CHM2047: ONE-SEMESTER GENERAL CHEMISTRY



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CHAPTER OVERVIEW

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1.1: Hypothesis, Theories, and Laws

Learning Objectives

- Describe the difference between hypothesis and theory as scientific terms.
- Describe the difference between a theory and scientific law.

Although many have taken science classes throughout the course of their studies, people often have incorrect or misleading ideas about some of the most important and basic principles in science. Most students have heard of hypotheses, theories, and laws, but what do these terms really mean? Prior to reading this section, consider what you have learned about these terms before. What do these terms mean to you? What do you read that contradicts or supports what you thought?

What is a Fact?

A fact is a basic statement established by experiment or observation. All facts are true under the specific conditions of the observation.

What is a Hypothesis?

One of the most common terms used in science classes is a "hypothesis". The word can have many different definitions, depending on the context in which it is being used:

- An educated guess: a scientific hypothesis provides a suggested solution based on evidence.
- Prediction: if you have ever carried out a science experiment, you probably made this type of hypothesis when you predicted the outcome of your experiment.
- Tentative or proposed explanation: hypotheses can be suggestions about why something is observed. In order for it to be scientific, however, a scientist must be able to test the explanation to see if it works and if it is able to correctly predict what will happen in a situation. For example, "if my hypothesis is correct, we should see ___ result when we perform ___ test."

> *A hypothesis is very tentative; it can be easily changed.*

What is a Theory?

The *United States National Academy of Sciences* describes what a theory is as follows:

> "Some scientific explanations are so well established that no new evidence is likely to alter them. The explanation becomes a scientific theory. In everyday language a theory means a hunch or speculation. Not so in science. In science, the word **theory** refers to a comprehensive explanation of an important feature of nature supported by facts gathered over time. Theories also allow scientists to make predictions about as yet unobserved phenomena."
>
> "A scientific theory is a well-substantiated explanation of some aspect of the natural world, based on a body of facts that have been repeatedly confirmed through observation and experimentation. Such fact-supported theories are not "guesses" but reliable accounts of the real world. The theory of biological evolution is more than "just a theory." It is as factual an explanation of the universe as the atomic theory of matter (stating that everything is made of atoms) or the germ theory of disease (which states that many diseases are caused by germs). Our understanding of gravity is still a work in progress. But the phenomenon of gravity, like evolution, is an accepted fact.

Note some key features of theories that are important to understand from this description:

- Theories are explanations of natural phenomena. They aren't predictions (although we may use theories to make predictions). They are explanations as to why we observe something.
- Theories aren't likely to change. They have a large amount of support and are able to satisfactorily explain numerous observations. Theories can, indeed, be facts. Theories can change, but it is a long and difficult process. In order for a theory to change, there must be many observations or pieces of evidence that the theory cannot explain.
- Theories are not guesses. The phrase "just a theory" has no room in science. To be a scientific theory carries a lot of weight; it is not just one person's idea about something

> *Theories aren't likely to change.*

What is a Law?

Scientific laws are similar to scientific theories in that they are principles that can be used to predict the behavior of the natural world. Both scientific laws and scientific theories are typically well-supported by observations and/or experimental evidence. Usually scientific laws refer to rules for how nature will behave under certain conditions, frequently written as an equation. Scientific theories are more overarching explanations of how nature works and why it exhibits certain characteristics. As a comparison, theories explain why we observe what we do and laws describe what happens.

For example, around the year 1800, Jacques Charles and other scientists were working with gases to, among other reasons, improve the design of the hot air balloon. These scientists found, after many, many tests, that certain patterns existed in the observations on gas behavior. If the temperature of the gas is increased, the volume of the gas increased. This is known as a natural law. A law is a relationship that exists between variables in a group of data. Laws describe the patterns we see in large amounts of data, but do not describe why the patterns exist.

What is a Belief?

A **belief** is a statement that is not scientifically provable. Beliefs may or may not be incorrect; they just are outside the realm of science to explore.

Laws vs. Theories

A common misconception is that scientific theories are rudimentary ideas that will eventually graduate into scientific laws when enough data and evidence has accumulated. A theory does not change into a scientific law with the accumulation of new or better evidence. Remember, **theories are explanations** and **laws are patterns** we see in large amounts of data, frequently written as an equation. A theory will always remain a theory; a law will always remain a law.



Video **1.1.1**: What's the difference between a scientific law and theory?

Summary

- A hypothesis is a tentative explanation that can be tested by further investigation.
- A theory is a well-supported explanation of observations.
- A scientific law is a statement that summarizes the relationship between variables.
- An experiment is a controlled method of testing a hypothesis.

Contributions & Attributions

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- Marisa Alviar-Agnew (Sacramento City College)
- Henry Agnew (UC Davis)

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1.2: The Scientific Method - How Chemists Think

Learning Objectives

- Identify the components of the scientific method.

Scientists search for answers to questions and solutions to problems by using a procedure called the scientific method. This procedure consists of making observations, formulating hypotheses, and designing experiments; which leads to additional observations, hypotheses, and experiments in repeated cycles (Figure 1.2.1).

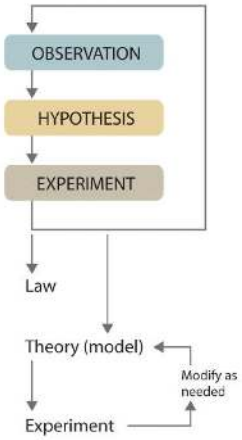


Figure 1.2.1: The Steps in the Scientific Method.

Step 1: Make observations

Observations can be qualitative or quantitative. **Qualitative observations** describe properties or occurrences in ways that do not rely on numbers. Examples of qualitative observations include the following: "the outside air temperature is cooler during the winter season," "table salt is a crystalline solid," "sulfur crystals are yellow," and "dissolving a penny in dilute nitric acid forms a blue solution and a brown gas." **Quantitative observations** are measurements, which by definition consist of both a number and a unit. Examples of quantitative observations include the following: "the melting point of crystalline sulfur is 115.21° Celsius," and "35.9 grams of table salt—the chemical name of which is sodium chloride—dissolve in 100 grams of water at 20° Celsius." For the question of the dinosaurs' extinction, the initial observation was quantitative: iridium concentrations in sediments dating to 66 million years ago were 20–160 times higher than normal.

Step 2: Formulate a hypothesis

After deciding to learn more about an observation or a set of observations, scientists generally begin an investigation by forming a hypothesis, a tentative explanation for the observation(s). The hypothesis may not be correct, but it puts the scientist's understanding of the system being studied into a form that can be tested. For example, the observation that we experience alternating periods of light and darkness corresponding to observed movements of the sun, moon, clouds, and shadows is consistent with either one of two hypotheses:

a. Earth rotates on its axis every 24 hours, alternately exposing one side to the sun.
b. The sun revolves around Earth every 24 hours.

Suitable experiments can be designed to choose between these two alternatives. For the disappearance of the dinosaurs, the hypothesis was that the impact of a large extraterrestrial object caused their extinction. Unfortunately (or perhaps fortunately), this hypothesis does not lend itself to direct testing by any obvious experiment, but scientists can collect additional data that either support or refute it.

Step 3: Design and perform experiments

After a hypothesis has been formed, scientists conduct experiments to test its validity. Experiments are systematic observations or measurements, preferably made under controlled conditions—that is—under conditions in which a single variable changes.

Step 4: Accept or modify the hypothesis

A properly designed and executed experiment enables a scientist to determine whether or not the original hypothesis is valid. If the hypothesis is valid, the scientist can proceed to step 5. In other cases, experiments often demonstrate that the hypothesis is incorrect or that it must be modified and requires further experimentation.

Step 5: Development into a law and/or theory

More experimental data are then collected and analyzed, at which point a scientist may begin to think that the results are sufficiently reproducible (i.e., dependable) to merit being summarized in a law, a verbal or mathematical description of a phenomenon that allows for general predictions. A law simply states what happens; it does not address the question of why.

One example of a law, the law of definite proportions, which was discovered by the French scientist Joseph Proust (1754–1826), states that a chemical substance always contains the same proportions of elements by mass. Thus, sodium chloride (table salt) always contains the same proportion by mass of sodium to chlorine, in this case 39.34% sodium and 60.66% chlorine by mass, and sucrose (table sugar) is always 42.11% carbon, 6.48% hydrogen, and 51.41% oxygen by mass.

Whereas a law states only what happens, a theory attempts to explain why nature behaves as it does. Laws are unlikely to change greatly over time unless a major experimental error is discovered. In contrast, a theory, by definition, is incomplete and imperfect, evolving with time to explain new facts as they are discovered.

Because scientists can enter the cycle shown in Figure 1.2.1 at any point, the actual application of the scientific method to different topics can take many different forms. For example, a scientist may start with a hypothesis formed by reading about work done by others in the field, rather than by making direct observations.

✔ Example 1.2.1

Classify each statement as a law, a theory, an experiment, a hypothesis, an observation.

a. Ice always floats on liquid water.
b. Birds evolved from dinosaurs.
c. Hot air is less dense than cold air, probably because the components of hot air are moving more rapidly.
d. When 10 g of ice were added to 100 mL of water at 25°C, the temperature of the water decreased to 15.5°C after the ice melted.
e. The ingredients of Ivory soap were analyzed to see whether it really is 99.44% pure, as advertised.

Solution

a. This is a general statement of a relationship between the properties of liquid and solid water, so it is a law.
b. This is a possible explanation for the origin of birds, so it is a hypothesis.
c. This is a statement that tries to explain the relationship between the temperature and the density of air based on fundamental principles, so it is a theory.
d. The temperature is measured before and after a change is made in a system, so these are observations.
e. This is an analysis designed to test a hypothesis (in this case, the manufacturer's claim of purity), so it is an experiment.

? Exercise 1.2.1

Classify each statement as a law, a theory, an experiment, a hypothesis, a qualitative observation, or a quantitative observation.

a. Measured amounts of acid were added to a Rolaids tablet to see whether it really "consumes 47 times its weight in excess stomach acid."
b. Heat always flows from hot objects to cooler ones, not in the opposite direction.
c. The universe was formed by a massive explosion that propelled matter into a vacuum.
d. Michael Jordan is the greatest pure shooter to ever play professional basketball.
e. Limestone is relatively insoluble in water, but dissolves readily in dilute acid with the evolution of a gas.

Answer a

experiment

Answer b

law

Answer c

theory

Answer d

hypothesis

Answer e

observation

Summary

The scientific method is a method of investigation involving experimentation and observation to acquire new knowledge, solve problems, and answer questions. The key steps in the scientific method include the following:

- Step 1: Make observations.
- Step 2: Formulate a hypothesis.
- Step 3: Test the hypothesis through experimentation.
- Step 4: Accept or modify the hypothesis.
- Step 5: Develop into a law and/or a theory.

Contributions & Attributions

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- Wikipedia

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1.3: Radiation and the Wave Nature of Light

Learning Objectives

- Explain the basic behavior of waves, including traveling waves and standing waves
- Describe the wave nature of light
- Use appropriate equations to calculate related light-wave properties such as period, frequency, wavelength

The nature of light has been a subject of inquiry since antiquity. In the seventeenth century, Isaac Newton performed experiments with lenses and prisms and was able to demonstrate that white light consists of the individual colors of the rainbow combined together. Newton explained his optics findings in terms of a "corpuscular" view of light, in which light was composed of streams of extremely tiny particles travelling at high speeds according to Newton's laws of motion. Others in the seventeenth century, such as Christiaan Huygens, had shown that optical phenomena such as reflection and refraction could be equally well explained in terms of light as waves travelling at high speed through a medium called "luminiferous aether" that was thought to permeate all space. Early in the nineteenth century, Thomas Young demonstrated that light passing through narrow, closely spaced slits produced interference patterns that could not be explained in terms of Newtonian particles but could be easily explained in terms of waves. Later in the nineteenth century, after James Clerk Maxwell developed his theory of electromagnetic radiation and showed that light was the visible part of a vast spectrum of electromagnetic waves, the particle view of light became thoroughly discredited. By the end of the nineteenth century, scientists viewed the physical universe as roughly comprising two separate domains: matter composed of particles moving according to Newton's laws of motion, and electromagnetic radiation consisting of waves governed by Maxwell's equations. Today, these domains are referred to as classical mechanics and classical electrodynamics (or classical electromagnetism). Although there were a few physical phenomena that could not be explained within this framework, scientists at that time were so confident of the overall soundness of this framework that they viewed these aberrations as puzzling paradoxes that would ultimately be resolved somehow within this framework. As we shall see, these paradoxes led to a contemporary framework that intimately connects particles and waves at a fundamental level called wave-particle duality, which has superseded the classical view.

Visible light and other forms of electromagnetic radiation play important roles in chemistry, since they can be used to infer the energies of electrons within atoms and molecules. Much of modern technology is based on electromagnetic radiation. For example, radio waves from a mobile phone, X-rays used by dentists, the energy used to cook food in your microwave, the radiant heat from red-hot objects, and the light from your television screen are forms of electromagnetic radiation that all exhibit wavelike behavior.

Waves

A wave is an oscillation or periodic movement that can transport energy from one point in space to another. Common examples of waves are all around us. Shaking the end of a rope transfers energy from your hand to the other end of the rope, dropping a pebble into a pond causes waves to ripple outward along the water's surface, and the expansion of air that accompanies a lightning strike generates sound waves (thunder) that can travel outward for several miles. In each of these cases, kinetic energy is transferred through matter (the rope, water, or air) while the matter remains essentially in place. An insightful example of a wave occurs in sports stadiums when fans in a narrow region of seats rise simultaneously and stand with their arms raised up for a few seconds before sitting down again while the fans in neighboring sections likewise stand up and sit down in sequence. While this wave can quickly encircle a large stadium in a few seconds, none of the fans actually travel with the wave-they all stay in or above their seats.

Waves need not be restricted to travel through matter. As Maxwell showed, electromagnetic waves consist of an electric field oscillating in step with a perpendicular magnetic field, both of which are perpendicular to the direction of travel. These waves can travel through a vacuum at a constant speed of 2.998×10^8 m/s, the speed of light (denoted by c).

All waves, including forms of electromagnetic radiation, are characterized by, a wavelength (denoted by λ, the lowercase Greek letter lambda), a frequency (denoted by ν, the lowercase Greek letter nu), and an amplitude. As can be seen in Figure 1.3.1, the wavelength is the distance between two consecutive peaks or troughs in a wave (measured in meters in the SI system). Electromagnetic waves have wavelengths that fall within an enormous range-wavelengths of kilometers (10^3 m) to picometers (10^{-12} m) have been observed. The frequency is the number of wave cycles that pass a specified point in space in a specified amount of time (in the SI system, this is measured in seconds). A cycle corresponds to one complete wavelength. The unit for frequency, expressed as cycles per second [s^{-1}], is the hertz (Hz). Common multiples of this unit are megahertz, (1 MHz = 1×10^6

Hz) and gigahertz (1 GHz = 1×10^9 Hz). The amplitude corresponds to the magnitude of the wave's displacement and so, in Figure, this corresponds to one-half the height between the peaks and troughs. The amplitude is related to the intensity of the wave, which for light is the brightness, and for sound is the loudness.

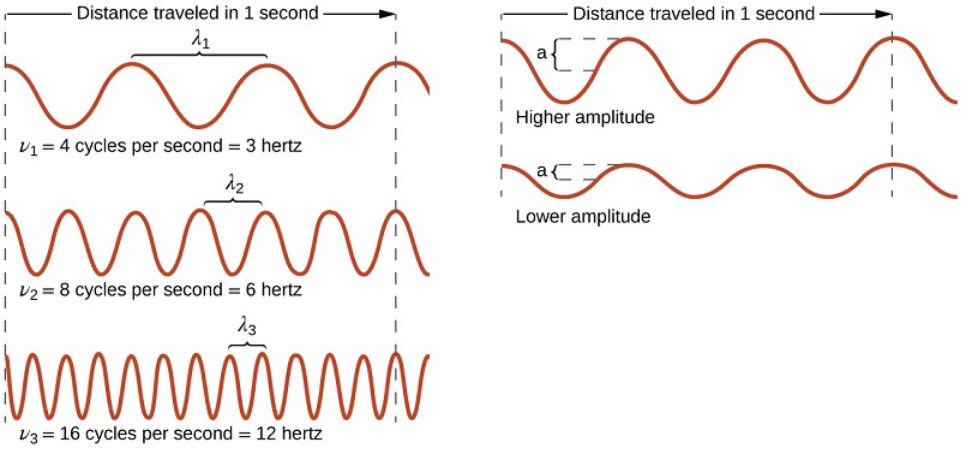


Figure 1.3.1: One-dimensional sinusoidal waves show the relationship among wavelength, frequency, and speed. The wave with the shortest wavelength has the highest frequency. Amplitude is one-half the height of the wave from peak to trough. (CC BY 4.0; OpenStax)

The product of a wave's wavelength (λ) and its frequency (ν), $\lambda\nu$, is the speed of the wave. Thus, for electromagnetic radiation in a vacuum:

$$c=\mathrm{2.998\times10^8\,ms^{-1}}=\lambda\nu \quad (6.2.1)$$

Wavelength and frequency are inversely proportional: As the wavelength increases, the frequency decreases. The inverse proportionality is illustrated in Figure 1.3.2. This figure also shows the electromagnetic spectrum, the range of all types of electromagnetic radiation. Each of the various colors of visible light has specific frequencies and wavelengths associated with them, and you can see that visible light makes up only a small portion of the electromagnetic spectrum. Because the technologies developed to work in various parts of the electromagnetic spectrum are different, for reasons of convenience and historical legacies, different units are typically used for different parts of the spectrum. For example, radio waves are usually specified as frequencies (typically in units of MHz), while the visible region is usually specified in wavelengths (typically in units of nm or angstroms).

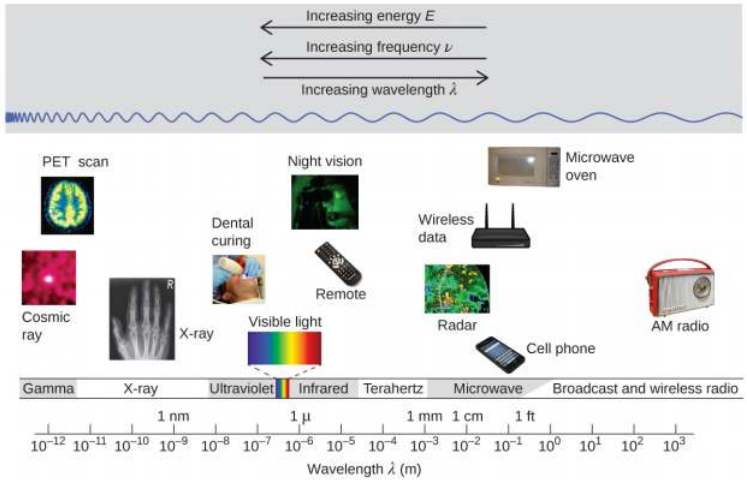


Figure 1.3.2: Portions of the electromagnetic spectrum are shown in order of decreasing frequency and increasing wavelength. Examples of some applications for various wavelengths include positron emission tomography (PET) scans, X-ray imaging, remote controls, wireless Internet, cellular telephones, and radios. (credit “Cosmic ray": modification of work by NASA; credit “PET scan": modification of work by the National Institute of Health; credit “X-ray": modification of work by Dr. Jochen Lengerke; credit “Dental curing": modification of work by the Department of the Navy; credit “Night vision": modification of work by the Department of the Army; credit “Remote": modification of work by Emilian Robert Vicol; credit “Cell phone": modification of work by Brett Jordan; credit “Microwave oven": modification of work by Billy Mabray; credit “Ultrasound": modification of work by Jane Whitney; credit “AM radio": modification of work by Dave Clausen)

When working with electromagnetic waves in different regions of the spectrum we use different units.

Unit	Symbol	Wavelength (m)	Type of Radiation
picometer	pm	10^{-12}	gamma ray
angstrom	Å	10^{-10}	x-ray
nanometer	nm	10^{-9}	UV, visible
micrometer	μm	10^{-6}	infrared
millimeter	mm	10^{-3}	infrared
centimeter	cm	10^{-2}	microwave
meter	m	10^{0}	radio

Table 1.3.1: Common Wavelength Units for Electromagnetic Radiation

Example 1.3.1: Determining the Frequency and Wavelength of Radiation

A sodium streetlight gives off yellow light that has a wavelength of 589 nm (1 nm = 1×10^{-9} m). What is the frequency of this light?

Solution

We can rearrange the Equation ??? to solve for the frequency:

$$\nu = \frac{c}{\lambda}$$

Since c is expressed in meters per second, we must also convert 589 nm to meters.

$$\nu = \left(\frac{2.998 \times 10^{8} \ \cancel{\text{m}}\,\text{s}^{-1}}{589 \ \cancel{\text{nm}}}\right)\left(\frac{1 \times 10^{9} \ \cancel{\text{nm}}}{1 \ \cancel{\text{m}}}\right) = 5.09 \times 10^{14}\,\text{s}^{-1}$$

Exercise 1.3.1

One of the frequencies used to transmit and receive cellular telephone signals in the United States is 850 MHz. What is the wavelength in meters of these radio waves?

Answer

0.353 m = 35.3 cm

Wireless Communication

Many valuable technologies operate in the radio (3 kHz-300 GHz) frequency region of the electromagnetic spectrum. At the low frequency (low energy, long wavelength) end of this region are AM (amplitude modulation) radio signals (540-2830 kHz) that can travel long distances. FM (frequency modulation) radio signals are used at higher frequencies (87.5-108.0 MHz). In AM radio, the information is transmitted by varying the amplitude of the wave (Figure 1.3.5). In FM radio, by contrast, the amplitude is constant and the instantaneous frequency varies.



Figure 1.3.3: Radio and cell towers are typically used to transmit long-wavelength electromagnetic radiation. Increasingly, cell towers are designed to blend in with the landscape, as with the Tucson, Arizona, cell tower (right) disguised as a palm tree. (credit left: modification of work by Sir Mildred Pierce; credit middle: modification of work by M.O. Stevens)

Other technologies also operate in the radio-wave portion of the electromagnetic spectrum. For example, 4G cellular telephone signals are approximately 880 MHz, while Global Positioning System (GPS) signals operate at 1.228 and 1.575 GHz, local area wireless technology (Wi-Fi) networks operate at 2.4 to 5 GHz, and highway toll sensors operate at 5.8 GHz. The frequencies associated with these applications are convenient because such waves tend not to be absorbed much by common building materials.

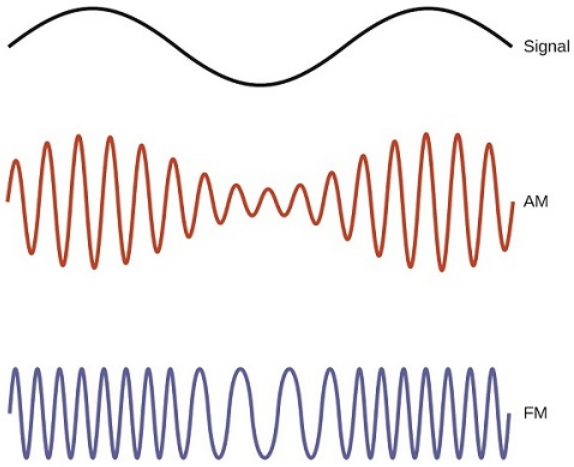


Figure 1.3.4: This schematic depicts how amplitude modulation (AM) and frequency modulation (FM) can be used to transmit a radio wave.

One particularly characteristic phenomenon of waves results when two or more waves come into contact: They interfere with each other. Figure 1.3.5 shows the interference patterns that arise when light passes through narrow slits closely spaced about a

wavelength apart. The fringe patterns produced depend on the wavelength, with the fringes being more closely spaced for shorter wavelength light passing through a given set of slits. When the light passes through the two slits, each slit effectively acts as a new source, resulting in two closely spaced waves coming into contact at the detector (the camera in this case). The dark regions in Figure 1.3.5 correspond to regions where the peaks for the wave from one slit happen to coincide with the troughs for the wave from the other slit (destructive interference), while the brightest regions correspond to the regions where the peaks for the two waves (or their two troughs) happen to coincide (constructive interference). Likewise, when two stones are tossed close together into a pond, interference patterns are visible in the interactions between the waves produced by the stones. Such interference patterns cannot be explained by particles moving according to the laws of classical mechanics.

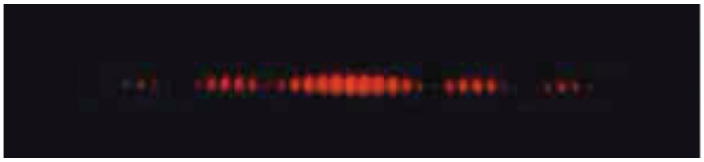


Figure 1.3.5: Interference fringe patterns are shown for light passing through two closely spaced, narrow slits. The spacing of the fringes depends on the wavelength, with the fringes being more closely spaced for the shorter-wavelength blue light. (credit: PASCO)

Dorothy Hodgkin

Because the wavelengths of X-rays (10-10,000 picometers [pm]) are comparable to the size of atoms, X-rays can be used to determine the structure of molecules. When a beam of X-rays is passed through molecules packed together in a crystal, the X-rays collide with the electrons and scatter. Constructive and destructive interference of these scattered X-rays creates a specific diffraction pattern. Calculating backward from this pattern, the positions of each of the atoms in the molecule can be determined very precisely. One of the pioneers who helped create this technology was Dorothy Crowfoot Hodgkin.

She was born in Cairo, Egypt, in 1910, where her British parents were studying archeology. Even as a young girl, she was fascinated with minerals and crystals. When she was a student at Oxford University, she began researching how X-ray crystallography could be used to determine the structure of biomolecules. She invented new techniques that allowed her and her students to determine the structures of vitamin B_{12}, penicillin, and many other important molecules. Diabetes, a disease that affects 382 million people worldwide, involves the hormone insulin. Hodgkin began studying the structure of insulin in 1934, but it required several decades of advances in the field before she finally reported the structure in 1969. Understanding the structure has led to better understanding of the disease and treatment options.

Not all waves are travelling waves. Standing waves (also known as stationary waves) remain constrained within some region of space. As we shall see, standing waves play an important role in our understanding of the electronic structure of atoms and molecules. The simplest example of a standing wave is a one-dimensional wave associated with a vibrating string that is held fixed at its two end points. Figure 1.3.6 shows the four lowest-energy standing waves (the fundamental wave and the lowest three harmonics) for a vibrating string at a particular amplitude. Although the string's motion lies mostly within a plane, the wave itself is considered to be one dimensional, since it lies along the length of the string. The motion of string segments in a direction perpendicular to the string length generates the waves and so the amplitude of the waves is visible as the maximum displacement of the curves seen in Figure 1.3.6. The key observation from the figure is that only those waves having an integer number, n, of half-wavelengths between the end points can form. A system with fixed end points such as this restricts the number and type of the possible waveforms. This is an example of quantization, in which only discrete values from a more general set of continuous values of some property are observed. Another important observation is that the harmonic waves (those waves displaying more than one-half wavelength) all have one or more points between the two end points that are not in motion. These special points are nodes. The energies of the standing waves with a given amplitude in a vibrating string increase with the number of half-wavelengths *n*. Since the number of nodes is $n - 1$, the energy can also be said to depend on the number of nodes, generally increasing as the number of nodes increases.

Figure 1.3.6: A vibrating string shows some one-dimensional standing waves. Since the two end points of the string are held fixed, only waves having an integer number of half-wavelengths can form. The points on the string between the end points that are not moving are called the nodes.

An example of two-dimensional standing waves is shown in Figure 1.3.7 which shows the vibrational patterns on a flat surface. Although the vibrational amplitudes cannot be seen like they could in the vibrating string, the nodes have been made visible by sprinkling the drum surface with a powder that collects on the areas of the surface that have minimal displacement. For one-dimensional standing waves, the nodes were points on the line, but for two-dimensional standing waves, the nodes are lines on the surface (for three-dimensional standing waves, the nodes are two-dimensional surfaces within the three-dimensional volume). Because of the circular symmetry of the drum surface, its boundary conditions (the drum surface being tightly constrained to the circumference of the drum) result in two types of nodes: radial nodes that sweep out all angles at constant radii and, thus, are seen as circles about the center, and angular nodes that sweep out all radii at constant angles and, thus, are seen as lines passing through the center. The upper left image in Figure 1.3.7 shows two radial nodes, while the image in the lower right shows the vibrational pattern associated with three radial nodes and two angular nodes.

Figure 1.3.7: *Two-dimensional standing waves can be visualized on a vibrating surface. The surface has been sprinkled with a powder that collects near the nodal lines. There are two types of nodes visible: radial nodes (circles) and angular nodes (radii). For a more animated video, check this link out.*

Exercise 1.3.3

Calculate the threshold energy in kJ/mol of electrons in aluminum, given that the lowest frequency photon for which the photoelectric effect is observed is $9.87 \times 10^{14}\ Hz$.

Answer

$3.94\ kJ/mol$

Summary

Light and other forms of electromagnetic radiation move through a vacuum with a constant speed, c, of 2.998×10^8 m s^{-1}. This radiation shows wavelike behavior, which can be characterized by a frequency, ν, and a wavelength, λ, such that $c = \lambda\nu$. Light is an example of a travelling wave. Other important wave phenomena include standing waves, periodic oscillations, and vibrations. Standing waves exhibit quantization, since their wavelengths are limited to discrete integer multiples of some characteristic lengths.

Key Equations

- $c = 2.998 \times 10^8\ \text{ms}^{-1} = \lambda\nu$

Glossary

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)

blackbody
idealized perfect absorber of all incident electromagnetic radiation; such bodies emit electromagnetic radiation in characteristic continuous spectra called blackbody radiation

continuous spectrum
electromagnetic radiation given off in an unbroken series of wavelengths (e.g., white light from the sun)

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

frequency (ν)
number of wave cycles (peaks or troughs) that pass a specified point in space per unit time

hertz (Hz)
the unit of frequency, which is the number of cycles per second, s^{-1}

intensity
property of wave-propagated energy related to the amplitude of the wave, such as brightness of light or loudness of sound

interference pattern
pattern typically consisting of alternating bright and dark fringes; it results from constructive and destructive interference of waves

line spectrum
electromagnetic radiation emitted at discrete wavelengths by a specific atom (or atoms) in an excited state

node
any point of a standing wave with zero amplitude

photon
smallest possible packet of electromagnetic radiation, a particle of light

quantization
occurring only in specific discrete values, not continuous

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

wave

oscillation that can transport energy from one point to another in space

wavelength (λ)

distance between two consecutive peaks or troughs in a wave

wave-particle duality

term used to describe the fact that elementary particles including matter exhibit properties of both particles (including localized position, momentum) and waves (including nonlocalization, wavelength, frequency)

Contributors and Attributions

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1.4: The failures of Classical Mechanics- the Particle Nature of Light

By the late 19th century, many physicists thought their discipline was well on the way to explaining most natural phenomena. They could calculate the motions of material objects using Newton's laws of classical mechanics, and they could describe the properties of radiant energy using mathematical relationships known as Maxwell's equations, developed in 1873 by James Clerk Maxwell, a Scottish physicist. The universe appeared to be a simple and orderly place, containing matter, which consisted of particles that had mass and whose location and motion could be accurately described, and electromagnetic radiation, which was viewed as having no mass and whose exact position in space could not be fixed. Thus matter and energy were considered distinct and unrelated phenomena. Soon, however, scientists began to look more closely at a few inconvenient phenomena that could *not* be explained by the theories available at the time.

The traditional introduction to quantum mechanics involves discussing the breakdown of classical mechanics and where quantum steps in. We have three examples of this: (1) blackbody radiation, (2) photoelectric effect and (3) hydrogen emission (of light). We discuss them here.

First Evidence of Classical Breakdown: Blackbody Radiation

It has been known for a long time that hot things radiate light!



Figure 1.4.1: Blackbody Radiation. When heated, all objects emit electromagnetic radiation whose wavelength (and color) depends on the temperature of the object. A relatively low-temperature object, such as a horseshoe forged by a blacksmith, appears red, whereas a higher-temperature object, such as the surface of the sun, appears yellow or white. Images used with permission from Wikipedia.

Blackbody Radiators

To begin analyzing heat radiation, we need to be specific about the body doing the radiating: the simplest possible case is an idealized body which is a perfect absorber, and therefore also (from the above argument) a perfect emitter. For obvious reasons, this is called a "blackbody". It is an idealized physical body that absorbs all incident electromagnetic radiation, regardless of frequency or angle of incidence.

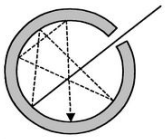


Figure 1.4.2: A cavity with a small hole that approximates a physical blackbody radiator. Images used with permission via MIT .

> *A blackbody radiator is an object or system that absorbs all radiation incident upon it and re-radiates energy which is characteristic of only the radiating system only, not on the type of radiation which is incident upon it.*

A physical realization of a blackbody is a cavity with a small hole with many reflections and absorptions. Very few entering photons (light rays) will get out. The inside of the cavity has radiation which is homogeneous and isotropic (the same in any direction, uniform everywhere).

Two experimental "laws" connected to black-body radiation:

1. **Stefan-Boltzmann Law:** The total (i.e., integrated) radiation intensity varies as T^4. That is

$$\int \text{all emitted light } d\nu \propto T^4 \tag{1.4.1}$$

> **Note**
>
> The symbol $\propto$ means "it is proportional to"

2. **Wien's Displacement Law**: As the temperature of a blackbody varies, so does the *frequency* at which the emitted radiation is most intense. In fact, that frequency is directly proportional to the absolute temperature:

$$\nu_{max} \propto T \tag{1.4.2}$$

where the proportionality constant is $5.879 \times 10^{10} Hz/K$.

The concept underlying Equation 1.4.2 is familiar to most people. When an iron is heated in a fire, the first visible radiation (at around 900 K) is deep red, the lowest frequency visible light. Further increase in *T* causes the color to change to orange then yellow, and finally blue at very high temperatures (10,000 K or more) for which the peak in radiation intensity has moved beyond the visible into the ultraviolet (Figure 1.4.3).

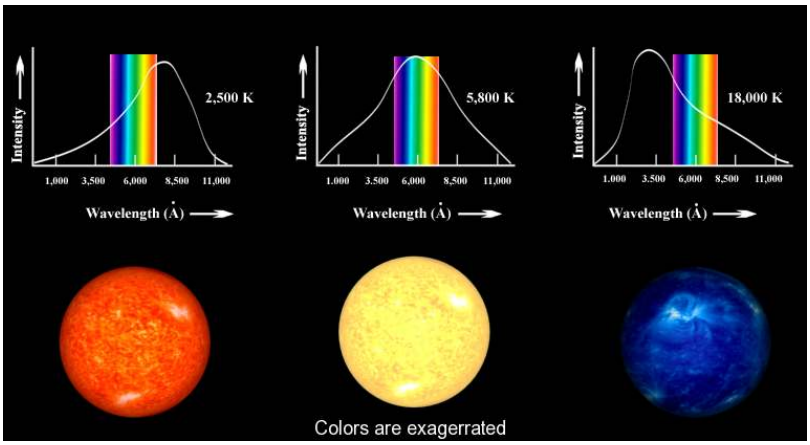


Figure 1.4.3: To estimate the surface temperature of a star, we can use the known relationship between the temperature of a blackbody, and the wavelength of light where its spectrum peaks (Equation 1.4.2). That is, as you increase the temperature of a blackbody, the peak of its spectrum moves to shorter (bluer) wavelengths of light. This is illustrated where the intensity of three hypothetical stars is plotted against wavelength. The "rainbow" indicates the range of wavelengths that are visible to the human eye. (GNU 1.2; KStars Handbook).

Classic Blackbody Radiation

Lord Rayleigh and J. H. Jeans developed an equation which explained blackbody radiation at low frequencies.The equation which seemed to express blackbody radiation was built upon all the known assumptions of physics at the time.

> *The big assumption which Rayleigh and Jean implied was that infinitesimal amounts of energy were continuously added to the system when the frequency was increased.*

Classical physics assumed that energy emitted by atomic oscillations could have any continuous value.This was true for anything that had been studied up until that point, including things like acceleration, position, or energy. The resulting *Rayleigh-Jeans law* was

$$d\rho\left(\nu,T\right)=\rho_{\nu}\left(T\right)d\nu=\underbrace{\frac{8\pi k_{B}T}{c^{3}}\nu^{2}}_{\text{Rayleigh-Jeans distribution}}\quad d\nu \tag{1.4.3}$$

The Classical Rayleigh-Jeans law

Assumed that energy emitted by atomic oscillations *could have any continuous value.*

Aside: Distributions

Equation 1.4.3 is a "distribution" not unlike the distribution of grades in a course. As such it has several properties of interest:

- **The integrated value (A)**: This is the sum over the distribution over all possible values of x. Graphically, this is the area under the distribution.

$$A=\int_{-\infty}^{\infty}D(x)\,dx \tag{1.4.4}$$

  If the range of x is less than $-\infty$ to ∞ (e.g., from a to b), then A is given by

$$A=\int_{a}^{b}D(x)\,dx \tag{1.4.5}$$

- **The expectation value ($\langle x\rangle$):** This is a different term that is used synonymously with the *average* (or *mean*) of x over the distribution. The mean is given by

$$\bar{x}=\langle x\rangle=\int_{a}^{b}xD(x)\,dx \tag{1.4.6}$$

  Notice the difference between Equations 1.4.5 and 1.4.6.
- **The most probable value (x_{mp}):** This is the value of x at the peak of $D(x)$. This is determined from basic calculus for determining extrema and via identifying when the derivative of the distribution is zero.

$$\left(\frac{dD(x)}{dx}\right)_{x_{mp}}=0 \tag{1.4.7}$$

- **The standard deviation (σ_x)**: This is the a measure of the spread of the distribution and is given by

$$\sigma_{x}^{2}=\int_{a}^{b}(x-\bar{x})^{2}D(x)\,dx \tag{1.4.8}$$

Experimental data performed on the black box showed slightly different results than what was expected by the *Rayleigh-Jeans law.* The law had been studied and widely accepted by many physicists of the day, but the experimental results did not lie, something was different between what was theorized and what actually happens.The experimental results showed a bell type of curve but according to the ***Rayleigh-Jeans law*** **the frequency diverged as it neared the ultraviolet region** (Equation 1.4.3). This inconsistency was termed the *ultraviolet catastrophe.*

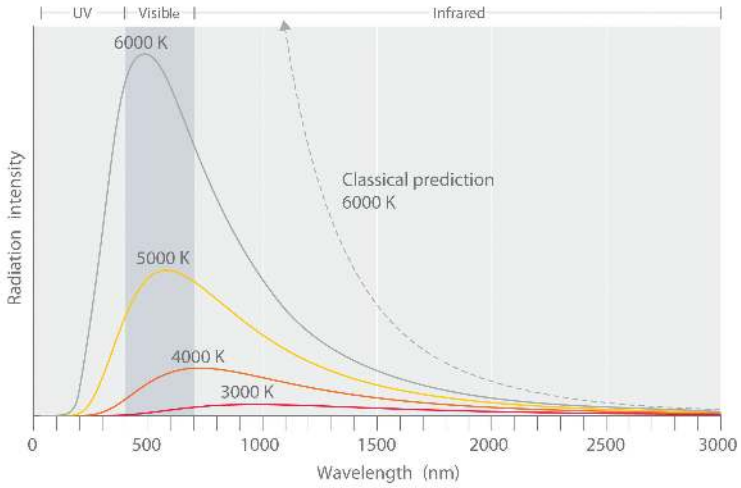


Figure 1.4.1 Relationship between the Temperature of an Object and the Spectrum of Blackbody Radiation It Emits. At relatively low temperatures, most radiation is emitted at wavelengths longer than 700 nm, which is in the infrared portion of the spectrum. As the temperature of the object increases, the maximum intensity shifts to shorter wavelengths, successively resulting in orange, yellow, and finally white light. At high temperatures, all wavelengths of visible light are emitted with approximately equal intensities.

Max Planck was the first person to properly explain this experimental data. Rayleigh and Jean made the assumption that energy is continuous, but Planck took a slightly different approach. He said energy must come in certain unit intervals instead of being any random unit or number. He instead "quantized" energy in the form of

$$E = nh\nu \tag{1.4.9}$$

where n is an integer, h is a constant, and ν is the frequency. This assumption proved to be the missing piece of the puzzle and Planck derived an expression which could explain the experimental data.

> Max Planck proposed that energy is emitted in discrete packets - he didn't know what they were though.

From this, the Planck distribution law, with respect to frequency, was derived from

$$d\rho(\nu, T) = \rho_\nu(T)d\nu = \underbrace{\frac{2h}{c^3} \cdot \frac{\nu^3}{e^{\frac{h\nu}{k_BT}} - 1}}_{\text{Planck's distribution}} d\nu \tag{1.4.10}$$

which is the "radiant energy density function".

using:

- π = 3.14159
- h = $6.626 \times 10^{-34} J \cdot s$
- c = $3.00 \times 10^{8} \frac{M}{s}$
- v = $\frac{1}{s}$
- k_B = $1.38 \times 10^{-23} \frac{J}{K}$
- T is absolute temperature (in Kelvin)

The resulting units of the radiant energy density function can be shown to be $J \cdot m^{-3}$ by using the constants and their respective units.

By setting the wavelength $\lambda = c \cdot \nu^{-1}$ and $d\nu = c \cdot \frac{-d\lambda}{\lambda^2}$, you can express $d\rho$ (1.4.10) in terms of λ rather than ν.

$$d\rho(\lambda, T) = \rho_\lambda(T)d\lambda = \underbrace{\frac{2hc^2}{\lambda^5} \cdot \frac{1}{e^{\frac{hc}{\lambda k_BT}} - 1}}_{\text{Planck's distribution}} d\lambda \tag{1.4.11}$$

Both the Stefan-Boltzmann Law and the Wien's Displacement Law can be derived from Planck's distribution.

Example 1.4.1: Peak Wavelength

The maximum of a curve has slope equal to zero, so to find λ_{max}, set

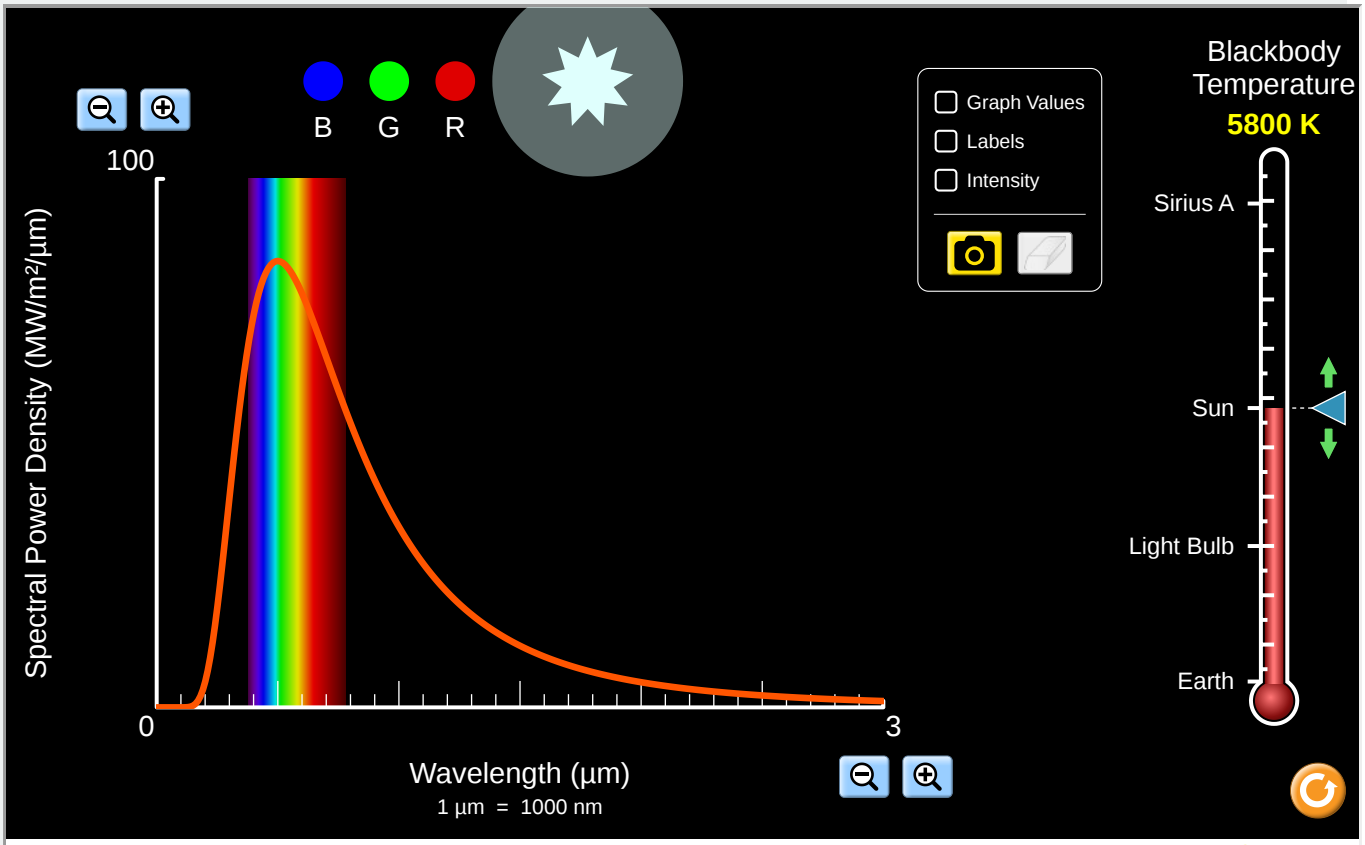
$$\frac{d\rho_\lambda(T)}{d\lambda} = 0 \tag{1.4.12}$$

which results in

$$\lambda_{max} = \frac{hc}{4.965 k_B T} \tag{1.4.13}$$

From this Equation 1.4.13, it is clear that temperature and the maximum wavelength are inversely proportional. A larger temperature gives a smaller λ_{max}, where a smaller temperature gives a larger λ_{max}.

Interactive: Blackbody Spectrum



Blackbody Spectrum

Template:HideTOC

The mathematics implied that the energy given off by a blackbody was not continuous, but given off at certain specific wavelengths, in regular increments. If Planck assumed that the energy of blackbody radiation was in the form

$$E = nh\nu \tag{1.4.14}$$

where n is an integer (now called a quantum number), then he could explain what the mathematics represented.

The traditional introduction to quantum mechanics involves discussing the breakdown of classical mechanics and where quantum steps in.

Example 1.4.2: Calculating the Energy of Radiation

When we see light from a neon sign, we are observing radiation from excited neon atoms. If this radiation has a wavelength of 640 nm, what is the energy of the photon being emitted?

Solution

We use the part of Planck's equation that includes the wavelength, λ, and convert units of nanometers to meters so that the units of λ and c are the same.

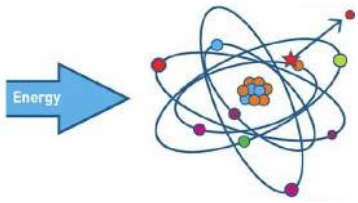
$$\begin{aligned} E &= \frac{hc}{\lambda} \\ &= \frac{(6.626 \times 10^{-34}\ \text{J}\ \cancel{\text{s}})(2.998 \times 10^{8}\ \text{m}\ \cancel{\text{s}^{-1}})}{(640\ \cancel{\text{nm}})\left(\frac{1\ \text{m}}{10^{9}\ \cancel{\text{nm}}}\right)} \\ &= 3.10 \times 10^{-19}\ \text{J} \end{aligned}$$

Exercise 1.4.2

The microwaves in an oven are of a specific frequency that will heat the water molecules contained in food. (This is why most plastics and glass do not become hot in a microwave oven-they do not contain water molecules.) This frequency is about 3×10^9 Hz. What is the energy of one photon in these microwaves?

Second Evidence of Classical Breakdown: The Photoelectric Effect

Ionization is the process by which an atom or a molecule acquires a negative or positive charge by gaining or losing electrons to form ions, often in conjunction with other chemical changes. You can read about the discussion of ionization energies.

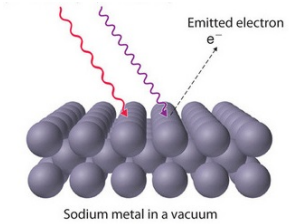


Key to an electron ionization event is that energy is introduced and an electron is ejected.

There are different ways to add energy to systems (heat, electricity, bombarding of particles). Moreover, not only atoms, but molecules and bulk matter can be ionzed. The process we are interested in is injecting energy via the absorption of light, which is called the **photoelectric effect**.

> *The photoelectric effect is the emission of electrons or other free carriers when light is shone onto a material. Electrons emitted in this manner can be called photo electrons.*

Only five years after Planck's proposed quantization, this hypothesis was used to explain a second phenomenon that conflicted with the accepted laws of classical physics. In 1886, the photoelectric effect was observed by Heinrich Hertz, by finding that when a metallic surface is exposed to ultraviolet light, electrons are emitted from the surface. When certain metals are exposed to light, electrons are ejected from their surface. Classical physics predicted that the number of electrons emitted and their kinetic energy should depend on only the intensity of the light, not its frequency.

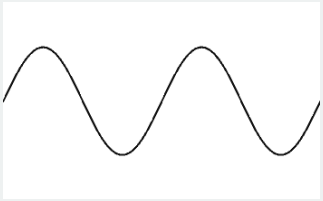


The Photoelectric Effect involves the irradiating a metal surface with photons of sufficiently high energy to causes electrons to be ejected from the metal. (CC BY-SA-NC; anonymous by request).

Before delving into the photoelectric effect, let's discussing the the wave perspective of light and how it transfers energy.

The classical wave perspective of light and its associated Energy

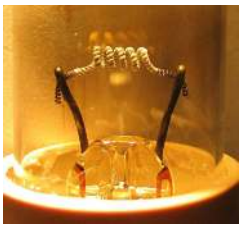
Classical theory of light is a wave picture. Both **amplitude** and **frequency** are the two factors that affect the energy transferred by a wave: the height of the wave, and the number of waves passed by each second.



- The **amplitude** tells you how much energy is in the wave. A high amplitude wave is a high-energy wave, and a low-amplitude wave is a low-energy wave. In the case of sound waves, a high amplitude sound will be loud, and a low amplitude sound will be quiet. Or with light waves, a high amplitude beam of light will be bright, and a low amplitude beam of light will be dim.
- The other factor is frequency. **Frequency** is the number of waves that pass by each second, measured in hertz. So a wave of a particular amplitude will transmit more energy per second if it has a higher frequency, simply because more waves are passing by in a given period of time.

Classical Picture of Photoelectron Effect (Thermionic Emission)

According to the classical perspective of photoelectric effect, when light shines on a surface, it slowly transfers energy into the substance. This increases the kinetic energy of the particles until finally, they give off excited electrons. This process is called *Thermionic Emission* and it was considered the most likely explanation for the photoelectric effect by physicists in in the early 20th century.



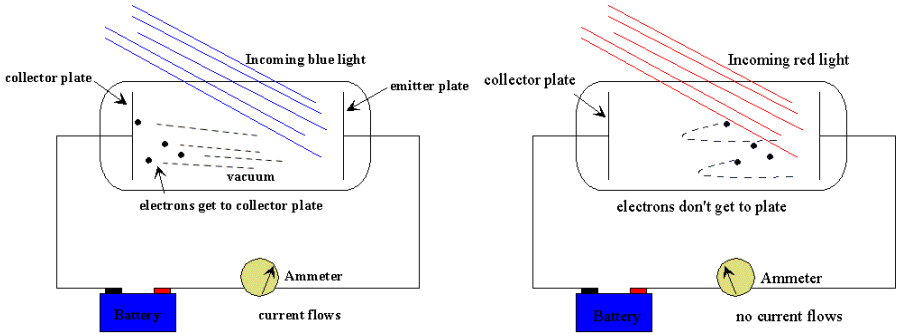
Thermionic Emission: Close up of the filament on a low pressure mercury gas discharge lamp showing white thermionic emission mix coating on the central portion of the coil. Typically made of a mixture of barium, strontium and calcium oxides, the coating is sputtered away through normal use, often eventually resulting in lamp failure. (CC-SA-BY 3.0; Deglr6328)

Expectations from Thermionic Emission based approach (The Classical Picture)

- **Increasing** light intensity, regardless of frequency, would result in photoelectrons with **higher** kinetic energies
- The photoelectric effect would **not** be observed immediately, since the substance must first reach a critical temperature before it can begin ejecting electrons.

Experimental Observations (Lenard's Experiment)

To test the theories proposed by classical mechanics, Lenard built the experimental device shown below (also http://www.thephysicsaviary.com/Physics/Programs/Labs/PhotoelectricEffect/index.html).



Lenard's experimental setup. Image by Fowler. In the above figure, the battery represents the potential Lenard used to charge the collector plate negatively, which would actually be a variable voltage source. Since the electrons ejected by the blue light are getting to the collector plate, evidently the potential supplied by the battery is less than V_{stop} for blue light. Show with an arrow on the wire the direction of the electric current in the wire.

The applied voltage from the battery (V) is used to stop the electron from getting to the end. This is due to the energy of this applied field

$$E_{battery} = eV \tag{1.4.15}$$

matching or exceeding the kinetic energy of the photoelectrons

$$KE = \frac{1}{2}mv^2 \tag{1.4.16}$$

On cranking up the negative voltage on the collector plate until the current just stops, that is, to V, the highest kinetic energy electrons must have had energy eV on leaving the cathode.

Interactive: Five Key Experimental Results

Recreate the Lenard's experiment using the Photoelectric Effect simulation:

https://phet.colorado.edu/en/simulation/photoelectric or http://www.thephysicsaviary.com/Physics/Programs/Labs/PhotoelectricEffect/index.html

1. Below a certain threshold frequency, no matter how intense the light was, there was *no* emission of electrons.
2. Above the threshold frequency, the current (i.e. the # of electrons reaching the anode) was directly *proportional* to the light intensity.
3. The current appeared almost *instantaneously* after the light was turned on
4. Higher frequency light increased the **kinetic energy** of the electrons,
5. Changing the light intensity had **no effect** on the kinetic energy.

> *Higher frequencies may increase the energy of the ejected photoelectrons and make it cross a distance faster, but the time between each successive photoelectron remains the same because the time between each successive photon impact remains the same for the same intensity. It does not increase the total number of photoelectrons per photon.*

Quantum Picture of the Photoelectron Effect

Einstein showed that the kinetic energy of the emitted electron depends on to the energy of the photon that hit the metallic surface and an effective "ionization energy" of the metal. This is shown by

$$KE = \frac{mv^2}{2} = h\nu - \Phi \tag{1.4.17}$$

where ϕ is the work function of the metal, and $\phi = h\nu_0$, where ν_0 is the threshold frequency. However, each electron will only absorb the energy and be ejected if the frequency of the light is of sufficient energy according to the equation

$$E = h\nu \tag{1.4.18}$$

where ν is the frequency of the incident light and h is Planck's constant ($h = 6.626 \times 10^{-34} Js$). The required energy to free an electron from an atom is called the work function and is designated by the symbol ϕ. The threshold frequency corresponds to a particle-light with the lowest energy needed to satisfy this work function (i.e. overcome the electron's affinity for the atom). Higher frequency light increases the kinetic energy (KE) of the ejected electron according to the equation:

$$KE = h\nu - \Phi \tag{1.4.19}$$

but it does not affect the number of photons ejected. To increase the number of electrons ejected, it is necessary to increase the number of photons (particle-light), since one photon is absorbed for each ejected electron.

Table 1 summarizes the work functions for several elements:

Table 1: Work Functions of Select Elements

Element	Work function Φ (eV)	Ionization Energy (eV)

Element	Work function Φ (eV)	Ionization Energy (eV)
Silver (Ag)	4.64	7.57
Aluminum (Al)	4.20	5.98
Gold (Au)	5.17	9.22
Boron (B)	4.45	8.298
Beryllium (Be)	4.98	9.32

Workfunctions and Ionization Energies are Different Concepts

In a particular textbook, the work function of a metal (in the context of the photoelectric effect) is defined as:

the minimum amount of energy necessary to remove an electron from the ***surface of the metal***

This sounds similar to ionization energy, which is:

the amount of energy required to remove an electron from ***an atom or molecule*** *in the* ***gaseous state***

These two energies are generally different (Table 1). For instance, Copper has a work function of about 4.7 eV but has a higher ionization energy of about 746 kJ mol^{-1} or 7.7 eV.

Work function deals with "free" electrons in the metallic bonding of the metal, while ionization energy addressed the valence electrons still bound within the atom. Is the difference due to the energy required to overcome the attraction of the positive nucleus?

Ramifications of Einstein's Photon Theory of the Photoelectron effect

Since every photon of sufficient energy excites only one electron, increasing the light's intensity (i.e. the number of photons/sec) only increases the **number of released** electrons and not their kinetic energy.

- No time is necessary for the atom to be heated to a critical temperature and therefore the release of the electron is nearly **instantaneous** upon absorption of the light.
- The photons must be above a certain energy $h\nu \geq h\nu_0$ to equal or exceed the workfunction, a threshold frequency exists below which no photoelectrons are observed.

Einstein's simple explanation completely accounted for the observed phenomenon in Lenard's experiment and began an investigation into the field we now call quantum mechanics. This new field seeks to provide a quantum explanation for classical mechanics and create a more unified theory of physics and thermodynamics. The study of the photoelectric effect has also lead to the creation of new photoelectron spectroscopy theory and applications.

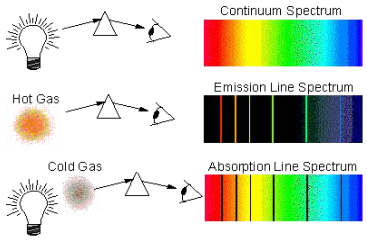
In 1911 R. A. Milliken measured the value of \h (R. A. Millikan, *Physical Review*, Vol. **7**, Issue 3, March 1916, pp. 355-388) obtaining a value of ($h = 6.57 \times 10^{-34} Js$), only a 0.85% error with respect to the currently accepted value of ($h = 6.626 \times 10^{-34} Js$).

The photoelectric effect concludes two important points

1. Photons are quantized, packets of energy.
2. Different metals have different work functions and threshold frequencies.

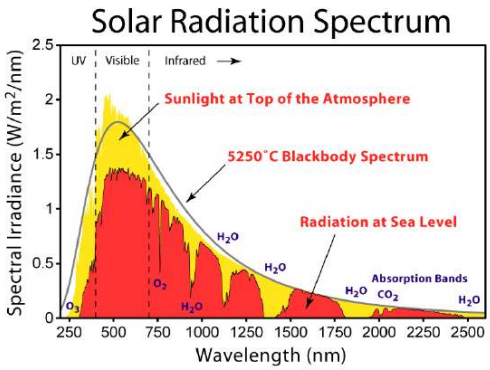
Third Evidence of Classical Breakdown: Atomic Spectra

Most of what is known about atomic (and molecular) structure and mechanics has been deduced from spectroscopy. A continuous spectrum can be produced by an incandescent solid or gas at high pressure. Blackbody radiation, for example, is a continuum since the degree of quantization from Planck's assumptions is so small the radiation curves look continuous (with other factors discussed later). An emission spectrum can be produced by a gas at low pressure excited by heat or by collisions with electrons. http://physics.bu.edu/~duffy/HTML5/emission_spectra.html or https://www.edumedia-sciences.com/en/media/661-emission-and-absorption-spectra



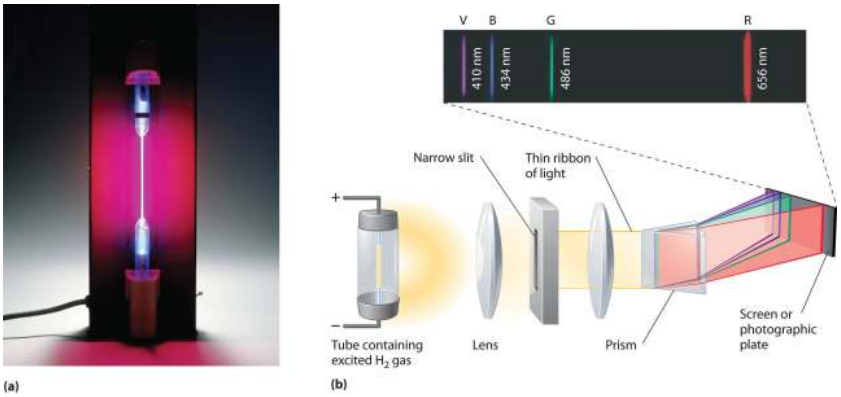
Continuous spectrum and two types of line spectra. from Wikipedia.

An absorption spectrum results when light from a continuous source passes through a cooler gas, consisting of a series of dark lines characteristic of the composition of the gas. Frauenhofer between 1814 and 1823 discovered nearly 600 dark lines in the solar spectrum viewed at high resolution. It is now understood that these lines are caused by absorption by the outer layers of the Sun and the Earth's atmosphere.



This figure shows the solar radiation spectrum for direct light at both the top of the Earth's atmosphere and at sea level. The sun produces light with a distribution similar to what would be expected from a 5525 K (5250 °C) blackbody, which is approximately the sun's surface temperature. As light passes through the atmosphere, some is absorbed by gases with specific absorption bands. from Wikipedia.

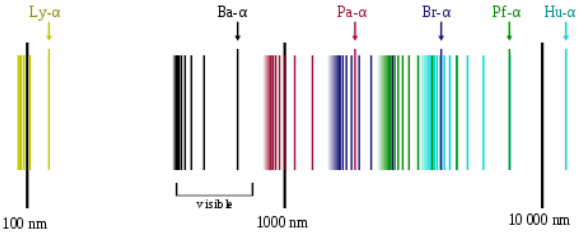
Gases heated to incandescence were found by Bunsen, Kirkhoff and others to emit light with a series of sharp wavelengths. The emitted light analyzed by a spectrometer (or even a simple prism) appears as a multitude of narrow bands of color. These so called *line spectra* are characteristic of the atomic composition of the gas.



(a) A sample of excited hydrogen atoms emits a characteristic red light. (b) When the light emitted by a sample of excited hydrogen atoms is split into its component wavelengths by a prism, four characteristic violet, blue, green, and red emission lines can be observed, the most intense of which is at 656 nm.

Experimental Observations (Hydrogen Gas)

The line spectrum of hydrogen *atoms* is shown below.



The spectral series of hydrogen, on a logarithmic scale. (CC BY Sa 3.0; OrangeDog);

The hydrogen spectrum is complex, comprising more than the three lines visible to the naked eye. It is possible to detect patterns of lines in both the ultraviolet and infrared regions of the spectrum as well. These fall into a number of "series" of lines named after the person who discovered them.

Lyman series: λ, vacuum (nm)	Balmer series: λ, vacuum (nm)	Paschen series: λ, vacuum (nm)	Brackett series: λ, vacuum (nm)	Pfund series: λ, vacuum (nm)	Humphreys : λ, vacuum (nm)
121.57	656.3	1875	1875	7460	12.37
102.57	486.1	1282	1282	4654	7.503
97.254	434.0	1094	1094	3741	5.908
94.974	410.2	1005	1005	3297	5.129
93.780	397.0	954.6	954.6	3039	4.673
91.175	364.6	922.9	922.9	2279	3.282

Three particular series are well observed in emission of hydrogen atoms

- The Lyman series (UV)
- The Balmer series (Visible)
- The Paschen series for (NIR)

The series can be phenomenologically described via the following relationships

- The Lyman series for $n_1 = 1$

$$\bar{\nu} = \frac{1}{\lambda} = R\left(\frac{1}{1} - \frac{1}{n_2^2}\right), n_2 > 1 \tag{1.4.20}$$

- The Balmer series for $n_1 = 2$

$$\bar{\nu} = \frac{1}{\lambda} = R\left(\frac{1}{4} - \frac{1}{n_2^2}\right), n_2 > 2 \tag{1.4.21}$$

- the Paschen series for $n_1 = 3$

$$\bar{\nu} = \frac{1}{\lambda} = R\left(\frac{1}{9} - \frac{1}{n_2^2}\right), n_2 > 3 \tag{1.4.22}$$

But what does n_2 represent?

The Rydberg Formula

The equations for the different series above that describe atomic spectra for a hydrogen atom can be consolidated into a single equation:

$$\tilde{\nu} = \frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad n_1 = 1, 2, 3..., n_2 > n_1 \tag{1.4.23}$$

$\tilde{\nu}$ is called the wavenumber ($\tilde{\nu}$) and is the number of waves that fit in one unit of length (typically cm). This constant is named after the Swedish physicist Rydberg who (in 1888) presented a generalization of formulas identified for the specific series (Equations 1.4.20- 1.4.22).

- For the Lyman series, $n_1 = 1$ and n_2 varies from 2 to ∞.
- For the Balmer series, $n_1 = 2$ and n_2 varies from 3 to ∞.
- For the Paschen series, $n_1 = 3$ and n_2 varies from 4 to ∞.

For each series, when n_2 approaches ∞, $\tilde{\nu}$ gets bigger and the lines become more dense (i.e., more lines per wavenumber). Furthermore, \widetilde {\nu} will reach an asymptotic value:

$$\tilde{\nu}_\infty = \lim_{n_2 \to \infty} R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = \frac{R}{n_1^2} \tag{1.4.24}$$

and since $\tilde{\nu} = \frac{1}{\lambda}$, λ gets successively smaller as n_2 increases.

But what do n_1 and n_2 represent?

Rydberg suggested that **all atomic spectra** formed families with pattern given by Equation 1.4.23. It turns out that there are families of spectra following Rydberg's pattern, notably in the alkali metals, sodium, potassium, etc., but not with the precision the hydrogen atom lines fit the formula in Equations 1.4.20- 1.4.22, and low values of n_1 give lines that deviate considerably. As we will discuss extensively later on this is if because there are **more than one electron** in these systems.

Summary

Electromagnetic radiation demonstrates properties of particles called photons. The energy of a photon is related to the frequency (or alternatively, the wavelength) of the radiation as $E = h\nu$ (or $E = \frac{hc}{\lambda}$), where h is Planck's constant. That light demonstrates both wavelike and particle-like behavior is known as wave-particle duality. All forms of electromagnetic radiation share these properties, although various forms including X-rays, visible light, microwaves, and radio waves interact differently with matter and have very different practical applications. Electromagnetic radiation can be generated by exciting matter to higher energies, such as by heating it. The emitted light can be either continuous (incandescent sources like the sun) or discrete (from specific types of excited atoms).

Contributors and Attributions

Adapted by Valeria D. Kleiman

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1.5: Early Experiments to Characterize the Atom

Learning Objectives

- To become familiar with the components and structure of the atom.

Long before the end of the 19th century, it was well known that applying a high voltage to a gas contained at low pressure in a sealed tube (called a gas discharge tube) caused electricity to flow through the gas, which then emitted light (Figure 1.5.1). Researchers trying to understand this phenomenon found that an unusual form of energy was also emitted from the cathode, or negatively charged electrode; this form of energy was called a cathode ray.

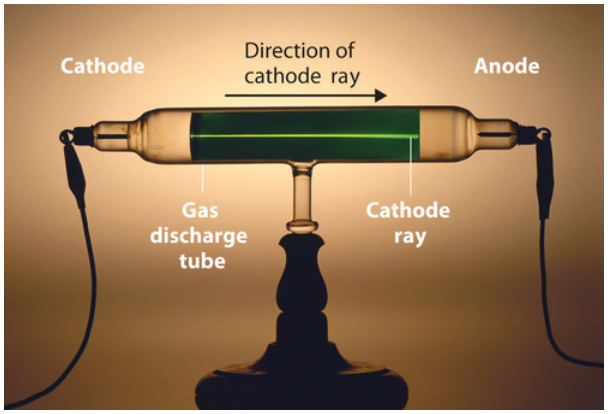


Figure 1.5.1: A Gas Discharge Tube Producing Cathode Rays. When a high voltage is applied to a gas contained at low pressure in a gas discharge tube, electricity flows through the gas, and energy is emitted in the form of light. Image used with Permission (CC BY-SA-NC).

In 1897, the British physicist J. J. Thomson (1856–1940) proved that atoms were not the most basic form of matter. He demonstrated that cathode rays could be deflected, or bent, by magnetic or electric fields, which indicated that cathode rays consist of charged particles (Figure 1.5.2). More important, by measuring the extent of the deflection of the cathode rays in magnetic or electric fields of various strengths, Thomson was able to calculate the mass-to-charge ratio of the particles. These particles were emitted by the negatively charged cathode and repelled by the negative terminal of an electric field. Because like charges repel each other and opposite charges attract, Thomson concluded that the particles had a net negative charge; these particles are now called electrons. Most relevant to the field of chemistry, Thomson found that the mass-to-charge ratio of cathode rays is independent of the nature of the metal electrodes or the gas, which suggested that electrons were fundamental components of all atoms.

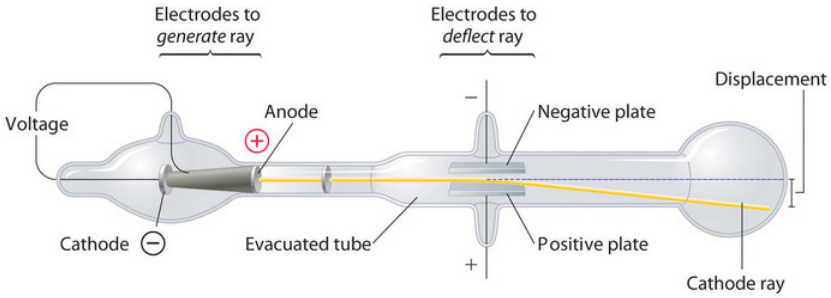


Figure 1.5.2: Deflection of Cathode Rays by an Electric Field. As the cathode rays travel toward the right, they are deflected toward the positive electrode (+), demonstrating that they are negatively charged. Image used with Permission (CC BY-SA-NC).
Schematic of cathode ray tube with deflection. Electrodes generate the ray. Another set of electrode plates deflect the ray, with the ray bending towards the positive plate.

Subsequently, the American scientist Robert Millikan (1868–1953) carried out a series of experiments using electrically charged oil droplets, which allowed him to calculate the charge on a single electron. With this information and Thomson's mass-to-charge ratio, Millikan determined the mass of an electron:

$$\frac{mass}{charge} \times charge = mass$$

It was at this point that two separate lines of investigation began to converge, both aimed at determining how and why matter emits energy. The video below shows how JJ Thompson used such a tube to measure the ratio of charge over mass of an electron



Measuring e/m For an Electron. Video from Davidson College demonstrating Thompson's e/m experiment.

Radioactivity

The second line of investigation began in 1896, when the French physicist Henri Becquerel (1852–1908) discovered that certain minerals, such as uranium salts, emitted a new form of energy. Becquerel's work was greatly extended by Marie Curie (1867–1934) and her husband, Pierre (1854–1906); all three shared the Nobel Prize in Physics in 1903. Marie Curie coined the term radioactivity (from the Latin *radius*, meaning "ray") to describe the emission of energy rays by matter. She found that one particular uranium ore, pitchblende, was substantially more radioactive than most, which suggested that it contained one or more highly radioactive impurities. Starting with several tons of pitchblende, the Curies isolated two new radioactive elements after months of work: polonium, which was named for Marie's native Poland, and radium, which was named for its intense radioactivity. Pierre Curie carried a vial of radium in his coat pocket to demonstrate its greenish glow, a habit that caused him to become ill from radiation poisoning well before he was run over by a horse-drawn wagon and killed instantly in 1906. Marie Curie, in turn, died of what was almost certainly radiation poisoning.



Figure 1.5.3: Radium bromide illuminated by its own radioactive glow. This 1922 photo was taken in the dark in the Curie laboratory.

Building on the Curies' work, the British physicist Ernest Rutherford (1871–1937) performed decisive experiments that led to the modern view of the structure of the atom. While working in Thomson's laboratory shortly after Thomson discovered the electron, Rutherford showed that compounds of uranium and other elements emitted at least two distinct types of radiation. One was readily absorbed by matter and seemed to consist of particles that had a positive charge and were massive compared to electrons. Because it was the first kind of radiation to be discovered, Rutherford called these substances α particles. Rutherford also showed that the particles in the second type of radiation, β particles, had the same charge and mass-to-charge ratio as Thomson's electrons; they are now known to be high-speed electrons. A third type of radiation, γ rays, was discovered somewhat later and found to be similar to the lower-energy form of radiation called x-rays, now used to produce images of bones and teeth.

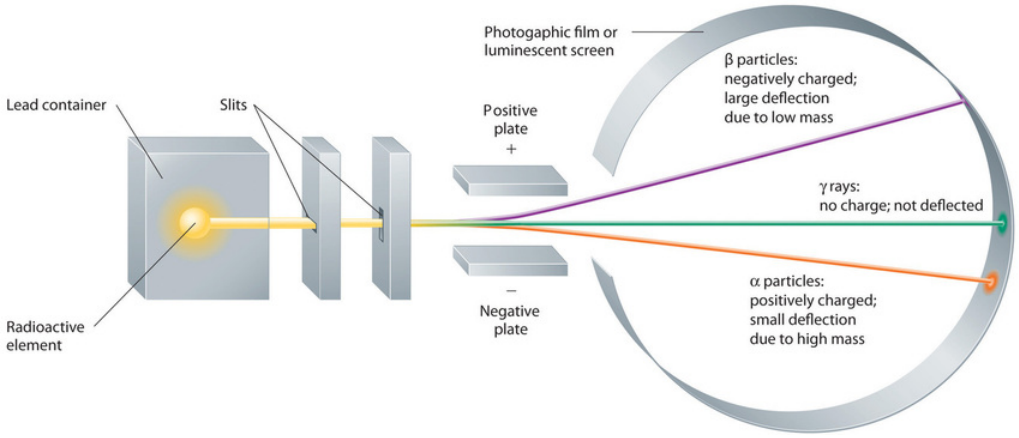


Figure 1.5.4: Effect of an Electric Field on α Particles, β Particles, and γ Rays. A negative electrode deflects negatively charged β particles, whereas a positive electrode deflects positively charged α particles. Uncharged γ rays are unaffected by an electric field. (Relative deflections are not shown to scale.) Image used with Permission (CC BY-SA-NC).

Schematic of a radioactive element in a lead container projected through slits to produce a narrow beam that impacts a photographic film. Two plates, one positive and one negative, deflect the beam depending on whether it is beta, gamma, or alpha. Beta particles deflect towards the positive plate and have a large deflection due to small mass. Alpha particles deflect towards the negative plate and have a small deflection due to high mass. Gamma rays do not deflect.

These three kinds of radiation—α particles, β particles, and γ rays—are readily distinguished by the way they are deflected by an electric field and by the degree to which they penetrate matter. As Figure 1.5.3 illustrates, α particles and β particles are deflected in opposite directions; α particles are deflected to a much lesser extent because of their higher mass-to-charge ratio. In contrast, γ rays have no charge, so they are not deflected by electric or magnetic fields. Figure 1.5.5 shows that α particles have the least penetrating power and are stopped by a sheet of paper, whereas β particles can pass through thin sheets of metal but are absorbed by lead foil or even thick glass. In contrast, γ-rays can readily penetrate matter; thick blocks of lead or concrete are needed to stop them.

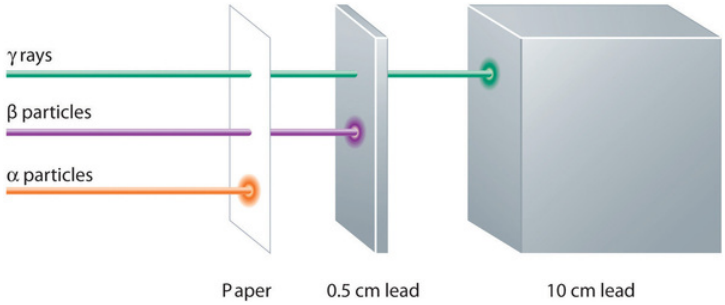


Figure 1.5.5: Relative Penetrating Power of the Three Types of Radiation. A sheet of paper stops comparatively massive α particles, whereas β particles easily penetrate paper but are stopped by a thin piece of lead foil. Uncharged γ rays penetrate the paper and lead foil; a much thicker piece of lead or concrete is needed to absorb them. Image used with Permission (CC BY-SA-NC).

Cartoon of gamma, alpha, and beta rays. The beta ray is stopped by paper. The alpha ray is stopped by .5 centimeter lead. The gamma ray is stopped by 10 centimeter lead.

The Atomic Model

Once scientists concluded that all matter contains negatively charged electrons, it became clear that atoms, which are electrically neutral, must also contain positive charges to balance the negative ones. Thomson proposed that the electrons were embedded in a uniform sphere that contained both the positive charge and most of the mass of the atom, much like raisins in plum pudding or chocolate chips in a cookie (Figure 1.5.6).

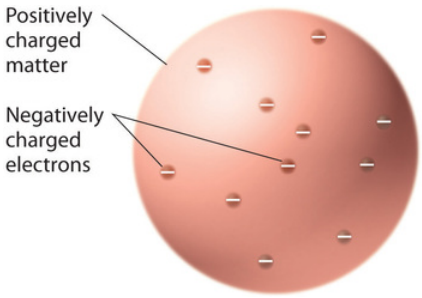


Figure 1.5.6: Thomson's Plum Pudding or Chocolate Chip Cookie Model of the Atom. In this model, the electrons are embedded in a uniform sphere of positive charge. Image used with Permission (CC BY-SA-NC).

Diagram of the plum-pudding model, with spheres of negatively charged electrons in a larger sphere of positively charged matter.

In a single famous experiment, however, Rutherford showed unambiguously that Thomson's model of the atom was incorrect. Rutherford aimed a stream of α particles at a very thin gold foil target (Figure 1.5.7*a*) and examined how the α particles were scattered by the foil. Gold was chosen because it could be easily hammered into extremely thin sheets, minimizing the number of atoms in the target. If Thomson's model of the atom were correct, the positively-charged α particles should crash through the uniformly distributed mass of the gold target like cannonballs through the side of a wooden house. They might be moving a little slower when they emerged, but they should pass essentially straight through the target (Figure 1.5.7*b*). To Rutherford's amazement, a small fraction of the α particles were deflected at large angles, and some were reflected directly back at the source (Figure 1.5.7*c*). According to Rutherford, "It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you."

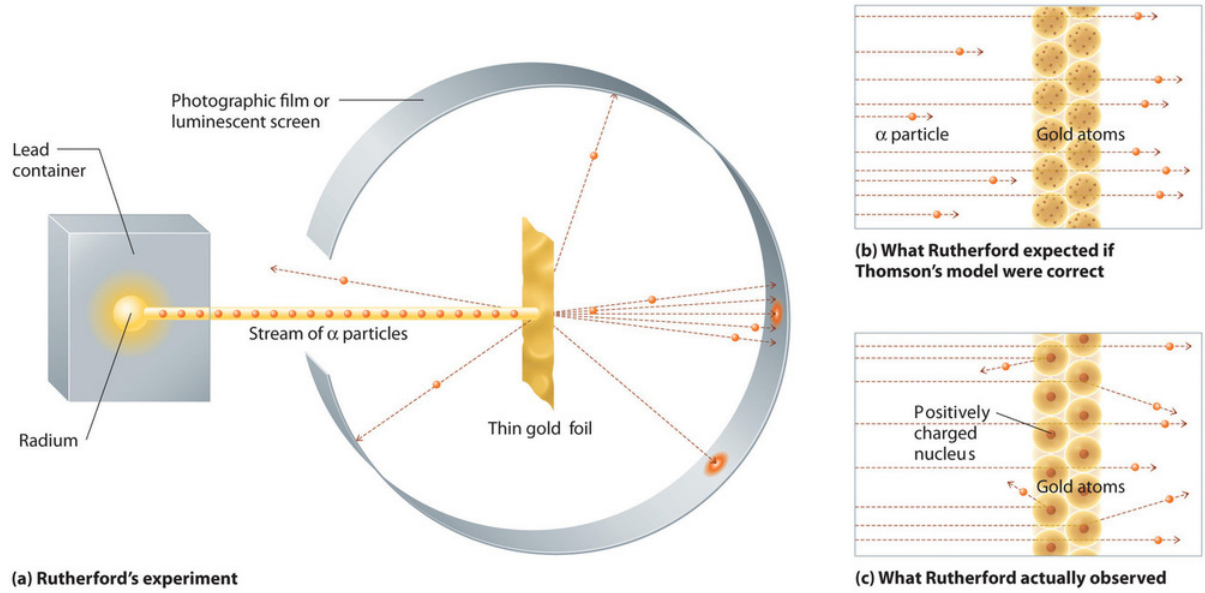


Figure 1.5.7: A Summary of Rutherford's Experiments. (a) A representation of the apparatus Rutherford used to detect deflections in a stream of α particles aimed at a thin gold foil target. The particles were produced by a sample of radium. (b) If Thomson's model of the atom were correct, the α particles should have passed straight through the gold foil. (c) However, a small number of α particles were deflected in various directions, including right back at the source. This could be true only if the positive charge were much more massive than the α particle. It suggested that the mass of the gold atom is concentrated in a very small region of space, which he called the nucleus. Image used with Permission (CC BY-SA-NC).

Schematic of Rutherford's gold foil experiment. Inset A: Radium fires a stream of alpha particles onto thin gold foil, showing particle deflection onto surrounding photographic film. Inset B: What Rutherford would have expected if Thomas' model were correct: alpha particles continuing through gold foil with no deflection. Inset C: What Rutherford actually observed: alpha particles deflected by nuclei of gold atoms.



The Nuclear Atom: The Nuclear Atom, YouTube(opens in new window) [youtu.be]

Rutherford's results were not consistent with a model in which the mass and positive charge are distributed uniformly throughout the volume of an atom. Instead, they strongly suggested that both the mass and positive charge are concentrated in a tiny fraction of the volume of an atom, which Rutherford called the nucleus. It made sense that a small fraction of the α particles collided with the dense, positively charged nuclei in either a glancing fashion, resulting in large deflections, or almost head-on, causing them to be reflected straight back at the source.

Although Rutherford could not explain why repulsions between the positive charges in nuclei that contained more than one positive charge did not cause the nucleus to disintegrate, he reasoned that repulsions between negatively charged electrons would cause the electrons to be uniformly distributed throughout the atom's volume.Today it is known that strong nuclear forces, which are much stronger than electrostatic interactions, hold the protons and the neutrons together in the nucleus. For this and other insights, Rutherford was awarded the Nobel Prize in Chemistry in 1908. Unfortunately, Rutherford would have preferred to receive the Nobel Prize in Physics because he considered physics superior to chemistry. In his opinion, "All science is either physics or stamp collecting."

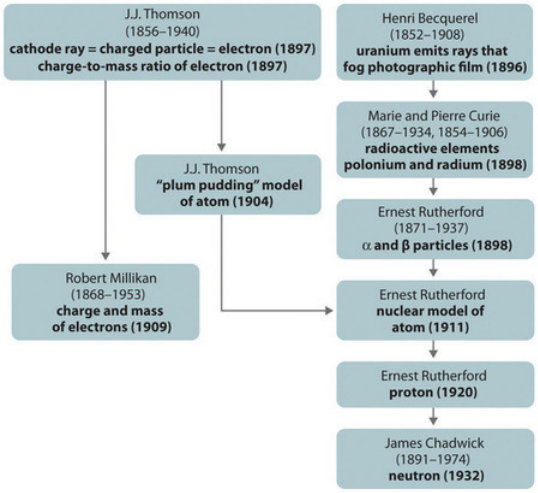


Figure 1.5.8: A Summary of the Historical Development of Models of the Components and Structure of the Atom. The dates in parentheses are the years in which the key experiments were performed. Image used with Permission (CC BY-SA-NC).

The historical development of the different models of the atom's structure is summarized in Figure 1.5.8. Rutherford established that the nucleus of the hydrogen atom was a positively charged particle, for which he coined the name proton in 1920. He also suggested that the nuclei of elements other than hydrogen must contain electrically neutral particles with approximately the same mass as the proton. The neutron, however, was not discovered until 1932, when James Chadwick (1891–1974, a student of Rutherford; Nobel Prize in Physics, 1935) discovered it. As a result of Rutherford's work, it became clear that an α particle contains two protons and neutrons, and is therefore the nucleus of a helium atom.

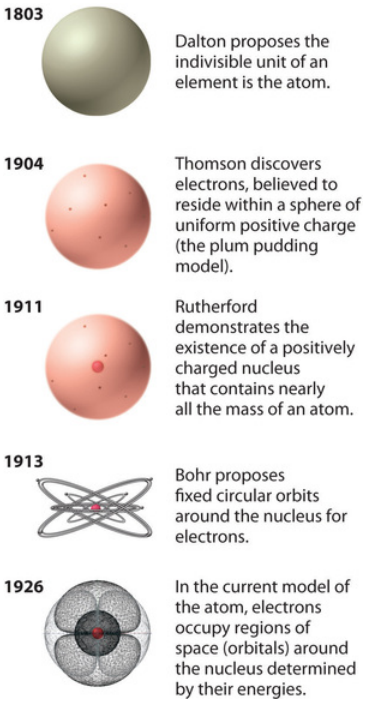


Figure 1.5.9: The Evolution of Atomic Theory, as Illustrated by Models of the Oxygen Atom. Bohr's model and the current model are described in Chapter 6, "The Structure of Atoms." Image used with Permission (CC BY-SA-NC).

Summary timeline of the evolution of atomic theory. Shows events at 1803 with Dalton's original proposal, 1904 with Thomson's model, 1911 with Rutherford's experiment, 1913 with Bohr's model, and 1926 with the current orbital model of the atom.

Rutherford's model of the atom is essentially the same as the modern model, except that it is now known that electrons are not uniformly distributed throughout an atom's volume. Instead, they are distributed according to a set of principles described by Quantum Mechanics. Figure 1.5.9 shows how the model of the atom has evolved over time from the indivisible unit of Dalton to the modern view taught today.

Summary

Atoms are the ultimate building blocks of all matter. The modern atomic theory establishes the concepts of atoms and how they compose matter. Atoms, the smallest particles of an element that exhibit the properties of that element, consist of negatively charged electrons around a central nucleus composed of more massive positively charged protons and electrically neutral neutrons. Radioactivity is the emission of energetic particles and rays (radiation) by some substances. Three important kinds of radiation are α particles (helium nuclei), β particles (electrons traveling at high speed), and γ rays (similar to x-rays but higher in energy).

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1.6: First attempts to model the H atom

Hydrogen Atoms Models

Model 1: The Rutherford model

The Coulomb force that exists between oppositely charge particles means that a positive nucleus and negative electrons should attract each other, and the atom should collapse. To prevent the collapse, the electron was postulated to be orbiting the positive nucleus. The Coulomb force (discussed below) is used to change the direction of the velocity, just as a string pulls a ball in a circular orbit around your head or the gravitational force holds the moon in orbit around the Earth. The origin for this hypothesis that suggests this perspective is plausible is the similarity of the gravity and Coulombic interactions. The expression for the force of gravity between two masses (Newton's Law of gravity) is

$$F_{gravity} \propto \frac{m_1 m_2}{r^2} \tag{1.6.1}$$

with

- m_1 and m_2 representing the **mass** of object 1 and 2, respectively and
- r representing the distance between the objects centers

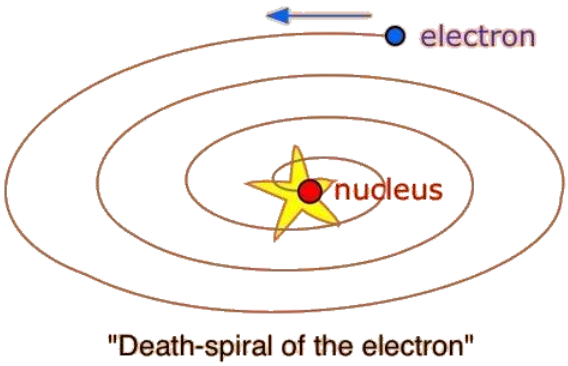
The expression for the Coulomb force between two charged species is

$$F_{Coulomb} \propto \frac{Q_1 Q_2}{r^2} \tag{1.6.2}$$

with

- Q_1 and Q_2 representing the **charge** of object 1 and 2, respectively and
- r representing the distance between the objects centers

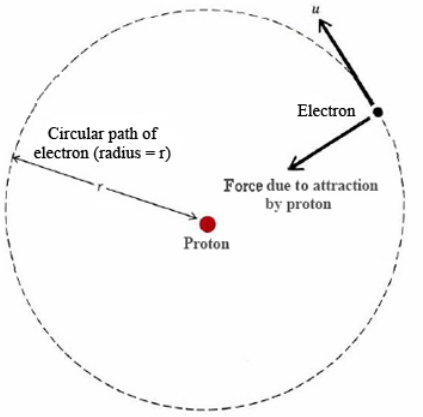
However this analogy has a problem too. An electron going around in a circle is constantly being accelerated because its velocity vector is changing. A charged particle that is being accelerated emits radiation. This property is essentially how a radio transmitter works. A power supply drives electrons up and down a wire and thus transmits energy (electromagnetic radiation) that your radio receiver picks up. The radio then plays the music for you that is encoded in the waveform of the radiated energy.



The classical death spiral of an electron around a nucleus.

Model 2A: The Classical Bohr Atom (Electron as a Particle)

The Bohr model is an early attempt to predict the allowed energies for single-electron atoms such as H, He^{+}, Li^{2+}, Be^{3+}, etc. Although Bohr's reasoning relies on classical concepts and hence, is not a correct explanation, the reasoning is interesting, and so we examine this model for its historical significance.



Bohr atom with an electron revolving around a fixed nucleus.

In 1911, Niels Bohr introduced his theory on the hydrogen atom. It assumed three main points.

1. Electrons move in circular orbitals.
2. Electrons are confined by Coulombic force
3. The wave nature of particles leads to quantization of energy levels of an atom.

Calculation of the orbits requires two assumptions.

Assumption 1: The electron is held in a circular orbit by electrostatic attraction

The Coulombic force of the attraction between the proton and electron can be written as

$$F_{coulombic} = \frac{e^2}{4\pi\epsilon_0 r^2} \tag{1.6.3}$$

where e is the charge of the electron, ϵ_0 is the perimittivity of free space, and r is the radius of the electron orbit. The Coulombic force is counterbalanced by centrifugal force

$$F_{centrifugal} = m_e \cdot \frac{v^2}{r} \tag{1.6.4}$$

where m_e is the mass of the electron, and v is the speed of the electron.

Assumption 2: The angular momentum is quantized

Bohr assumed that angular momentum of the electron was quantized (more below)

$$L = m_e v r = \frac{nh}{2\pi} \tag{1.6.5}$$

Setting Equations 1.6.3 and 1.6.4 equal to each other and solving for r and introducing Equation 1.6.5, the radius of the electron's orbit, gives

$$r = \frac{\epsilon_0 h^2 n^2}{\pi m_e e^2} \tag{1.6.6}$$

The symbol $\hbar$ is more commonly used in quantum mechanics, which is equivalent to $\frac{h}{2\pi}$, so the equation for the radius of the orbit can be written as

$$r = \frac{4\pi\epsilon_0 \hbar^2 n^2}{m_e e^2} \tag{1.6.7}$$

Using n = 1, you get an r value of $5.29 \times 10^{-11} m$. So Equation 1.6.7 can be rewritten as

$$r = n^2 a_o \tag{1.6.8}$$

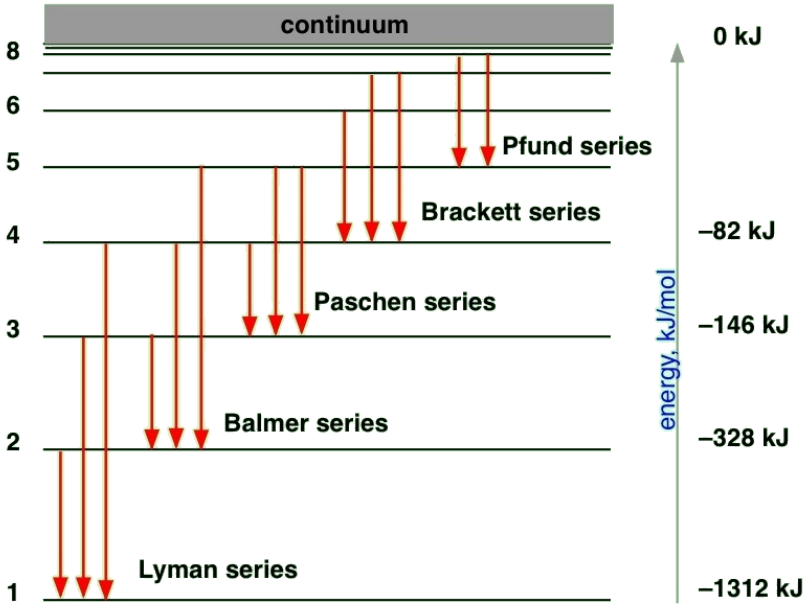
where

$$a_o = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = 5.29 \times 10^{-11} m \tag{1.6.9}$$

a_o is often called the **Bohr radius** (i.e. radius of an unexcited hydrogen atom).

Example 1.6.2: Quantized Orbits

A hydrogen atom is in its first excited state ($n = 2$). Using the Bohr theory of the atom, calculate the radius of the orbit.



Energy levels predicted by the Bohr model. Electron transitions and their resulting wavelengths for hydrogen. Energy levels are not to scale. from Stephen Lower.

The total energy of any system can be denoted by

$$E = T + V \tag{1.6.11}$$

the summation of the systems kinetic and potential energy, respectively. Setting the system to be an electron allows for the total energy of the electron in a Hydrogen atom to be calculated. In this case, the kinetic energy is

$$T = \frac{m_e v^2}{2} \tag{1.6.12}$$

and

$$V = -\frac{e^2}{4\pi\epsilon_0 r}. \tag{1.6.13}$$

Thus,

$$E = \frac{m_e v^2}{2} - \frac{e^2}{4\pi\epsilon_0 r} \tag{1.6.14}$$

By substituting $m_e v^2$ by equating $F_{coulombic}$ and $F_{centrifugal}$, and plugging in the Bohr radius for r (Equation 1.6.7) results in

$$E_n = \frac{-m_e e^4}{8\epsilon_0^2 h^2} \cdot \frac{1}{n^2} \tag{1.6.15}$$

or

$$E_n = -R\frac{1}{n^2} \tag{1.6.16}$$

where R is the Rydberg constant, which is sometimes referred to as R_∞ or R_H.

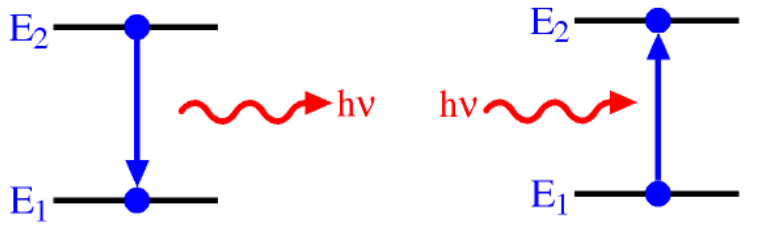
The energy of an orbital is **negative** indicating that the negatively charged electron is bound by the positive nucleus, and therefore it requires energy to free the electron from the atom. When assuming the nuclear mass is infinite compared to the mass of the electron, the value of R_∞ is $109737 cm^{-1}$ or $13.6\ eV$. When properly taking the nuclear mass into account, R_H is $109677 cm^{-1}$.

Example 1.6.3: Quantized Energies

A hydrogen atom is in its first excited state ($n = 2$). Using the Bohr theory of the atom, calculate the energy of the electron in this orbit.

State-to-state Transitions

A Hydrogen atom **emits** radiation when the e$^-$ makes a transition from a higher energy orbit (state, orbital) to a lower one. Alternatively, the electron can **absorb** a photon by "jumping" (changing) from one quantum state to another.



For emission, the conservation of energy in the **absorption** transition would look like

$$E_{n_i} + hv = E_{n_f} \tag{1.6.18}$$

and similarly for **emission** transition

$$E_{n_i} - hv = E_{n_f} \tag{1.6.19}$$

where the energy of the state is a function of the n_i and n_f integers for the initial and final states. For emission, we can now expand Equation 1.6.19 using Equation 1.6.15

$$\nu = \frac{E_{n_i} - E_{n_f}}{h} = \frac{e^4 m_e}{8\epsilon_0^2 h^3}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \tag{1.6.20}$$

Note

It is important to differentiate the energy of a photon $E = hv$ corresponding to a wave that propagates with speed c, frequency v and wavelength λ and the transition energy between 2 states $E_{n_f} - E_{n_i} = \Delta E$. Given that a transition (absorption pr emission) occurs when the change in Energy ΔE equals the energy of a photon, we can write Equation 1.6.19.

We can now identify the Rydberg constant R_H and it is not phenomenological, but can be expressed in terms of basic physical constants on the right hand side of Equation 1.6.20

$$R_H = \frac{m_e e^4}{8\epsilon_0^2 h^3}$$

$$\approx 2.19 \times 10^{-18} J$$

and in terms of wavenumbers using the $c = \lambda\nu$ relationship

$$R_H = \frac{m_e e^4}{8\epsilon_0^2 h^3 c}$$

$$\approx 109,737\, cm^{-1}$$

> *A demo of both wavelength and particle like Bohr atoms: http://www.walter-fendt.de/html5/phe...hrmodel_en.htm*

Contributions and Attributions

Adapted by Valeria D. Kleiman

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1.7: Matter as Waves

So far we have seen that to fully understand some experimental results with light we cannot simply treat them as *waves* but sometimes we have to consider that they also have properties of *particles* (photons). It turns out that for particles like the electrons, there are some experimental results whose results can only be understood if we treat those particles as waves.

Light Waves

Many of the properties of light (e.g., surface of water or acoustics) including **reflection, refraction, diffraction, and interference** can be explained, both qualitatively and quantitatively, in terms of light viewed as a wave.

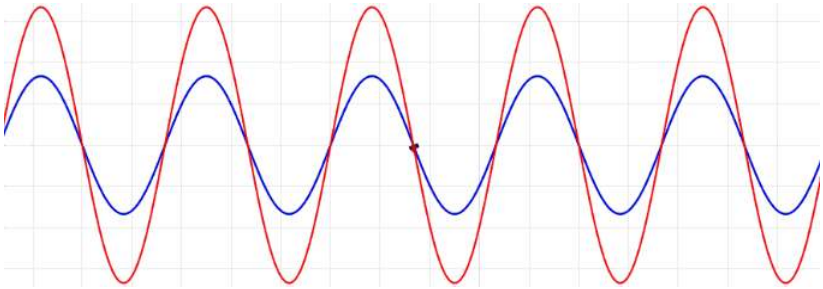


Figure: Linear Interference: The phenomenon of interference between waves is based on this idea. When two or more waves traverse the same space, the net amplitude at each point is the sum of the amplitudes of the individual waves. In some cases, such as in noise-cancelling headphones, the summed variation has a smaller amplitude than the component variations; this is called destructive interference. In other cases, such as in Line Array, the summed variation will have a bigger amplitude than any of the components individually; this is called constructive interference. (CC BY-SA 4.0 Internation; Lookangmany via Wikipedia)

The amplitudes of waves add. **Constructive interference** is obtained when identical waves are in phase and **destructive interference** occurs when identical waves are exactly out of phase, or shifted by half a wavelength.

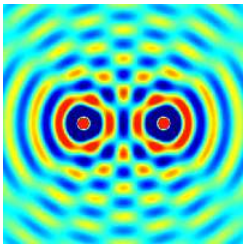


Figure: 2-D Interference: Interference of waves from two point sources. Image use with permission (Public Domain; Oleg Alexandrov)

Quantum Matter Waves

Continuing with our analysis of experiments that lead to the new quantum theory, we now look at the phenomenon of electron diffraction. It is well-known that *light* has the ability to diffract around objects in its path, leading to an interference pattern that is particular to the object. This is, in fact, how holography works (the interference pattern is created by allowing the diffracted light to interfere with the original beam so that the hologram can be viewed by shining the original beam on the image). A simple illustration of diffraction is the Young double slit experiment pictured below:

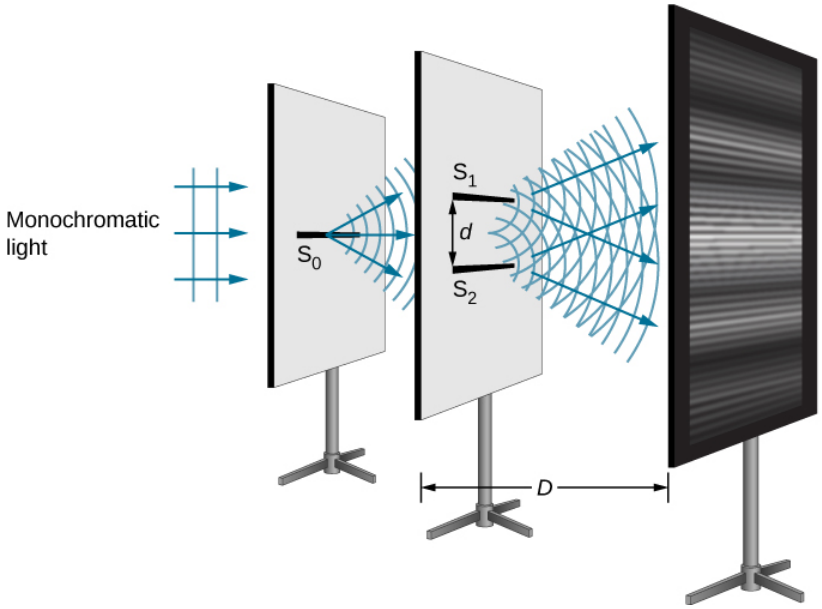


Figure: The double-slit interference experiment using monochromatic light and narrow slits. Fringes produced by interfering Huygens wavelets from slits S_1 and S_2 are observed on the screen. (CC-BY-SA; OpenStax).

Amazingly, if electrons are used instead of light in the double-slit experiment, and a fluorescent screen is used, one finds the same kind of interference pattern! This is shown in the electron double-slit diffraction pattern below:

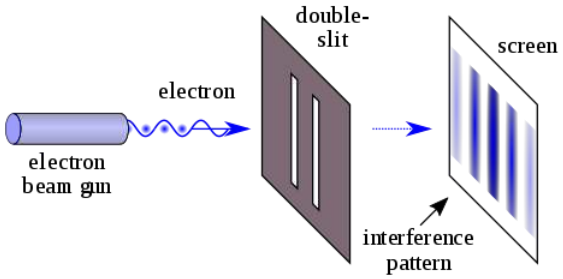


Figure: Particles of matter (like an electron) produce a wave pattern when two slits are used. (Public domain; NekoJaNekoJa).

Obviously, classical mechanics is not able to predict such a result. If the electrons are treated as classical particles, one would predict an intensity pattern corresponding to particles that can pass through one slit or the other, landing on the screen directly opposite the slit (i.e., no intensity maximum at the center of the screen):



Video: De Broglie's Theory can be seen in Young's Double Slit Experiment. https://youtu.be/O55XiriEaQI

Through such experiments, the idea that electrons can behave as waves, creating interference patterns normally associated with light, is now well-established. The fact that particles can behave as waves but also as particles, depending on which experiment you perform on them, is known as the *particle-wave duality*.

Deriving the De Broglie Wavelength

De Broglie derived his equation using well established theories through the following series of substitutions:

1. De Broglie first used Einstein's famous equation relating matter and energy:

$$E = mc^2 \tag{1.7.1}$$

with

- E = energy,
- m = mass,
- c = speed of light

2. Using Planck's theory which states every quantum of a wave has a discrete amount of energy given by Planck's equation:

$$E = h\nu \tag{1.7.2}$$

with

- E = energy,
- h = Plank's constant (6.62607 x 10^{-34} J s),
- ν= frequency

3. Since de Broglie believed particles and wave have the same traits, he hypothesized that the two energies would be equal:

$$mc^2 = h\nu \tag{1.7.3}$$

4. Because real particles do not travel at the speed of light, De Broglie submitted velocity (v) for the speed of light (c).

$$mv^2 = h\nu \tag{1.7.4}$$

5. Since the speed of a wave relates its frequency to its wavelength, de Broglie substituted v/λ for ν and arrived at the final expression that relates wavelength and particle with speed.

$$mv^2 = \frac{hv}{\lambda} \tag{1.7.5}$$

Hence:

$$\lambda = \frac{hv}{mv^2} = \frac{h}{mv} = \frac{h}{p} \tag{1.7.6}$$

At this stage, a majority of Wave-Particle Duality problems are simply "plug and chug" using Equation 1.7.6 with some variation of canceling out units

Example 1.7.1: Wavelength of a Baseball in Motion

Calculate the wavelength of a baseball, which has a mass of 149 g and a speed of 100 mi/h.

Given: mass and speed of object

Asked for: wavelength

Strategy:

A. Convert the speed of the baseball to the appropriate SI units: meters per second.
B. Substitute values into Equation 1.7.6 and solve for the wavelength.

Solution:

The wavelength of a particle is given by $\lambda = h/mv$. We know that m = 0.149 kg, so all we need to find is the speed of the baseball:

$$v = \left(\frac{100\ \cancel{mi}}{\cancel{h}}\right)\left(\frac{1\ \cancel{h}}{60\ \cancel{min}}\right)\left(\frac{1.609\ \cancel{km}}{\cancel{mi}}\right)\left(\frac{1000\ m}{\cancel{km}}\right)$$

B Recall that the joule is a derived unit, whose units are (kg•m^2)/s^2. Thus the wavelength of the baseball is

$$\lambda = \frac{6.626\times10^{-34}\ J\cdot s}{(0.149\ kg)\,(44.69\ m\cdot s)} = \frac{6.626\times10^{-34}\ \cancel{kg}\cdot m^{\cancel{2}}\cdot \cancel{s}^{\cancel{-2}}\cdot \cancel{s}}{\left(0.149\ \cancel{kg}\right)\left(44.69\ \cancel{m}\cdot \cancel{s^{-1}}\right)} = 9.95\times10^{-35}\ m \tag{1.7.7}$$

(You should verify that the units cancel to give the wavelength in meters.) Given that the diameter of the nucleus of an atom is approximately 10^{-14} m, the wavelength of the baseball is almost unimaginably small.

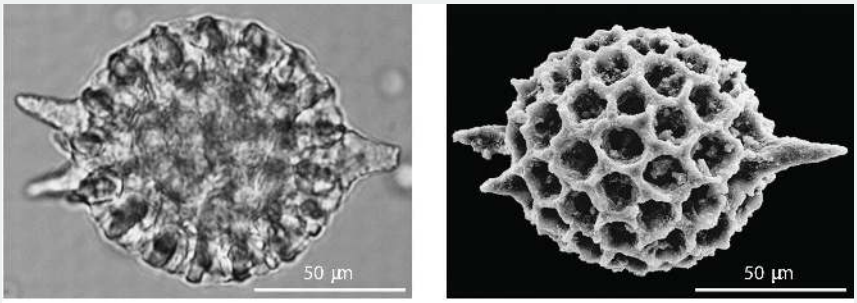
Example 1.7.2: Wavelength of an Electron in Motion

Find the de Broglie wavelength for an electron moving at the speed of $5.0\times10^6\ m/s$ (mass of an electron is $9.1\times10^{-31}\ kg$).

Size matters in Quantum Mechanics

As you calculated in Example 1.7.1, objects such as a baseball have such short wavelengths that they are best regarded primarily as particles. In contrast, objects with very small masses (such as photons) have large wavelengths and can be viewed primarily as waves. Objects with intermediate masses, however, such as electrons (Example 1.7.2), exhibit the properties of both particles *and* waves.To effectively diffract a wave, the wavelength of the wave must be comparable to the dimensions of the diffraction device!

Although we still usually think of electrons as particles, the wave nature of electrons is employed in an *electron microscope*, which has revealed most of what we know about the microscopic structure of living organisms and materials. Because the wavelength of an electron beam is much shorter than the wavelength of a beam of visible light, this instrument can resolve smaller details than a light microscope can:



(a) Radiolarian under light microscope (b) Radiolarian under electron microscope

A Comparison of Images Obtained Using a Light Microscope and an Electron Microscope. Because of their shorter wavelength, high-energy electrons have a higher resolving power than visible light. Consequently, an electron microscope (b) is able to resolve finer details than a light microscope (a). Radiolaria, which are shown here, are unicellular planktonic organisms. (CC BY-SA-NC; Anonymous by request).

Standing Waves

De Broglie also investigated why only certain orbits were allowed in Bohr's model of the hydrogen atom. He hypothesized that the electron behaves like a **standing wave** (a wave that does not travel in space). An example of a standing wave is the motion of a string of a violin or guitar. When the string is plucked, it vibrates at certain fixed frequencies because it is fastened at both ends (Figure 1.7.3). If the length of the string is L, then the lowest-energy vibration (the fundamental) has wavelength

$$\frac{\lambda}{2} = L$$
$$\lambda = 2L \tag{1.7.9}$$

Higher-energy vibrations are called *overtones* (the vibration of a standing wave that is higher in energy than the fundamental vibration) and are produced when the string is plucked more strongly; they have wavelengths given by

$$\lambda = \frac{2L}{n} \tag{1.7.10}$$

where n has any integral value. When plucked, all other frequencies die out immediately. Only the resonant frequencies survive and are heard. Thus, we can think of the resonant frequencies of the string as being quantized. Notice in Figure 1.7.3 that all overtones have one or more nodes, points where the string does not move. The amplitude of the wave at a node is zero.

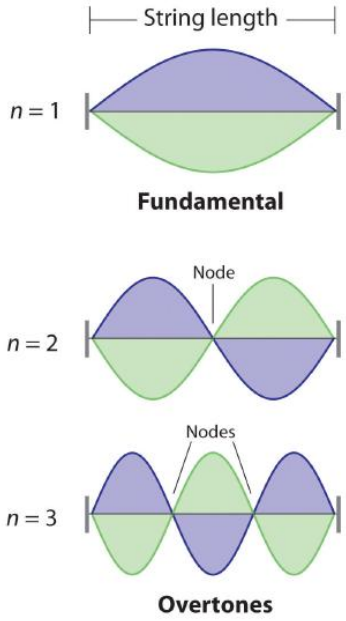


Figure 1.7.3: Standing Waves on a Vibrating String. The vibration with \(*n* = 1\) is the fundamental and contains no nodes. Vibrations with higher values of *n* are called overtones; they contain \(*n* − 1\) nodes.

Quantized vibrations and overtones containing nodes are not restricted to one-dimensional systems, such as strings. A two-dimensional surface, such as a drumhead, also has quantized vibrations. Similarly, when the ends of a string are joined to form a circle, the only allowed vibrations are those with wavelength

$$2\pi r = n\lambda \tag{1.7.11}$$

where r is the radius of the circle. De Broglie argued that Bohr's allowed orbits could be understood if the electron behaved like a *standing circular wave* (Figure 1.7.4). The standing wave could exist only if the circumference of the circle was an integral multiple of the wavelength such that the propagated waves were all in phase, thereby increasing the net amplitudes and causing *constructive interference*. Otherwise, the propagated waves would be out of phase, resulting in a net decrease in amplitude and causing *destructive interference*. The nonresonant waves interfere with themselves! De Broglie's idea explained Bohr's allowed orbits and energy levels nicely: in the lowest energy level, corresponding to $n = 1$ in Equation 1.7.11, one complete wavelength would close the circle. Higher energy levels would have successively higher values of *n* with a corresponding number of nodes.

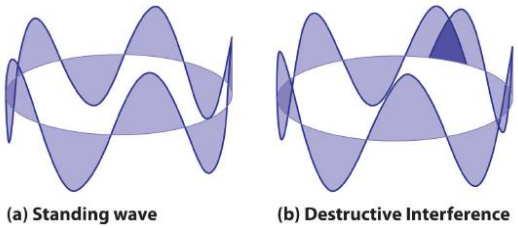


Figure 1.7.4: Standing Circular Wave and Destructive Interference. (a) In a standing circular wave with \(*n* = 5\), the circumference of the circle corresponds to exactly five wavelengths, which results in constructive interference of the wave with itself when overlapping occurs. (b) If the circumference of the circle is not equal to an integral multiple of wavelengths, then the wave does not overlap exactly with itself, and the resulting destructive interference will result in cancellation of the wave. Consequently, a standing wave cannot exist under these conditions.

Like all analogies, although the standing wave model helps us understand much about why Bohr's theory worked, it also, if pushed too far, can mislead. As you will see, some of de Broglie's ideas are retained in the modern theory of the electronic structure of the

atom: the wave behavior of the electron and the presence of nodes that increase in number as the energy level increases. Unfortunately, his (and Bohr's) explanation also contains one major feature that we now know to be incorrect: in the currently accepted model, the electron in a given orbit is *not* at the same distance from the nucleus.

Summary

An electron possesses both particle and wave properties. The modern model for the electronic structure of the atom is based on recognizing that an electron possesses particle and wave properties, the so-called **wave–particle duality**. Louis de Broglie showed that the wavelength of a particle is equal to Planck's constant divided by the mass times the velocity of the particle.

$$\lambda = \frac{h}{mv}$$

The electron in Bohr's circular orbits could thus be described as a **standing wave**, one that does not move through space. Standing waves are familiar from music: the lowest-energy standing wave is the **fundamental** vibration, and higher-energy vibrations are **overtones** and have successively more **nodes**, points where the amplitude of the wave is always zero.

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CHAPTER OVERVIEW

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2.3: The Schrödinger Equation for a Wave
2.4: Operators, Observables and Wavefunctions
2.5: Overview of Particle in a box
2.6: A Particle in a Multidimensional Box

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2.1: Describing Matter-Waves

Wavefunctions

In 1926 Max Born proposed a probabilistic description of the wave behavior of a particle. To understand the Born Interpretation, we can use an analogy with classical waves: the wavefunction $\Psi(x,t)$ is a function that describes the wave properties of a particle, and the behavior of this wave in space and time is governed by a wave equation.

Born described the wavefunction $\boldsymbol{(\Psi(x,y,z,t))}$ as a **Probability Amplitude**, and the square of the absolute value of this amplitude, $\boldsymbol{|\Psi(x,y,z,t)|^2}$, as a **Probability Density**. Whereas the value of the Amplitude has no physical meaning, the Probability Density is proportional to the probability of finding a particle/wave in a point in space at the time *t*. When doing an actual measurement, we always measure a specific volume of space, thus the Probability to find a particle in a given volume will be given by $|\Psi(x,y,z,t)|^2 \Delta V$ or, to be more precise

$$P = \int |\Psi(x,y,z,t)|^2 d\tau \tag{2.1.1}$$

where $d\tau$ is the volume element in three-dimensional space

From this interpretation, there are a few things that we can learn

If the value of $|\Psi(x_1,y_1,z_1,t)|^2$ is larger than $|\Psi(x_2,y_2,z_2,t)|^2$ then the probability to find the particle at position x_1, y_1, z_1 is larger than a position x_2, y_2, z_2.

If the value of $|\Psi(x_1,y_1,z_1,t)|^2$ is equal to the value of $|\Psi(x_2,y_2,z_2,t)|^2$ then the probability to find the particle at position (x_1,y_1,z_1) is equal than a position (x_2,y_2,z_2) at time t.

As a consequence of the probabilistic interpretation there are some important properties for the wavefunction

For each point in space $x_1,y_1,z_1)$, there is a single value of $|\Psi(x_1,y_1,z_1,t)|^2$, since it is not possible to have two different probabilities to find the particle in one point in space at a given time.

If we know that the particle exists within a limited space, then the total probability to find it within that space must be unity.

$$\int_{-\infty}^{\infty} |\Psi(x_1,t)|^2 = 1 \tag{2.1.2}$$

There are points in space where the wavefunction changes sign and thus $|\Psi(x_1,y_1,z_1,t)|^2 = 0$. These points are called **Nodes**. The probability to find the particle at a node is null.

The simplest particle-wave: a Free Electron

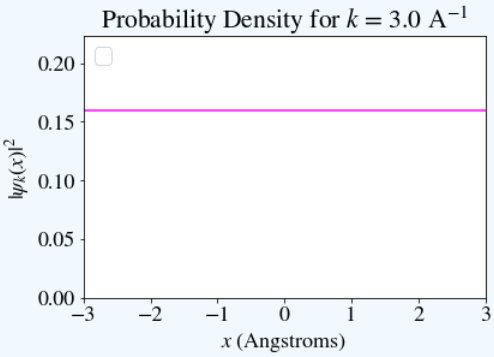
We start by describing a free electron: a particle that is not under the influence of a potential.
As any other particle, the state of a ***Free electron*** is described with a wavefunction $\psi(x)$ and we want to answer the question: "Where is the electron?"

Like any other free particle moving, this electron will have momentum $p = \frac{h}{\lambda}$. If the electron is described by a single wave, then it has a single value of the momentum $p = hk$, where $k = \frac{1}{\lambda}$ is called the wave-vector.

We can evaluate the probability of finding the electron at a given point in space, or, even better, we can plot the probability density as a function of position for a range of x values, to see what is the probability to find in different places at a given time.

Example 2.1.1 : A free electron with fully defined momentum

For an electron with a momentum $p = 3.16 \cdot 10^{-24} \frac{kg\,m}{s}$ the wave-vector is $k = 3.0$ Å^{-1} the probability density $|\psi(x)|^2$ as a function of position is shown below

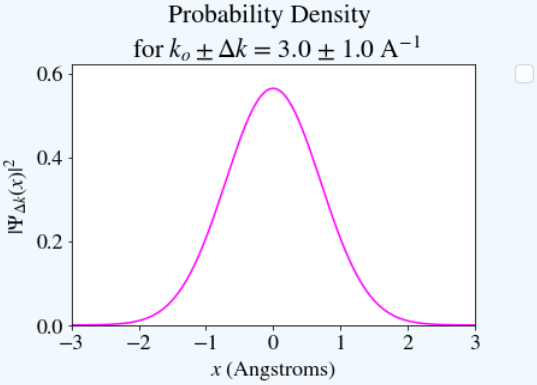


This plot shows that the probability to find a free electron is exactly the same for ALL values of x, i.e. $|\psi(-3)|^2 = |\psi(0)|^2 = |\psi(-1.2)|^2$, etc) . Even though we know exactly the momentum of the electron, we know nothing specific about its position. At the time of the measurement, it has the same probability of being found at any possible point in this one-dimensional space.

Example 2.1.2: A free electron with some uncertainty in the momentum

What happens if instead of having the free electron with an exact value of momentum, we allow the momentum to have a range of values (uncertainty in the momentum $= \Delta p$)?

For an electron with wave-vector momentum $k = 3.0 \pm 1.0$Å^{-1} (or momentum $p = 3.16 \pm 1.05 \cdot 10^{-24} \frac{kg \cdot m}{s}$, we can evaluate the values of the probability density $|\psi(x)|^2$ as a function of position as shown below

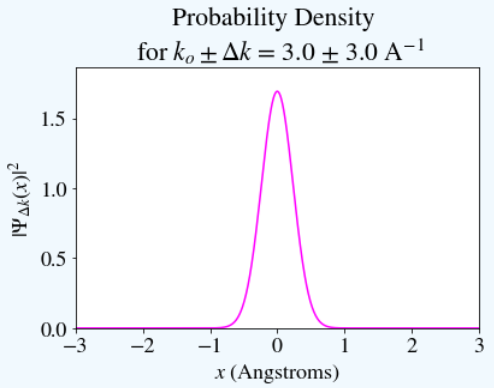


Now, the probability to find the electron at $x = 0$ Å is larger than at $x = 1.2$ Å and much larger than at $x = 3$ Å. This is telling us that it is very likely to find the electron near $x = 0.$, but it will be very unlikely to find the electron at large values of x. We can also say that the probability to find the particle somewhere between $x = -2$ Å and $x = 2$ Å is almost 100%, whereas the probability to find it at values of $x \leq -2$ Å or $x \geq 3$ Å is almost 0.

Example 2.1.3: A free electron with a large uncertainty in the momentum

What happens if we now allow the electron to have a very large range of values of momenta (very large Δp)?

For an electron with wave-vector momentum $k = 3.0 \pm 3.0$Å^{-1} (or moment with any value from $p = 0$ to $7.32 \cdot 10^{-24} \frac{kg \cdot m}{s}$, we can evaluate the values of the probability density $|\psi(x)|^2$ as a function of position as shown below



Now the probability to find the electron at $x = 0$ Å is much larger than at $x = 1.2 or x = 3$ Å. When the particle can have these varying values of momenta, we have almost (not quite, but close to) 100% probability to find it somewhere between $x = -1$ Å and $x = 1$ Å, meaning that the position of the particle is much more certain than before.
Even though we now know less about the exact value of the momentum, we know a bit more precisely where to look for the electron.

Obervation:

By plotting the probability density for the free electron we observe that as the uncertainty on the momentum increases (larger Δp, the uncertainty in the position of the electron decreases. This relationship is described by **Heisenberg Uncertainty Principle**.

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2.2: The Uncertainty Principle

The Heisenberg Uncertainty Principle

Because a wave is a disturbance that travels in space, it has no fixed position. One might therefore expect that it would also be hard to specify the exact position of a *particle* that exhibits wavelike behavior. A characteristic of light is that is can be bent or spread out by passing through a narrow slit. You can literally see this by half closing your eyes and looking through your eye lashes. This reduces the brightness of what you are seeing and somewhat fuzzes out the image, but the light bends around your lashes to provide a complete image rather than a bunch of bars across the image. This is called diffraction.

This behavior of waves is captured in Maxwell's equations (1870 or so) for electromagnetic waves and was and is well understood. An "uncertainty principle" for light is, if you will, merely a conclusion about the nature of electromagnetic waves and nothing new. De Broglie's idea of wave-particle duality means that particles such as electrons which exhibit wavelike characteristics will also undergo diffraction from slits whose size is on the order of the electron wavelength.

This situation was described mathematically by the German physicist Werner Heisenberg (1901–1976; Nobel Prize in Physics, 1932), who related the position of a particle to its momentum. Referring to the electron, Heisenberg stated that “at every moment the electron has only an inaccurate position and an inaccurate velocity, and between these two inaccuracies there is this uncertainty relation.” Mathematically, the **Heisenberg uncertainty principle** states that the uncertainty in the position of a particle (Δx) multiplied by the uncertainty in its momentum [$\Delta(mv)$] is greater than or equal to Planck’s constant divided by 4π:

$$(\Delta x)\,(\Delta\,[mv]) \geq \frac{h}{4\pi} \tag{2.2.1}$$

Because Planck’s constant is a very small number, the Heisenberg uncertainty principle is important only for particles such as electrons that have very low masses. These are the same particles predicted by de Broglie’s equation to have measurable wavelengths.

If the precise position x of a particle is known absolutely ($\Delta x = 0$), then the uncertainty in its momentum must be infinite:

$$(\Delta\,[mv]) = \frac{h}{4\pi\,(\Delta x)} = \frac{h}{4\pi\,(0)} = \infty \tag{2.2.2}$$

Because the mass of the electron at rest (m) is both constant and accurately known, the uncertainty in $\Delta(mv)$ must be due to the Δv term, which would have to be infinitely large for $\Delta(mv)$ to equal infinity. That is, according to Equation 2.2.2, the more accurately we know the exact position of the electron (as $\Delta x \rightarrow 0$), the less accurately we know the speed and the kinetic energy of the electron (1/2 mv^2) because $\Delta(mv) \rightarrow \infty$. Conversely, the more accurately we know the precise momentum (and the energy) of the electron [as $\Delta(mv) \rightarrow 0$], then $\Delta x \rightarrow \infty$ and we have no idea where the electron is.

Bohr’s model of the hydrogen atom violated the Heisenberg uncertainty principle by trying to specify *simultaneously* both the position (an orbit of a particular radius) and the energy (a quantity related to the momentum) of the electron. Moreover, given its mass and wavelike nature, the electron in the hydrogen atom could not possibly orbit the nucleus in a well-defined circular path as predicted by Bohr. You will see, however, that the *most probable radius* of the electron in the hydrogen atom is exactly the one predicted by Bohr’s model.

Example 2.2.1: Quantum Nature of Baseballs

Calculate the minimum uncertainty in the position of a pitched baseball that has a mass of exactly 149 g and a speed of 100 ± 1 mi/h.

Given: mass and speed of object

Asked for: minimum uncertainty in its position

Strategy:

A. Rearrange the inequality that describes the Heisenberg uncertainty principle (Equation 2.2.1) to solve for the minimum uncertainty in the position of an object (Δx).
B. Find Δv by converting the velocity of the baseball to the appropriate SI units: meters per second.
C. Substitute the appropriate values into the expression for the inequality and solve for Δx.

Solution:

A The Heisenberg uncertainty principle (Equation 2.2.1) tells us that

$$(\Delta x)(\Delta(mv)) = h/4\pi \tag{2.2.3}$$

. Rearranging the inequality gives

$$\Delta x \geq \left(\frac{h}{4\pi}\right)\left(\frac{1}{\Delta(mv)}\right)$$

B We know that h = 6.626 × 10^{-34} J•s and m = 0.149 kg. Because there is no uncertainty in the mass of the baseball, Δ(mv) = mΔv and Δv = ±1 mi/h. We have

$$\Delta u = \left(\frac{1\ \cancel{mi}}{\cancel{h}}\right)\left(\frac{1\ \cancel{h}}{60\ \cancel{min}}\right)\left(\frac{1\ \cancel{min}}{60\ s}\right)\left(\frac{1.609\ \cancel{km}}{\cancel{mi}}\right)\left(\frac{1000\ m}{\cancel{km}}\right) = 0.4469\ m/s \tag{2.2.4}$$

C Therefore,

$$\Delta x \geq \left(\frac{6.626 \times 10^{-34}\ J \cdot s}{4\,(3.1416)}\right)\left(\frac{1}{(0.149\ kg)\,(0.4469\ m \cdot s^{-1})}\right) \tag{2.2.5}$$

Inserting the definition of a joule (1 J = 1 kg•m^2/s^2) gives

$$\Delta x \geq \left(\frac{6.626 \times 10^{-34}\ \cancel{kg} \cdot m^{\cancel{2}} \cdot s}{4\,(3.1416)\left(\cancel{s^2}\right)}\right)\left(\frac{1\ \cancel{s}}{\left(0.149\ \cancel{kg}\right)(0.4469\ \cancel{m})}\right) \tag{2.2.6}$$

$$\Delta x \geq 7.92 \pm \times 10^{-34}\ m \tag{2.2.7}$$

This is equal to 3.12×10^{-32} inches. We can safely say that if a batter misjudges the speed of a fastball by 1 mi/h (about 1%), he will not be able to blame Heisenberg's uncertainty principle for striking out.

Exercise 2.2.2

Calculate the minimum uncertainty in the position of an electron traveling at one-third the speed of light, if the uncertainty in its speed is ±0.1%. Assume its mass to be equal to its mass at rest.

Answer

6 × 10^{-10} m, or 0.6 nm (about the diameter of a benzene molecule)

Videos and Examples

- de Broglie Waves - Sixty Symbols - a bit of history and explanation (as well as wave particle duality can be explained)
- Calculating the wavelength of a proton - Josh Samson
- Calculating the wavelength of a small car - Prof. Heath
- What is the Uncertainty Principle? - Minute Physics
- AP Chem Heisenberg Uncertainty Principle - Mind Bite
- deBroglie Example - about education
- Heisenberg uncertainty principle quiz worked out - C Craig
- Quantum Chemistry - Ohio State
- Quantum Chemistry Quizzes - mhe education
- AP Chemistry Chapter 7 Review - Science Geek

Answers for these quizzes are included.

Summary

Werner Heisenberg's **uncertainty principle** states that it is impossible to precisely describe both the location and the speed of particles that exhibit wavelike behavior.

$$(\Delta x)\,(\Delta\,[mv]) \geqslant \frac{h}{4\pi}$$

Contributors and Attributions

- Modified by Joshua Halpern (Howard University)

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2.3: The Schrödinger Equation for a Wave

The time-independent Schrödinger equation

When matter is described as waves, we can use a wave-equation to describe it mathematically. The wave equation will describe how the wave evolves in time and in space. In here, we will focus on the properties of the wave in space, thus the governing equation for a wave-particle in a one dimensional space (first proposed by Edwin Schrödinger in 1926) is

$$-\frac{\hbar}{2m}\frac{d^2\psi(x)}{dx^2}+V(x)\,\psi(x)=E\cdot\psi(x) \tag{2.3.1}$$

Caution

Don't panic. We want to understand the equation but we will not use its math

There are 3 components to this equation

- $\psi(x)$ is the function of the wave that describes the particle (wavefunction). If we know how to express $\psi(x)$ and how to evaluate it for values of x, then we can evaluate all the properties of the particle-wave that can be measured in a laboratory. For a given particle-wave, a specific wavefunction $\psi(x)$ is called a **state**. For an atom or molecule, each $\psi(x)$ is called an **orbital**.
- E is the numerical value (in units of energy) that corresponds to the energy of the particle-wave in the specific state represented by $\psi(x)$.
- $-\frac{\hbar}{2m}\frac{d^2}{dx^2}$ and$V(x)$ are called operators. The sum$-\frac{\hbar}{2m}\frac{d^2}{dx^2}+V(x)=H$ is called the Hamiltonian operator.

Example 2.3.1: The wavefunction of a particle in a box

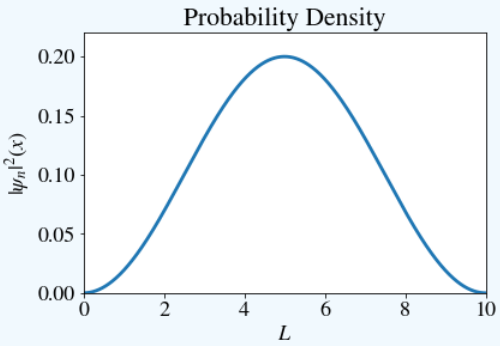
Consider an electron that can move in one-dimensional space (moving within a line). If this electron is confined within a 1-D box of length 10 Å its state will be described by

$$\psi_1(x)=\sqrt{\frac{2}{10\text{Å}}}sin(\frac{\pi}{10\text{Å}}\cdot x) \tag{2.3.2}$$

Solution

Since we know the wavefunction for the particular state 1, we can plot the probability density for all possible positions in the box where the particle could be found.

$$|\psi_1(x)|^2=\frac{2}{10\text{Å}}\left(sin(\frac{\pi}{10\text{Å}}\cdot x)\right)^2 \tag{2.3.3}$$



If we were to measure in the lab the position of this particle, there would be a 0.07 probability to find it at $x=8$Å. The energy of state 1 is given by $E=6.025\cdot10^{-20}Joules$

To describe particle-waves that can move in 3 dimensions (for example, the H atom, with 1 electron and 1 proton), we use a 3-dimensional wavefunction $\psi(x,y,z)$ with the Schrödinger equation also written for 3 dimensions. The probability density would

be plotted in 4 dimensions (one for each coordinate x, y, z, and a 4th for the value of Probability Density at each point in space $|\psi(x, y, z)|^2$.

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2.4: Operators, Observables and Wavefunctions

What are Operators?

Operators are rules to convert a function or number into another a function or number. Operators are symbolized by a ^ above a letter.

The symbol +represents the operator **sum** , which takes 2 numbers and adds them together, the symbol · corresponds to the operator **multiplication**, which multiplies two numbers or functions together to obtain a new number or new function. Other examples of operators are

- Differentiation = $\hat{D} = \frac{d}{dx}$ applied to the function $f(x)$ yields the derivative of that function

$$\frac{d}{dx} f(x) = \frac{df(x)}{dx} = f'(x) \tag{2.4.1}$$

$$\hat{D}^2 = \frac{d^2}{dx^2} f(x) = \frac{d}{dx}\frac{df(x)}{dx} = f\text{''}(x) \tag{2.4.2}$$

- Multiplication This operator multiplies a number or a function to another function

$$\hat{x} f(x) = x \cdot f(x) = x f(x) \qquad \text{or} \qquad 3 \cdot f(x) = 3 f(x) \tag{2.4.3}$$

In Quantum Mechanics, operators are used to write the Schrödinger equation for a particle-wave.

Example 2.4.1

What is the result of applying the operator $\frac{d}{dx}$ to the function $f(x) = 4x^3 - 22x$

Solution

$$\frac{d}{dx} f(x) = \frac{d}{dx}(4x^3 - 22x) = \frac{d(4x^3 - 22x)}{dx} = \frac{d(4x^3)}{dx} - \frac{d(22x)}{dx} = 3 \cdot 4x^2 - 22 = 12x^2 - 22$$

Observables

In Quantum Mechanics, each **observable property** (something that we can measure in the lab, like the energy, the momentum, the position, etc) has a corresponding **operator**.

Energy

If we want to measure the energy of a particle, we look for the corresponding operator, that is the Hamiltonian, $\hat{H}$

The Hamiltonian $\hat{H}$ has two components,, one associated with kinetic energy $\hat{T}$ and one associated with potential energy $\hat{V}$.

$$\hat{H} = \hat{T} + \hat{V} \tag{2.4.4}$$

For a particle-wave that is moving in one-dimension, $\hat{T} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$. If the particle is moving in 3-dimensions, the operator associated with the Kinetic Energy becomes

$$\hat{T} = -\frac{\hbar^2}{2m} \cdot \left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2} \right) \tag{2.4.5}$$

The operator associated with Potential Energy will depend on each specific system (whether the system is rotating or oscillating, or whether it includes 1, 2 or multiple particles, etc). For each system there will be a specific $\hat{V}$ that will be use to describe the particular conditions of the particle-wave, thus for each specific system there is a particular Hamiltonian.

For each system there is one specific Schrödinger equation where we apply the Hamiltonian operator to the function of the wave and obtain as a result the energy of the system.

$$\hat{H}\psi(x) = E \cdot \psi(x) \tag{2.4.6}$$

Equation 2.4.6 is a differential equation, and quantum mechanics is devoted to find the functions that are proper solutions to this differential equation. This means to find the functions $\psi(x)$ that when we apply the Hamiltonian to it, we obtain a number E corresponding to the energy, multiplied by the same function $\psi(x)$.

Since for each Hamiltonian, there are always an infinite number of $\psi(x)$ and E solutions, each pair corresponds to a **state** of the system (ground state, excited state 1 excited state 2, etc) and is identified by its quantum numbers.

Momentum

If we want to measure the momentum of a particle, we look for the corresponding operator, that is the momentum operator, $\hat{p}$.

The momentum operator is given by $\hat{P} = -i\hbar\frac{d}{dx}$

There is an equivalent equation for the momentum

$$\hat{P}\psi(x) = p \cdot \psi(x) \tag{2.4.7}$$

where p corresponds to the numerical value of the momentum that we would measure in the lab if the system is found in a state described by the wavefucntion $\psi(x)$.

Wavefunctions

Although this time-independent Schrödinger Equation can be useful to describe a matter wave in free space, we are most interested in waves when confined to a small region, such as an electron confined in a small region around the nucleus of an atom. Several different models have been developed that provide a means by which to study a matter-wave when confined to a small region: the particle in a box (infinite well), the Hydrogen atom, molecules. We will discuss each of these in order to develop a greater understanding for how a wave behaves when it is in a bound state.

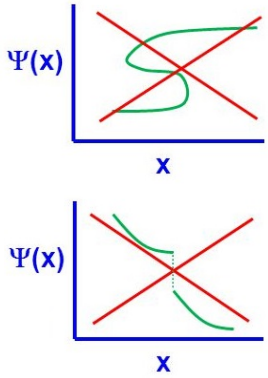


Figure 2.4.1 : Two unacceptable wavefunctions. (left) This is not a single-valued function and (right) this is a non-continuous function

There are four general aspects that are applicable to an acceptable wavefunction

1. An acceptable wavefunction will be the solution of the Schrödinger equation (either Equations 2.4.6).
2. An acceptable wavefunction must be normalizable so will approaches zero as position approaches infinity.
3. An acceptable wavefunction must be a continuous function of position.
4. An acceptable wavefunction will have a continuous slope (Figure 2.4.2).

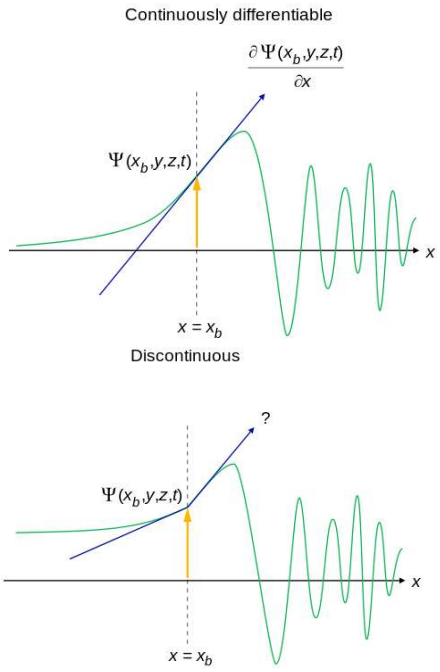


Figure 2.4.2:Wavefunction continuity in space.

Interpretation

As we saw before, the physical significance cannot be found from the function itself, instead the absolute square of the wavefunction, which also is called the square of the modulus is used.

$$|\psi(r,t)|^2 \tag{2.4.8}$$

where r is a vector (x, y, z) specifying a point in three-dimensional space. The square is used, rather than the modulus itself, just like the intensity of a light wave depends on the square of the electric field. At one time it was thought that for an electron described by the wavefunction $\psi(r)$, the quantity $e\psi^*(ri)\psi(r_i)d\tau$ was the amount of charge to be found in the volume $d\tau$ located at r_i. However, Max Born found this interpretation to be inconsistent with the results of experiments.

The Born interpretation, which generally is accepted today, is that $|\psi(r,t)|^2\ d\tau$ is the probability that the electron is in the volume $d\tau$ located at r_i at time t. The Born interpretation therefore calls the wavefunction the probability amplitude, the absolute square of the wavefunction is called the probability density, and the probability density times a volume element in three-dimensional space ($d\tau$) is the probability.

Normalization

A probability is a real number between 0 and 1. An outcome of a measurement which has a probability 0 is an impossible outcome, whereas an outcome which has a probability 1 is a certain outcome. The probability of a measurement of x yielding a result between $-\infty$ and $+\infty$ is

$$P_{x\in-\infty:\infty} = \int_{-\infty}^{\infty} |\psi(x)|^2 dx. \tag{2.4.9}$$

However, a measurement of x *must* yield a value between $-\infty$ and $+\infty$, since the particle has to be located somewhere. It follows that $P_{x\in-\infty:\infty}(t) = 1$, or

$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx = 1, \tag{2.4.10}$$

which is generally known as the *normalization condition* for the wavefunction.

Summary

For each **observable property**, we can construct an equation that will connect the **operator** to the **wavefunction** describing the specific state of a system. When studying a quantum mechanical system, we start a problem by finding the Hamiltonian that describes the system, and then we look for all the possible wavefunctions $\psi(x)$ that can solve Equation 2.4.6. Each solution corresponds to one **state** of the system.

Contributions and Attributions

- Valeria D. Kleiman
- The wavefunction section is from David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")

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2.5: Overview of Particle in a box

A One-Dimension Box

The system consists of a particle (one electron, one molecule, etc) that can only reside **inside** a one dimensional box (a line of length L). Outside the box there is an infinite potential, thus the particle cannot escape. Inside the box, no force or potential acts on the particle, thus inside the box, it is free to move.

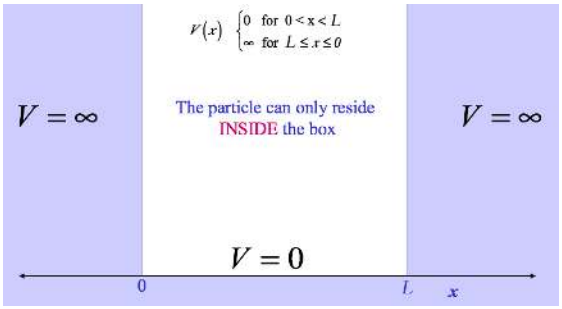


Figure 2.5.1: Diagram of a One-dimensional box with infinite potential walls. (Copyright: Valeria D. Kleiman)

Since the $|\psi(x)|^2$ gives the probability of finding the particle in space, that probability must be zero outside the box. If the probability density is null, that means $\psi(x) = 0$ outside the box and

$$\psi(x) = 0 \text{ for any position } x < 0 \text{ and for any position } x > 0. \tag{2.5.1}$$

Since the Probability density outside the box is $= 0$ and the probability inside the box is $= 0$, this means that at the edges,

$$\psi(0) = 0 \text{ and } \psi(L) = 0 \tag{2.5.2}$$

. This is called the **Boundary Condition**.

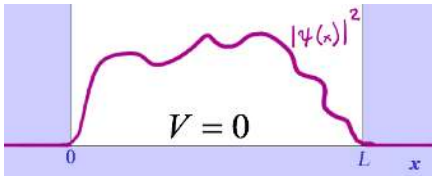


Figure 2.5.2: The wavefunction can have any value inside the box, but it must be null outside . (Copyright; Valeria D. Kleiman)

The Schrödinger equation for a 1D box allows us to find all the possible analytical forms of $\psi(x)$ inside the box and the energy of each of those possible states. In this case the equation is

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = E \cdot \psi(x) \tag{2.5.3}$$

where $\hbar$ is Planck's constant divided by 2π and m is the mass of the particle.

Although we don't need to know *how* to solve this equation, it is very useful to take a look and understand the solutions which are of the form

$$\psi_n(x) = \sqrt{\frac{2}{L}} sin(\frac{n\,\pi}{L} \cdot x) \tag{2.5.4}$$

where L is the length of the box, x is the variable in the wavefunction, and n is the quantum number that identifies each possible state. The are infinite solutions for Equation 2.5.3, each one for a different value of n. If we choose one state (i.e. $n = 1$) and we replace $\psi_1(x)$ into Equation 2.5.3 we obtain the $energy(E_1)$ for that specific state.

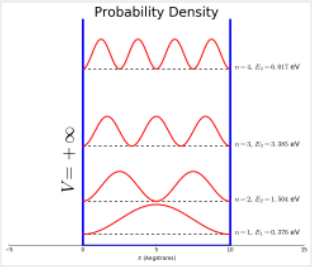
$$E_n = \frac{h^2}{8mL^2}n^2 \tag{2.5.5}$$

Each of these solutions will have a different probability density and a different energy.

Example 2.5.1

What are the first 4 possible states for the particle in a box of length 10Å

Solution

n	$\psi_n(x)$	E_n	Probability Density
1	$\sqrt{\frac{2}{L}}sin(\frac{\pi}{L}\cdot x)$	$E_n = \frac{h^2}{8mL^2}1 = 0.376eV$	
2	$\sqrt{\frac{2}{L}}sin(\frac{2\pi}{L}\cdot x)$	$E_n = \frac{h^2}{8mL^2}4 = 1.504eV$	
3	$\sqrt{\frac{2}{L}}sin(\frac{3\pi}{L}\cdot x)$	$E_n = \frac{h^2}{8mL^2}9 = 3.385eV$	
4	$\sqrt{\frac{2}{L}}sin(\frac{4\pi}{L}\cdot x)$	$E_n = \frac{h^2}{8mL^2}16 = 6.017eV$	

The graph shows the probability density for each state. It is plotted with each curve vertically displaced to emphasized that $E_4 > E_3 > E_2 > E_1$.

The Position of the Particle

For each of those states, we can always ask the question: Where will we find the particle? or What is the probability to find the particle between two values of x? That information can obtained from the **Probability Density**.
We start by looking at the state with $n = 1$, which has the lowest energy and it is call the **ground state**.

To find the particle between $x = 3$Å and $x = 5$Å we would need to solve the integral $\int_3^5 |\psi(x)|^2 dx$, which is represented in Figure $2.5.3$ by the shaded area in red.

What is the probability to find the particle between $\boldsymbol{x = 5}$Å and $\boldsymbol{x = 7}$Å and how does it compare with the probability to find it between $\boldsymbol{x = 3}$Å and $\boldsymbol{x = 5}$Å?

To answer this question we can look at the shaded areas in the probability density plot.

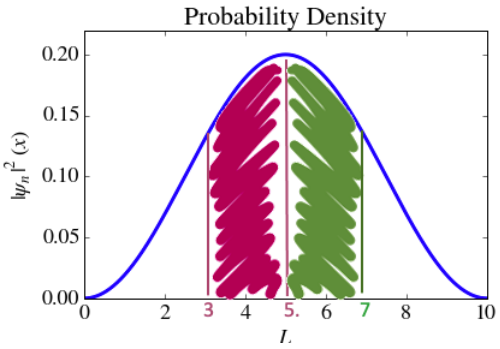


Figure 2.5.3: Probability density for a particle in a 1-D box in state with n=1. The red shaded area represents the probability to find the particle between $x = 3$ and $x = 5$Å, the green shaded area represents the probability to find the particle between $x = 5$ and $x = 7$Å. This graphical representation shows that both probabilities are the same. (Copyright; Valeria D. Kleiman)

Sometimes it is useful to compare two different regions. Figure $2.5.3$ shows the two regions shaded with different colors, and it is clear that the probability to find the particle on one side is the same as finding it on the other side. Is the particle on the left? or is it on the right?
The particle behaves as a wave, and as such we cannot say that it is on the left or on the right. If we do a a single measurement we might find it on the left (or on the right), but if we continue doing multiple measurements in systems that are similarly prepared (always a particle in a 1D box, always in the state with $n = 1$ and energy $0.376eV$) half of the times we will find it on the left side

and half of the times we will find it on the right side. This is the probabilistic interpretation of the wavefunction. The probability density provides statistical information of the possible outcome of the measurements.

If we prepare the particle on a different state, let's say $n = 2$, with energy= $1.504eV$, the Probability Density will have a different shape, and the outcome of the experiments will yield a different result.

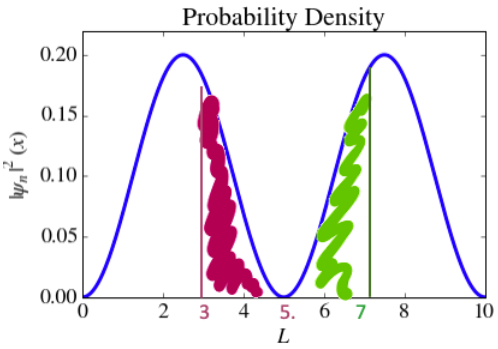


Figure 2.5.4: Probability density for a particle in a 1-D box in state with n=2. The red shaded area represents the probability to find the particle between $x = 3$ and $x = 5$Å, the green shaded area represents the probability to find the particle between $x = 5$ and $x = 7$Å. This graphical representation shows that both probabilities are the same. (Copyright; Valeria D. Kleiman)

Figure 2.5.4 again shows two regions with equally shaded areas ($x = 3$ to $x = 5$Å and $x = 5$ to $x = 7$Å) indicating that the probability to find the particle is the same when we measure in regions of equal lengths on both sides of the box.

Can we ever do a measurement and find the particle at $x = 5$Å?

The Probability Density of $n = 2$ shows an interesting characteristic. Figure 2.5.4 shows that there is a **node** at that position, that is $|\psi(5\text{Å})|^2 = 0$, indicating that the probability of finding the particle at that specific point in space is **exactly 0.** It doesn't matter how many measurements we performed, we will never find the particle at $x = 5$Å! But...how does the particle move from left to right if it can never go through the center? In reality, this question is wrongly posed. When the particle is in the state $n = 2$ its standing wave has no amplitude at $x = 5$Å, so it can never be found at that point.

> *Figure 2.5.3 shows that as the value of n increases, the number of nodes also increases. We can even read the value of n by counting how many nodes are in the Probability Density plot*

The Energies of the Particle

Table 2.5.1 shows the energies for the first 4 states of the particle. The generalized solution is given in Equation 2.5.5, where $n = 1, 2, 3, \ldots \infty$

This equation shows that the values of the energy do not change continuously but instead they vary in units of n: the Energy is **quantized**.

How much Energy is required to transfer the particle from the ground state to the first excited state ($n = 1 \rightarrow n = 2$)?

$$\Delta E = E_{final} - E_{initial} \tag{2.5.6}$$

$$= \frac{h^2}{8mL^2} n_f^2 - \frac{h^2}{8mL^2} n_i^2 \tag{2.5.7}$$

$$= \frac{h^2}{2mL^2} (n_f^2 - n_i^2) \tag{2.5.8}$$

$$= \frac{h^2}{mL^2} (4 - 1) \tag{2.5.9}$$

$$= \frac{h^2}{mL^2} 3 \tag{2.5.10}$$

We can find a general equation that describes the difference in energy between two consecutive state considering that $n_f = n_i + 1$

$$\Delta E = E_{final} - E_{initial} \tag{2.5.11}$$

$$= \frac{h^2}{2mL^2}[(n+1)^2 - n^2] \tag{2.5.12}$$

$$= \frac{h^2}{mL^2}(2n+1) \tag{2.5.13}$$

Equation 2.5.13 shows that transitions between two states corresponds to quantized values of energies. As the states increase (higher n), the value of the energy increases with a linear dependence in n, or in other words, the energy spacing between states is not the same. The transition from $n = 7 \rightarrow n = 8$ requires more energy than the transition from $n = 1 \rightarrow n = 2$.

The particle in a box only has Kinetic Energy (there is not potential inside the box) , therefore the calculated energy corresponds to Kinetic Energy. Of course that will not be the case if we are studying a different system like an electron in the H atom, or a molecule vibrating.

The probability density plot in Figure 2.5.3 shows the presence of multiple nodes for higher values of n. When the value of the quantum number $n$increases, the Kinetic Energy increases and the number of nodes increases.

A higher number of nodes in a standing wave corresponds to a higher frequency (shorter wavelength). Recalling deBroglie, where $\lambda = \frac{h}{p}$, we know that shorter λ is equivalent to larger momentum and larger momentum implies higher Kinetic Energy, since $K.E. = \frac{1}{2}mv^2 = \frac{p^2}{2m}$.

Note

We can even read the value of n by counting how many nodes are in the Probability Density plot and knowing that for a Particle in a 1-D box, the number of nodes will be $n - 1$

Can the particle have $\boldsymbol{Energy = 0}$?

The minimum energy a particle can have is for the ground state, with $n = 1$,

$$E = \frac{h^2}{8mL^2} \cdot 1 = K.E. \tag{2.5.14}$$

Since all this energy corresponds to kinetic energy, the particle is NEVER at rest, it will always have a non-zero value of momentum.

Correspondence Principle

In 1920 Bohr described the Correspondence Principle. The idea behind it is that there must be a set of conditions for which the "new" Theory (Quantum Mechanics) and the "old" Theory (Classical Mechanics) must provide similar results, a point of contact between both models to desribe matter.

We can understand that region of *correspondence* between the two theories by comparing the results of the particle in a 1-Dimensional box, under conditions that we would expect to use classical mechanics (heavy masses or large boxes).

Figure 2.5.5, left panel shows the energy levels for an electron in a box of length 10 Å and a box of length 100 Å. As the box becomes much wider, the spacing between the energy levels becomes very small. If the length of the box continues to increase, at some point that spacing will almost disappear, and the energy of the particle could be described as a continuous.

The right panel in Figure 2.5.5 shows the consequence of increasing the mass of the particle. Again we see how the spacing between states corresponds into a continuum ef energies as the mass becoems heavier.

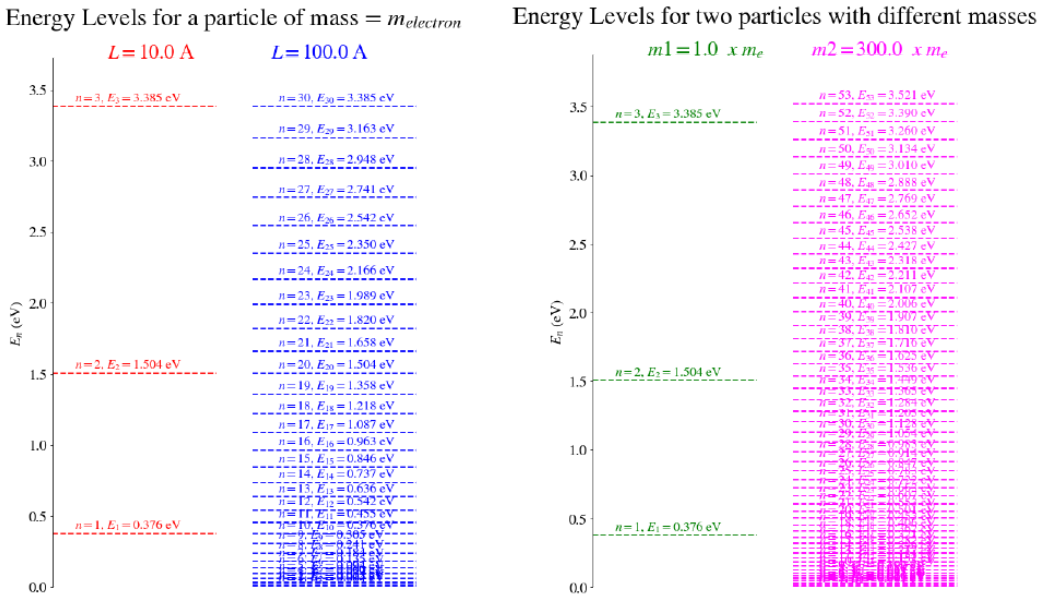


Figure 2.5.5: Left:Energy levels for an electron in a box of length 10 Å (red) and 100 Å (blue). Right: Energy levels for a particle of mass=mass of electron (green) and 300 times heavier (magenta).(Copyright; Valeria D. Kleiman)

When we look at the probability to find the particle in space, the correspondence principle can also be understood analyzing the results for a particle in a box.

Figure 2.5.6 compares the probability density for a particle in a state with $n = 3$ and $n = 75$. The probability to find the electron between $x = 3$Å and $x = 4$Å is very different than the probability to find the electron between $x = 4$Å and $x = 5$Å,when the system is in a low n state, but those probabilities becomes the same for very large values of the quantum number. In the plot on the right, the probability to find the particle is the same in any region of the box, a result corresponding to the classical treatment of a particle.

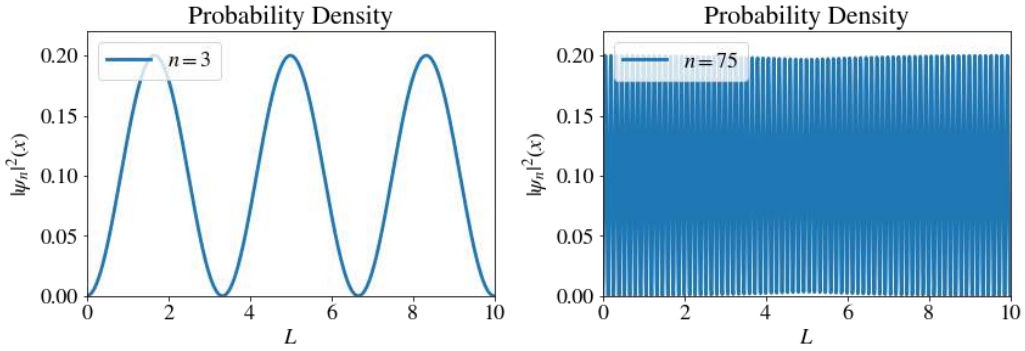


Figure 2.5.6: Probability density for a particle with $n = 3$ and $n = 75$ (a very high quantum number). (Copyright; Valeria D. Kleiman)

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2.6: A Particle in a Multidimensional Box

In quantum mechanics it is easy to expand the number of dimensions where a particle can exist.

2-Dimensional box

Consider a particle that can move in 2 independent directions, x, y. When each coordinate can be treated independently, the solution to the 2-D Schcrödinger equation yields a wavefunction $\psi(x,y)$ which depends on both coordinates and its characterized by 2 independent quantum numbers n_x and n_y.

$$\Psi_{n_x,n_y}(x,y) = \psi_{n_x}(x) \cdot \psi_{n_y}(y) = \sqrt{\frac{2}{L_x} \cdot \frac{2}{L_y}} \cdot \sin(\frac{n_x \pi}{L_x} x) \cdot \sin(\frac{n_y \pi}{L_y} y) \tag{2.6.1}$$

The energy of the states depends on those two quantum numbers

$$E_{n_x,n_y} = \frac{h^2}{8mL_x^2} n_x^2 + \frac{h^2}{8mL_y^2} n_y^2 = \frac{h^2}{8m} \cdot (\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2}) \tag{2.6.2}$$

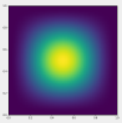
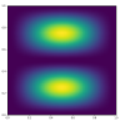
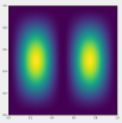
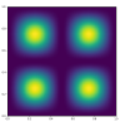
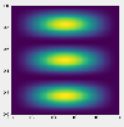
where m is the mass of the particle, L_x and L_y are the length of the box in the x and y directions, respectively. Each state of the system is given by a specific combination of quantum numbers n_x and n_y which are integer numbers that vary independently.

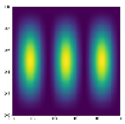
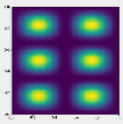
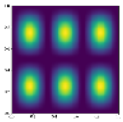
Looking at a square box (where $L_x = L_y = L$ we can evaluate the probability density and the energy of each state, with

$$|\Psi_{n_x,n_y}(x,y)|^2 = |\frac{2}{L} \cdot \sin(\frac{n_x \pi}{L} x) \cdot \sin(\frac{n_y \pi}{L} y)|^2 \qquad E_{n_x,n_y} = \frac{h^2}{8mL^2} \cdot (n_x^2 + n_y^2) \tag{2.6.3}$$

.

The presence of two quantum numbers provides the possibility of **degeneracy**, which occurs when different states, each one with its own probability density, have the same total energy. In this case, the states described by $\Psi_{a,b}(x,y)$ and $\Psi_{b,a}(x,y)$ will have different probability densities, but the same energy.

n_x, n_y	$\Psi_{n_x,n_y}(x,y)\|^2$	E_{n_x,n_y}
(1,1)		$E_{1,1} = 0.752\ eV$
(1,2)		$E_{1,2} = 1.880\ eV$
(2,1)		$E_{2,1} = 1.880\ eV$
(2,2)		$E_{2,2} = 3.008\ eV$
(1,3)		$E_{1,3} = 3.761\ eV$

(3,1)		$E_{3,1} = 3.761\ eV$
(2,3)		$E_{2,3} = 4.889\ eV$
(3,2)		$E_{2,3} = 4.889\ eV$

3-Dimensional box

Moving into 3 dimensions is done in a similar fashion, where the wavefucntion will depend on 3 coordinates (x, y, z); three independent quantum numbers will identify each state (n_x, n_y, n_z) and the energies will dependend on those 3 independent quantum numbers (each one with values $1, 2, \ldots, \infty$. The additional dimension increases the possibility of more degenerate states. For example, for a cubic box (all side lenghts being equal), we obtain $E_{1,3,6} = E_{1,6,3} = E_{3,6,1} = E_{3,1,6} = E_{6,1,3} = E_{6,3,1}$, although each of those states will have a different probability density in space.

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CHAPTER OVERVIEW

3: Atoms, Orbitals and Electronic Configurations

3.1: The Schroedinger equation for the H atom
3.2: Quantum Numbers for Atomic Orbitals
3.3: Atomic Orbitals
3.4: Many-Electron Atoms
3.5: Electron Configurations
3.6: Electron Configurations and the Periodic Table

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3.1: The Schroedinger equation for the H atom

The Hamiltonian of H atom

The H atom is the simplest atomic system, consisting of two particles, an electron and a proton, with opposite charges. Since the proton is so much heavier than the electron (about 1800 times) we could treat the proton as fixed in space and located at the center of coordinates, and the electron at a distance r from that proton. This leads to a small variation in the energy, something that is negligible in the overall understanding of the the H atom for our chemistry purposes.

Note

A better description reduces the system into a single particle with reduced mass μ, where

$$\frac{1}{\mu} = \frac{1}{m_{electron}} + \frac{1}{m_{nucleus}}. \tag{3.1.1}$$

This particle moves with respect to the center of coordinates.

The Schröedinger equation for the H atom provides the wave equation to understand the probability density for the electron in different states as well as the energy of each of those states. Although we don't need to learn to solve the mathematical equations, seeing their structure help us understand important properties of the H atom.

We start by considering that the energy observable will have its associated operator: the Hamiltonian. This Hamiltonian will have contributions from the Kinetic operator (associated with kinetic energy) and Potential operator (associated with the observable potential energy).

$$\hat{H} = \hat{T} + \hat{V} \tag{3.1.2}$$

where $\hat{T}$ is the kinetic operator and $\hat{V}$ is the potential operator. For the H atom, the potential operator $\hat{V}$ is unique and includes the electrostatic interaction between the two particles with opposite charge. According to Coulomb's law

$$V(r) = \frac{q_1 \cdot q_2}{4\pi\epsilon_o r}$$

were q_i corresponds to the charge of each particle, r is the distance between them and ϵ_o is the constant of permittivity in vaccuum. Given that the electron and the proton have the same charge $e = 1.60217662 \cdot 10^{-19} C$ with opposite sign, the Coulomb potential becomes

$$\hat{V} = -\frac{e^2}{4\pi\epsilon_o \hat{r}}$$

If we compare the electrostatic interaction between one electron and a nucleus that has a charge $Z \cdot (-e)$, then the complete potential operator will become

$$\hat{V} = -\frac{Ze^2}{4\pi\epsilon_o \hat{r}} \tag{3.1.3}$$

.

Equation 3.1.3 can be used for the interaction of a single electron at any nucleus with atom of atomic number Z.

The kinetic operator always has the same form, with a contribution from each coordinate leading to

$$\hat{T} = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial x^2}\right) \tag{3.1.4}$$

where the symbol $\frac{\partial}{\partial x}$ represents the partial derivative with respect to x.

The way it is written, the kinetic component is in Cartesian coordinates, but to combine both components of $\hat{H}$ we need to have them in the same system of coordinates. Since the H-atom has a centro-symmetrical symmetry it is more convenient to use everything in spherical coordinates r, θ, ϕ where

$$\begin{aligned} x &= r \cdot \cos\phi \cdot \sin\theta \\ y &= r \cdot \sin\phi \cdot \sin\theta \\ z &= r \cdot \cos\theta \end{aligned} \tag{3.1.5}$$

The Schrödinger Equation of H-like Atoms and its Solutions

Once we combine both contributions, the full Schrödinger equation can be written. This equation goes beyond a General Chemistry text, and it is shown here to provide a reference for the work ahead.

$$\hat{H}\Psi(r,\theta,\phi) = E \cdot \Psi(r,\theta\phi) \tag{3.1.6}$$

$$\frac{-\hbar^2}{2\mu}\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{\sin\theta}\left(\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin\theta}\frac{\partial^2}{\partial\phi^2}\right]\Psi(r,\theta,\phi) = E \cdot \Psi(r,\theta\phi) \tag{3.1.7}$$

The solution to this equation provides an infinite number of wavefunctions,

$$\Psi_{n,l,m_l}(r,\theta,\phi) \tag{3.1.8}$$

each solution is a function of the coordinates r, θ, ϕ and each solution is characterized by 3 quantum numbers: $\boldsymbol{n, l, m_l}$. Each wavefunction is called an **Orbital**, and its probability density $|Psi_{n,l,m}(r,\theta,\phi)|^2$ provides the probability to find the electron at a particular point in space when it is in the state labeld by $\boldsymbol{n, l, m_l}$.

Why 3 quantum numbers?

When solving the Schrödinger equation the wavefucntion must obey the Boundary Conditions. These are specific conditions that provide physical meaning to the problem. (For the particle in a 1-D box, we saw that the wavefunction evaluated at the edges of the box had to be zero $\psi(0) = \psi(l) = 0$. This was a requirement to have a smooth wavefunction that outside the box could not exist).

For the H atom, we know that as the radius r goes to $infty$, electron and nucleus are so far apart that the potential interaction will $\rightarrow 0$, which also means that $\Psi(r_{\rightarrow 0}, \theta, \phi) \rightarrow = 0$. This **boundary condition** sets some limits on the wavefunction and as a consequence, the quantum number n and l have specific values. An additional boundary condition considers that the value of a wavefunction has to be unique, therefore

$$|\Psi(r,\theta,\phi)|^2 = |\Psi(r,\theta+2\pi,\phi)|^2 \tag{3.1.9}$$

which leads to specific values on the quantum number m_l.

The possible values for these quantum numbers are

$$\begin{aligned} &n, \text{ Principal quantum number } 1, 2, 3..., \infty \\ &l, \text{ Angular momentum or Azimuthal quantum number } 0, 1, 2, \ldots, n-1 \\ &m_l, \text{ Magnetic moment quantum number } 0, \pm 1, \pm 2, \ldots, \pm l \end{aligned} \tag{3.1.10}$$

The Energies

Although each orbital is defined by a set of quantum numbers, the energy of the H-like wavefunctions only depends on the principal quantum number n.

$$E_n = -\frac{\mu e^4}{8h^2\epsilon_o}\frac{1}{n^2} = -hcR_H\frac{1}{n^2} \tag{3.1.11}$$

where R_H is the Rydberg constant for the H atom. The equation shows that the energy of the states of H-like atoms is quantized, and the energy required to change between two states is given by

$$\Delta E = E_{final} - E_{initial} \tag{3.1.12}$$

$$= -hcR_H\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \tag{3.1.13}$$

which resembles the phenomenological equation used to model the line emission spectra of H. If we take into account that ΔE of the transition must have the same energy as the emitted photons $\Delta E = E_{photon} = h\nu$ and that the experimentally known lines correspond to different combination of n_{final} and $n_{initial}$ we conclude that starting from the fundamental properties of quantum mechanics we were able to understand an experimental measurement that could not be properly explained by classical mechanics.

It is useful to note that

- The energies are all negative, describing the binding nature of the electron-nucleus interactions
- The energy depends on the inverse of n^2
- Since the energy does not depend on l or m_l, there might be multiple states (orbitals) with different combinations of l, m_l corresponding to the same n value and therefore having the same energies (degeneracy)
- As the value of n increases, the energy of the orbital gets closer to zero (less negative values).

Example 3.1.1

Calculate the minimum energy required to extract an electron from the H atom in its ground state.

Solution

To solve this problem we need to identify the initial and final states. The ground state corresponds to the state with lowest energy, which is $n = 1$. To identify the final state we consider that after the electron is removed from an atom there is no more potential interaction between electron and nucleus. The electron is not bound anymore, thus its energy cannot be negative (A free particle always has positive energies). The minimum energy to unbind the electron must be when $E_{final} \to 0$ which corresponds to $n \to \infty$.

$$\begin{aligned} \Delta E &= -hcR_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \\ &= -hcR_H \left(\frac{1}{n(\to \infty)^2} - \frac{1}{1^2} \right) \\ &= -hcR_H \cdot (-1) \end{aligned} \tag{3.1.14}$$

Using the tabulated values for h, c, R_H we obtain

$$\Delta E = 2.18 \cdot 10^{-18} Joules = 13.6 eV \tag{3.1.15}$$

In the gas phase this energy corresponds to the reaction

$$H \to H^+ + e-$$

which is known as the ionization of Hydrogen. If we multiply by Avogadro's number we obtain the ionization energy, *IE*, per mole of atoms.

$$IE = 2.18 \cdot 10^{-18} \frac{J}{atom} \cdot 6.022 \cdot 10^{23} \frac{atoms}{mol} = 1.31 \cdot 10^{-6} \frac{J}{mol} \tag{3.1.16}$$

3.1: The Schroedinger equation for the H atom is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

3.2: Quantum Numbers for Atomic Orbitals

Learning Objectives

- To apply the results of quantum mechanics to chemistry.

Although quantum mechanics uses sophisticated mathematics, you do not need to understand the mathematical details to follow our discussion of its general conclusions. We focus on the properties of the *wavefunctions* that are the solutions of Schrödinger's equations.

- **Describing the electron distribution as a standing wave leads to sets of *quantum numbers* that are characteristic of each wavefunction.**
- **Each wavefunction is associated with a particular energy.** The energy of an electron in an atom is quantized; it can have only certain allowed values.

Quantum Numbers

Schrödinger's approach uses three quantum numbers (n, l, and m_l) to specify any wavefunction. The quantum numbers provide information about the spatial distribution of an electron. Although n can be any positive integer, only certain values of l and m_l are allowed for a given value of n.

The Principal Quantum Number

The **principal quantum number** (n) tells the average relative distance of an electron from the nucleus:

$$n = 1, 2, 3, 4, \ldots \tag{3.2.1}$$

As n increases for a given atom, so does the average distance of an electron from the nucleus. A negatively charged electron that is, on average, closer to the positively charged nucleus is attracted to the nucleus more strongly than an electron that is farther out in space. This means that electrons with higher values of n are easier to remove from an atom. All wavefunctions that have the same value of n are said to constitute a principal shell because those electrons have similar average distances from the nucleus. As you will see, the principal quantum number n corresponds to the n used by Bohr to describe electron orbits and by Rydberg to describe atomic energy levels.

The Azimuthal Quantum Number

The second quantum number is often called the **azimuthal quantum number (l)**. The value of l describes the *shape* of the region of space occupied by the electron. The allowed values of l depend on the value of n and can range from 0 to n − 1:

$$l = 0, 1, 2, \ldots, n-1 \tag{3.2.2}$$

For example, if n = 1, l can be only 0; if n = 2, l can be 0 or 1; and so forth. For a given atom, all wavefunctions that have the same values of both n and l form a subshell. The regions of space occupied by electrons in the same subshell usually have the same shape, but they are oriented differently in space.

The Magnetic Quantum Number

The third quantum number is the magnetic quantum number (m_l). The value of m_l describes the *orientation* of the region in space occupied by an electron with respect to an applied magnetic field. The allowed values of m_l depend on the value of l: m_l can range from $-l$ to l in integral steps:

$$m_l = -l, -l+1, \ldots, 0, \ldots, l-1, l \tag{3.2.3}$$

For example, if $l = 0$, m_l can be only 0; if l = 1, m_l can be −1, 0, or +1; and if l = 2, m_l can be −2, −1, 0, +1, or +2.

Each wavefunction with an allowed combination of n, l, and m_l values describes an atomic **orbital**, a particular spatial distribution for an electron. For a given set of quantum numbers, each principal shell has a fixed number of subshells, and each subshell has a fixed number of orbitals.

Example3.2.1: n=4 Shell Structure

How many subshells and orbitals are contained within the principal shell with $n = 4$?

Given: value of n

Asked for: number of subshells and orbitals in the principal shell

Strategy:

A. Given $n = 4$, calculate the allowed values of l. From these allowed values, count the number of subshells.
B. For each allowed value of l, calculate the allowed values of m_l. The sum of the number of orbitals in each subshell is the number of orbitals in the principal shell.

Solution:

A We know that l can have all integral values from 0 to $n − 1$. If $n = 4$, then l can equal 0, 1, 2, or 3. Because the shell has four values of l, it has four subshells, each of which will contain a different number of orbitals, depending on the allowed values of m_l.

B For $l = 0$, m_l can be only 0, and thus the $l = 0$ subshell has only one orbital. For $l = 1$, m_l can be 0 or ±1; thus the $l = 1$ subshell has three orbitals. For $l = 2$, m_l can be 0, ±1, or ±2, so there are five orbitals in the $l = 2$ subshell. The last allowed value of l is $l = 3$, for which m_l can be 0, ±1, ±2, or ±3, resulting in seven orbitals in the $l = 3$ subshell. The total number of orbitals in the $n = 4$ principal shell is the sum of the number of orbitals in each subshell and is equal to $n^2 = 16$

Exercise 3.2.1: n=3 Shell Structure

How many subshells and orbitals are in the principal shell with $n = 3$?

Answer

three subshells; nine orbitals

Rather than specifying all the values of n and l every time we refer to a subshell or an orbital, chemists use an abbreviated system with lowercase letters to denote the value of l for a particular subshell or orbital:

l =	0	1	2	3
Designation	*s*	*p*	*d*	*f*

The principal quantum number is named first, followed by the letter *s*, *p*, *d*, or *f* as appropriate. (These orbital designations are derived from historical terms for corresponding spectroscopic characteristics: *s*harp, *p*rinciple, *d*iffuse, and *f*undamental.) A 1*s* orbital has $n = 1$ and $l = 0$; a 2*p* subshell has $n = 2$ and $l = 1$ (and has three 2*p* orbitals, corresponding to $m_l = −1$, 0, and +1); a 3*d* subshell has $n = 3$ and $l = 2$ (and has five 3*d* orbitals, corresponding to $m_l = −2$, −1, 0, +1, and +2); and so forth.

We can summarize the relationships between the quantum numbers and the number of subshells and orbitals as follows (Table 6.5.1):

- Each principal shell has n subshells. For $n = 1$, only a single subshell is possible (1*s*); for $n = 2$, there are two subshells (2*s* and 2*p*); for $n = 3$, there are three subshells (3*s*, 3*p*, and 3*d*); and so forth. Every shell has an *ns* subshell, any shell with $n \geq 2$ also has an *np* subshell, and any shell with $n \geq 3$ also has an *nd* subshell. Because a 2*d* subshell would require both $n = 2$ and $l = 2$, which is not an allowed value of l for $n = 2$, a 2*d* subshell does not exist.
- Each subshell has $2l + 1$ orbitals. This means that all *ns* subshells contain a single *s* orbital, all *np* subshells contain three *p* orbitals, all *nd* subshells contain five *d* orbitals, and all *nf* subshells contain seven *f* orbitals.

> *Each principal shell has n subshells, and each subshell has 2l + 1 orbitals.*

Table 3.2.1: Values of n, l, and ml through n = 4

n	l	Subshell Designation	m_l	Number of Orbitals in Subshell	Number of Orbitals in Shell
1	0	1*s*	0	1	1
2	0	2*s*	0	1	4
	1	2*p*	−1, 0, 1	3	
3	0	3*s*	0	1	9
	1	3*p*	−1, 0, 1	3	
	2	3*d*	−2, −1, 0, 1, 2	5	
4	0	4*s*	0	1	16
	1	4*p*	−1, 0, 1	3	
	2	4*d*	−2, −1, 0, 1, 2	5	
	3	4*f*	−3, −2, −1, 0, 1, 2, 3	7	

Summary

Wavefunctions have important properties:

1. the wavefunction uses three variables (Cartesian axes *x*, *y*, and *z*, or r, θ, ϕ) to describe the position of an electron;
2. describing electron distributions as standing waves leads naturally to the existence of sets of **quantum numbers** characteristic of each wavefunction; and
3. each spatial distribution of the electron described by a wavefunction with a given set of quantum numbers has a particular energy.

Quantum numbers provide important information about the energy and spatial distribution of an electron. The **principal quantum number** *n* can be any positive integer; as *n* increases for an atom, the average distance of the electron from the nucleus also increases. All wavefunctions with the same value of *n* constitute a **principal shell** in which the electrons have similar average distances from the nucleus. The **azimuthal quantum number** *l* can have integral values between 0 and $n - 1$; it describes the shape of the electron distribution. wavefunctions that have the same values of both *n* and *l* constitute a **subshell**, corresponding to electron distributions that usually differ in orientation rather than in shape or average distance from the nucleus. The **magnetic quantum number** m_l can have $2l + 1$ integral values, ranging from $-l$ to $+l$, and describes the orientation of the electron distribution. Each wavefunction with a given set of values of *n*, *l*, and m_l describes a particular spatial distribution of an electron in an atom, an **atomic orbital**.

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Adapted by Valeria D. Kleiman

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3.3: Atomic Orbitals

Learning Objectives

- To understand the 3D representation of electronic orbitals

Although quantum mechanics uses sophisticated mathematics, you do not need to understand the mathematical details to follow our discussion of its general conclusions. We focus on the properties of the *wavefunctions* that are the solutions of Schrödinger's equations.

Wavefunctions

A wavefunction (Ψ) is a mathematical function that relates the location of an electron at a given point in space (identified by x, y, and z coordinates) to the amplitude of its wave, which corresponds to its energy. Thus each wavefunction is associated with a particular energy E. The properties of wavefunctions derived from quantum mechanics are summarized here:

- **A wavefunction uses three variables to describe the position of an electron.** A fourth variable is usually required to fully describe the location of objects in motion. Three specify the position in space (as with the Cartesian coordinates x, y, and z, *or spherical coordinates* r, θ, ϕ), and one specifies the time at which the object is at the specified location. For example, if you were the captain of a ship trying to intercept an enemy submarine, you would need to know its latitude, longitude, and depth, as well as the time at which it was going to be at this position (Figure 3.3.1). For electrons, we can ignore the time dependence because we will be using standing waves, which by definition do not change with time, to describe the position of an electron.

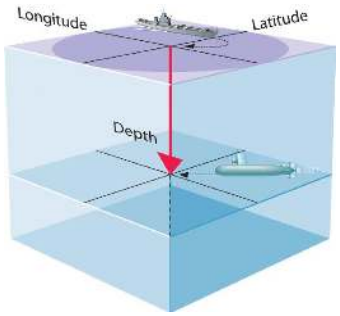


Figure 3.3.1: The Four Variables (Latitude, Longitude, Depth, and Time) required to precisely locate an object

- **The magnitude of the wavefunction at a particular point in space is proportional to the amplitude of the wave at that point.**
- **The square of the wavefunction at a given point is proportional to the probability of finding an electron at that point, which leads to a distribution of probabilities in space.** The probability of finding an electron at any point in space depends on several factors, including the distance from the nucleus and, in many cases, the atomic equivalent of latitude and longitude. As one way of graphically representing the probability distribution, the probability of finding an electron is indicated by the density of colored dots, as shown for the ground state of the hydrogen atom in Figure 3.3.2.
- **Describing the electron distribution as a standing wave leads to sets of *quantum numbers* that are characteristic of each wavefunction.**
- **Each wavefunction is associated with a particular energy.** The energy of an electron in an atom is quantized; it can have only certain allowed values.

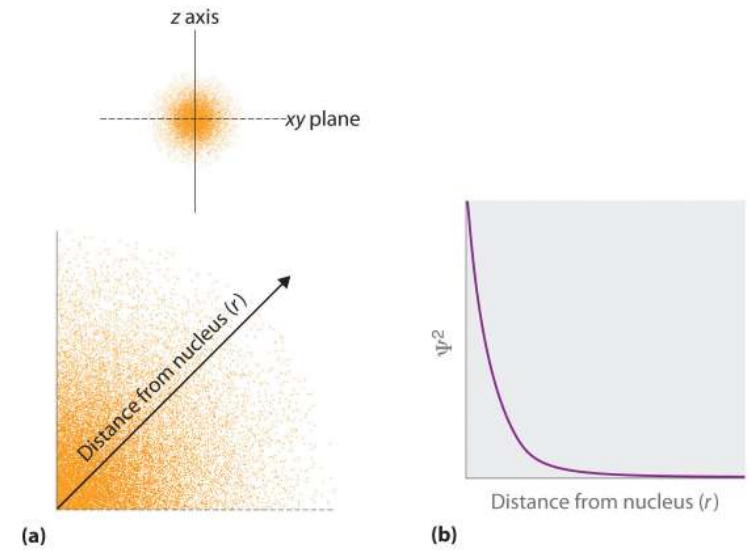


Figure 3.3.2: Probability of Finding the Electron in the Ground State of the Hydrogen Atom at Different Points in Space. (a) The density of the dots shows electron probability. (b) In this plot of Ψ^2 versus r for the ground state of the hydrogen atom, the electron probability density is greatest at $r = 0$ (the nucleus) and falls off with increasing r. Because the line never actually reaches the horizontal axis, the probability of finding the electron at very large values of r is very small but *not* zero.

Orbitals are mathematically derived regions of space with different **probabilities** of containing an electron.

One way of representing electron probability distributions was illustrated previously for the 1**s** orbital of hydrogen. Because Ψ^2 gives the probability of finding an electron in a given volume of space (such as a cubic picometer), a plot of Ψ^2 versus distance from the nucleus (**r**) is a plot of the **probability density**. The 1**s** orbital is spherically symmetrical, so the probability of finding a 1**s** electron at any given point depends **only** on its distance from the nucleus. The probability density is greatest at \($r = 0$\) (at the nucleus) and decreases steadily with increasing distance. At very large values of **r**, the electron probability density is very small but **not** zero.

In contrast, we can calculate the **radial probability** (the probability of finding a 1s electron at a distance r from the nucleus) by adding together the probabilities of an electron being at all points on a series of **x** spherical shells of radius $\mathbf{r}_1$, $\mathbf{r}_2$, $\mathbf{r}_3$,…, $\mathbf{r}_{x-1}$, $\mathbf{r}_x$. In effect, we are dividing the atom into very thin concentric shells, much like the layers of an onion (Figure 3.3.1*a*), and calculating the probability of finding an electron on each spherical shell. Recall that the electron probability density is greatest at $r = 0$ (Figure 3.3.1*b*), so the density of dots is greatest for the smallest spherical shells in part (a) in Figure 3.3.1. In contrast, the surface area of each spherical shell is equal to $4\pi r^2$, which increases very rapidly with increasing r (Figure 3.3.1*c*). Because the surface area of the spherical shells increases more rapidly with increasing r than the electron probability density decreases, the plot of radial probability has a maximum at a particular r distance (Figure 3.3.1*d*). Most important, when r is very small, the surface area of a spherical shell is so small that the **total** probability of finding an electron close to the nucleus is very low; at the nucleus, the electron probability vanishes (Figure 3.3.1*d*).

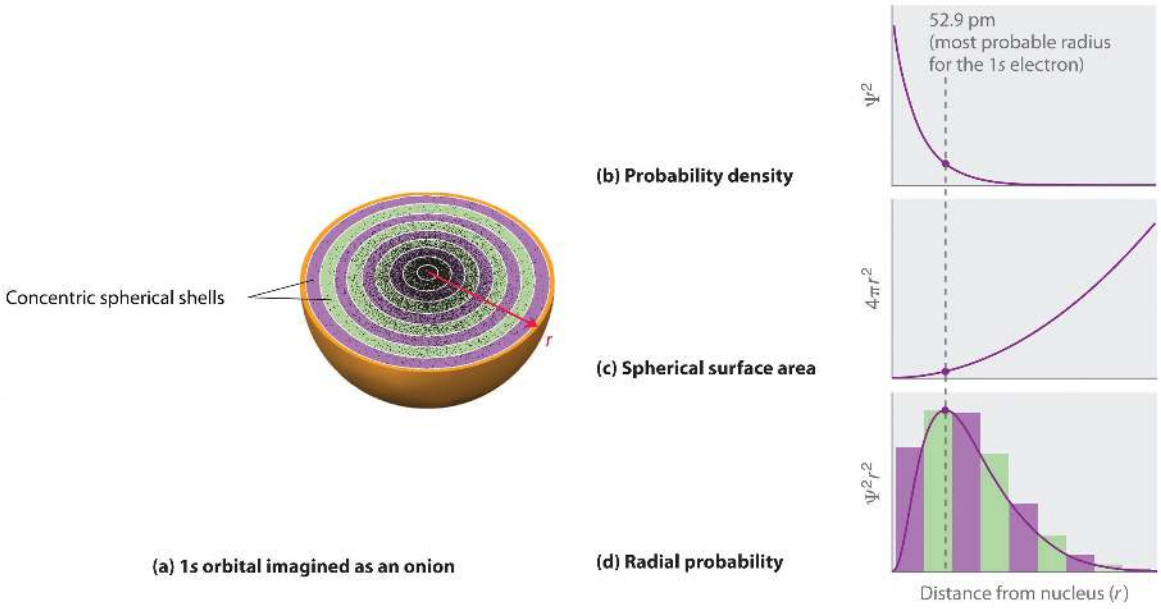


Figure 3.3.1: Most Probable Radius for the Electron in the Ground State of the Hydrogen Atom. (a) Imagine dividing the atom's total volume into very thin concentric shells as shown in the onion drawing. (b) A plot of electron probability density Ψ^2 versus r shows that the electron probability density is greatest at $r = 0$ and falls off smoothly with increasing r. The density of the dots is therefore greatest in the innermost shells of the onion. (c) The surface area of each shell, given by $4\pi r^2$, increases rapidly with increasing r. (d) If we count the number of dots in each spherical shell, we obtain the total probability of finding the electron at a given value of r. Because the surface area of each shell increases more rapidly with increasing r than the electron probability density decreases, a plot of electron probability versus r (the **radial probability**) shows a peak. This peak corresponds to the most probable radius for the electron, 52.9 pm, which is exactly the radius predicted by Bohr's model of the hydrogen atom.

For the hydrogen atom, the peak in the radial probability plot occurs at $r = 0.529$ Å (52.9 pm), which is exactly the radius calculated by Bohr for the **n** = 1 orbit. Thus the **most probable radius** obtained from quantum mechanics is identical to the radius calculated by classical mechanics. In Bohr's model, however, the electron was assumed to be at this distance 100% of the time, whereas in the Schrödinger model, it is at this distance only some of the time. The difference between the two models is attributable to the wavelike behavior of the electron and the Heisenberg uncertainty principle.

Figure 3.3.2 compares the electron probability densities for the hydrogen 1**s**, 2**s**, and 3**s** orbitals. Note that all three are spherically symmetrical. For the 2**s** and 3**s** orbitals, however (and for all other **s** orbitals as well), the electron probability density does not fall off smoothly with increasing r. Instead, a series of minima and maxima are observed in the radial probability plots (Figure 3.3.2*c*). The minima correspond to spherical **nodes** (regions of zero electron probability), which alternate with spherical regions of nonzero electron probability. The existence of these nodes is a consequence of changes of wave **phase** in the wavefunction Ψ.

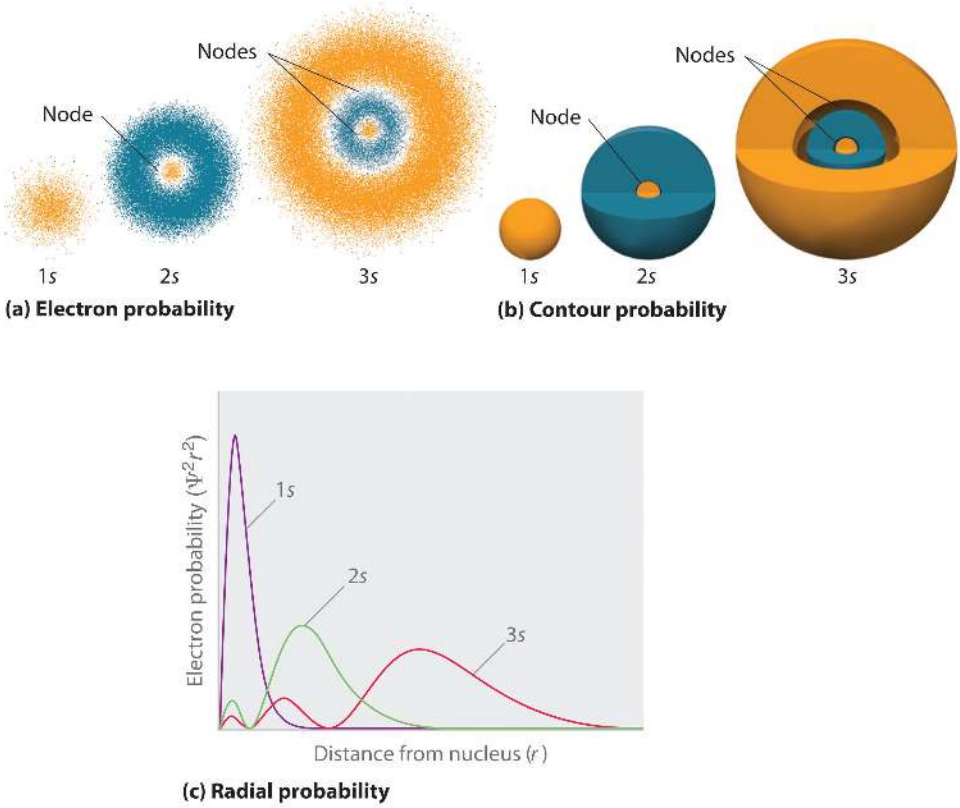


Figure 3.3.2: Probability Densities for the 1**s**, 2**s**, and 3**s** Orbitals of the Hydrogen Atom. (a) The electron probability density in any plane that contains the nucleus is shown. Note the presence of circular regions, or nodes, where the probability density is zero. (b) Contour surfaces enclose 90% of the electron probability, which illustrates the different sizes of the 1**s**, 2**s**, and 3**s** orbitals. The cutaway drawings give partial views of the internal spherical nodes. The orange color corresponds to regions of space where the phase of the wave function is positive, and the blue color corresponds to regions of space where the phase of the wave function is negative. (c) In these plots of electron probability as a function of distance from the nucleus (**r**) in all directions (radial probability), the most probable radius increases as **n** increases, but the 2**s** and 3**s** orbitals have regions of significant electron probability at small values of r.

s Orbitals (l=0)

Three things happen to **s** orbitals as **n** increases (Figure 3.3.2):

1. They become larger, extending farther from the nucleus.
2. They contain more nodes. This is similar to a standing wave that has regions of significant amplitude separated by nodes, points with zero amplitude.
3. For a given atom, the **s** orbitals also become higher in energy as **n** increases because of their increased distance from the nucleus.

Orbitals are generally drawn as three-dimensional surfaces that enclose 90% of the electron density, as was shown for the hydrogen 1**s**, 2**s**, and 3**s** orbitals in part (b) in Figure 3.3.2. Although such drawings show the relative sizes of the orbitals, they do not normally show the spherical nodes in the 2**s** and 3**s** orbitals because the spherical nodes lie inside the 90% surface. Fortunately, the positions of the spherical nodes are not important for chemical bonding.

p Orbitals (l=1)

Only **s** orbitals are spherically symmetrical. As the value of **l** increases, the number of orbitals in a given subshell increases, and the shapes of the orbitals become more complex. Because the 2**p** subshell has **l** = 1, with three values of $\mathbf{m_l}$ (−1, 0, and +1), there are three 2**p** orbitals.

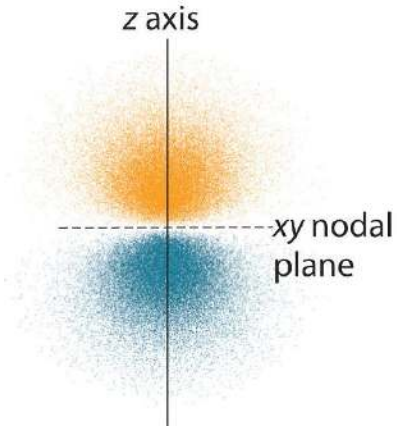


Figure 3.3.3: Electron Probability Distribution for a Hydrogen 2**p** Orbital. The nodal plane of zero electron density separates the two lobes of the 2**p** orbital. As in Figure 3.3.2, the colors correspond to regions of space where the phase of the wave function is positive (orange) and negative (blue).

The electron probability distribution for one of the hydrogen 2**p** orbitals is shown in Figure 3.3.3. Because this orbital has two lobes of electron density arranged along the **z** axis, with an electron density of zero in the **xy** plane (i.e., the **xy** plane is a nodal plane), it is a $2p_z$ orbital. As shown in Figure 3.3.4, the other two 2**p** orbitals have identical shapes, but they lie along the **x** axis ($2p_x$) and y axis ($2p_y$), respectively. Note that each **p** orbital has just one **nodal plane**. In each case, the phase of the wave function for each of the 2**p** orbitals is positive for the lobe that points along the positive axis and negative for the lobe that points along the negative axis. It is important to emphasize that these signs correspond to the **phase** of the wave that describes the electron motion, **not** to positive or negative charges.

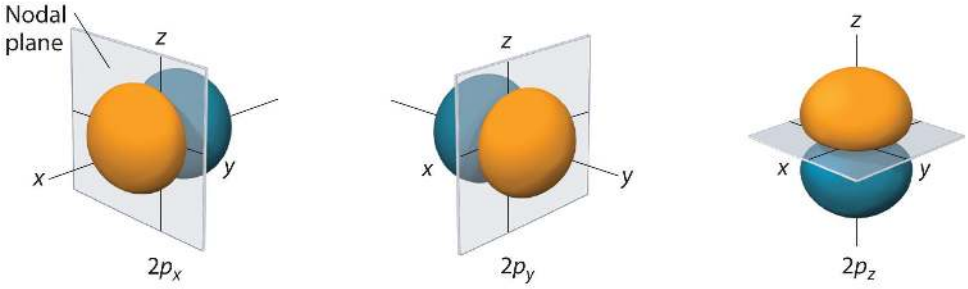


Figure 3.3.4 The Three Equivalent 2**p** Orbitals of the Hydrogen Atom

The surfaces shown enclose 90% of the total electron probability for the $2\mathbf{p_x}$, $2\mathbf{p_y}$, and $2\mathbf{p_z}$ orbitals. Each orbital is oriented along the axis indicated by the subscript and a nodal plane that is perpendicular to that axis bisects each 2**p** orbital. The phase of the wave function is positive (orange) in the region of space where **x**, **y**, or **z** is positive and negative (blue) where **x**, **y**, or **z** is negative. Just as with the **s** orbitals, the size and complexity of the **p** orbitals for any atom increase as the principal quantum numbe *r* **n** increases. The shapes of the 90% probability surfaces of the 3**p**, 4**p**, and higher-energy **p** orbitals are, however, essentially the same as those shown in Figure 3.3.4.

d Orbitals (l=2)

Subshells with **l** = 2 have five **d** orbitals; the first principal shell to have a **d** subshell corresponds to **n** = 3. The five **d** orbitals have $\mathbf{m_l}$ values of −2, −1, 0, +1, and +2.

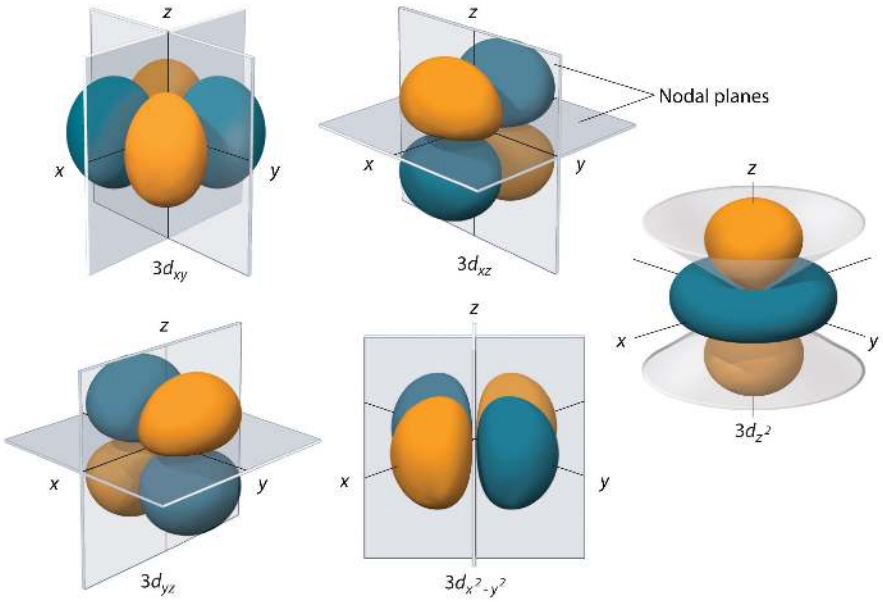


Figure 3.3.5: The Five Equivalent 3d Orbitals of the Hydrogen Atom. The surfaces shown enclose 90% of the total electron probability for the five hydrogen 3d orbitals. Four of the five 3d orbitals consist of four lobes arranged in a plane that is intersected by two perpendicular nodal planes. These four orbitals have the same shape but different orientations. The fifth 3d orbital, $3d_{z^2}$, has a distinct shape even though it is mathematically equivalent to the others. The phase of the wave function for the different lobes is indicated by color: orange for positive and blue for negative.

The hydrogen 3d orbitals, shown in Figure 3.3.5, have more complex shapes than the 2p orbitals. All five 3d orbitals contain two nodal surfaces, as compared to one for each p orbital and zero for each s orbital. In three of the d orbitals, the lobes of electron density are oriented between the x and y, x and z, and y and z planes; these orbitals are referred to as the $3d_{xy}$, \)3d_{xz}\), and $3d_{yz}$ orbitals, respectively. A fourth d orbital has lobes lying along the x and y axes; this is the $3d_{x^2-y^2}$ orbital. The fifth 3d orbital, called the $3d_{z^2}$ orbital, has a unique shape: it looks like a $2p_z$ orbital combined with an additional doughnut of electron probability lying in the xy plane. Despite its peculiar shape, the $3d_{z^2}$ orbital is mathematically equivalent to the other four and has the same energy. In contrast to p orbitals, the phase of the wave function for d orbitals is the same for opposite pairs of lobes. As shown in Figure 3.3.5, the phase of the wave function is positive for the two lobes of the dz^2 orbital that lie along the z axis, whereas the phase of the wave function is negative for the doughnut of electron density in the xy plane. Like the s and p orbitals, as n increases, the size of the d orbitals increases, but the overall shapes remain similar to those depicted in Figure 3.3.5.

f Orbitals (l=3)

Principal shells with **n** = 4 can have subshells with **l** = 3 and $\mathbf{m_l}$ values of −3, −2, −1, 0, +1, +2, and +3. These subshells consist of seven **f** orbitals. Each **f** orbital has three nodal surfaces, so their shapes are complex. Because **f** orbitals are not particularly important for our purposes, we do not discuss them further, and orbitals with higher values of **l** are not discussed at all.

Orbital Energies

Although we have discussed the shapes of orbitals, we have said little about their comparative energies. We begin our discussion of orbital energies by considering atoms or ions with only a single electron (such as H or He^+).

The relative energies of the atomic orbitals with **n** ≤ 4 for a hydrogen atom are plotted in Figure 3.3.6; note that the orbital energies depend on **only** the principal quantum number **n**. Consequently, the energies of the 2**s** and 2**p** orbitals of hydrogen are the same; the energies of the 3**s**, 3**p**, and 3**d** orbitals are the same; and so forth. Quantum mechanics predicts that in the hydrogen atom, all orbitals with the same value of **n** (e.g., the three 2**p** orbitals) are **degenerate**, meaning that they have the same energy. The orbital energies obtained for hydrogen using quantum mechanics are exactly the same as the allowed energies calculated by Bohr. In contrast to Bohr's model, however, which allowed only one orbit for each energy level, quantum mechanics predicts that there are **4** orbitals with different electron density distributions in the **n** = 2 principal shell (one 2**s** and three 2**p** orbitals), **9** in the **n** = 3 principal shell, and **16** in the **n** = 4 principal shell.The different values of **l** and $\mathbf{m_l}$ for the individual orbitals within a given principal shell are not important for understanding the emission or absorption spectra of the hydrogen atom under most conditions, but they do explain the splittings of the main lines that are observed when hydrogen atoms are placed in a magnetic

field. Figure 3.3.6 shows that the energy levels become closer and closer together as the value of **n** increases, as expected because of the $1/\mathbf{n}^2$ dependence of orbital energies.

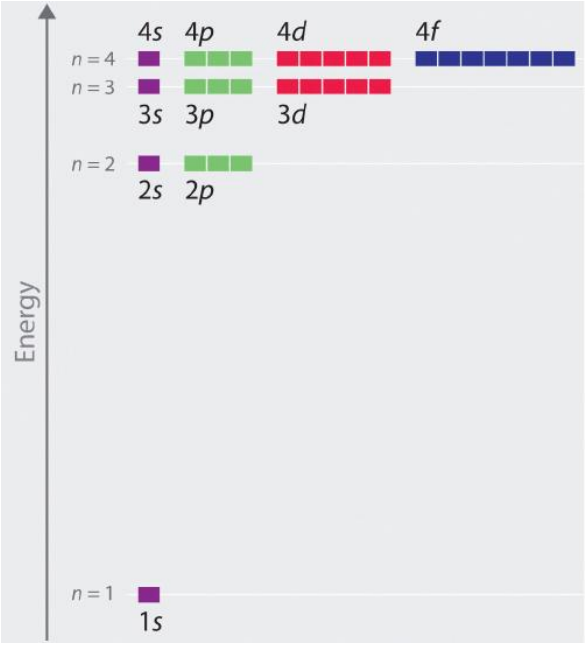


Figure 3.3.6: Orbital Energy Level Diagram for the Hydrogen Atom with a single electron. Each box corresponds to one orbital. Note that the difference in energy between orbitals decreases rapidly with increasing values of **n**.

The energies of the orbitals in any species with only one electron can be calculated by a minor variation of Bohr's equation, which can be extended to other single-electron species by incorporating the nuclear charge Z (the number of protons in the nucleus):

$$E = -\frac{Z^2}{n^2} Rhc \tag{3.3.1}$$

In general, both energy and radius decrease as the nuclear charge increases. Thus the most stable orbitals (those with the lowest energy) are those closest to the nucleus. For example, in the ground state of the hydrogen atom, the single electron is in the 1s orbital, whereas in the first excited state, the atom has absorbed energy and the electron has been promoted to one of the n = 2 orbitals. In ions with only a single electron, the energy of a given orbital depends on only n, and all subshells within a principal shell, such as the p_x, p_y, and p_z orbitals, are degenerate.

Summary

The four chemically important types of atomic orbital correspond to values of $\ell = 0$, 1, 2, and 3. Orbitals with $\ell = 0$ are s orbitals and are spherically symmetrical, with the greatest probability of finding the electron occurring at the nucleus. All orbitals with values of $n > 1$ and $ell = 0$ contain one or more nodes. Orbitals with $\ell = 1$ are p orbitals and contain a nodal plane that includes the nucleus, giving rise to a dumbbell shape. Orbitals with $\ell = 2$ are d orbitals and have more complex shapes with at least two nodal surfaces. Orbitals with $\ell = 3$ are f orbitals, which are still more complex.

Because its average distance from the nucleus determines the energy of an electron, each atomic orbital with a given set of quantum numbers has a particular energy associated with it, the **orbital energy**.

$$E = -\frac{Z^2}{n^2} Rhc$$

In atoms or ions with only a single electron, all orbitals with the same value of n have the same energy (they are degenerate), and the energies of the principal shells increase smoothly as n increases. An atom or ion with the electron(s) in the lowest-energy orbital(s) is said to be in its ground state, whereas an atom or ion in which one or more electrons occupy higher-energy orbitals is said to be in an excited state.

Contributors and Attributions

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3.4: Many-Electron Atoms

Learning Objectives

- To write the electron configuration of any element and relate its electron configuration to its position in the periodic table.

The quantum mechanical model allowed us to determine the energies of the hydrogen atomic orbitals; now we would like to extend this to describe the electronic structure of every element in the Periodic Table. The process of describing each atom's electronic structure consists, essentially, of beginning with hydrogen and adding one proton and one electron at a time to create the next heavier element in the table; however, interactions between electrons make this process a bit more complicated than it sounds. All stable nuclei other than hydrogen also contain one or more neutrons. Because neutrons have no electrical charge, however, they can be ignored in the following discussion. Before demonstrating how to do this, however, we must introduce the concept of electron spin and the Pauli principle.

Orbitals and their Energies

Unlike in hydrogen-like atoms with only one electron, in multielectron atoms the values of quantum numbers *n and l* determine the energies of an orbital. The energies of the different orbitals for a typical multielectron atom are shown in Figure 3.4.1. Within a given principal shell of a multielectron atom, the orbital energies increase with increasing *l*. An *ns* orbital always lies below the corresponding *np* orbital, which in turn lies below the *nd* orbital.



Figure 3.4.1: Orbital Energy Level Diagram for a Typical Multielectron Atom

These energy differences are caused by the effects of *shielding* and *penetration*, the extent to which a given orbital lies inside other filled orbitals. For example, an electron in the 2*s* orbital penetrates inside a filled 1*s* orbital more than an electron in a 2*p* orbital

does. Since electrons, all being negatively charged, repel each other, an electron closer to the nucleus partially *shields* an electron farther from the nucleus from the attractive effect of the positively charged nucleus. Hence in an atom with a filled 1*s* orbital, the effective nuclear charge (Z_{eff}) experienced by a 2*s* electron is greater than the Z_{eff} experienced by a 2*p* electron. Consequently, the 2*s* electron is more tightly bound to the nucleus and has a lower energy, consistent with the order of energies shown in Figure 3.4.1.

> *Due to electron shielding, Z_{eff} increases more rapidly going across a row of the periodic table than going down a column.*

Notice in Figure 3.4.1 that the difference in energies between subshells can be so large that the energies of orbitals from different principal shells can become approximately equal. For example, the energy of the 3*d* orbitals in most atoms is actually *between* the energies of the 4*s* and the 4*p* orbitals.

Electron Spin: The Fourth Quantum Number

When scientists analyzed the emission and absorption spectra of the elements more closely, they saw that for elements having more than one electron, nearly all the lines in the spectra were actually *pairs* of very closely spaced lines. Because each line represents an energy level available to electrons in the atom, there are twice as many energy levels available as would be predicted solely based on the quantum numbers n, l, and m_l. Scientists also discovered that applying a magnetic field caused the lines in the pairs to split farther apart. In 1925, two graduate students in physics in the Netherlands, George Uhlenbeck (1900–1988) and Samuel Goudsmit (1902–1978), proposed that the splittings were caused by an electron spinning about its axis, much as Earth spins about its axis. When an electrically charged object spins, it produces a magnetic moment parallel to the axis of rotation, making it behave like a magnet. Although the electron cannot be viewed solely as a particle, spinning or otherwise, it is indisputable that it does have a magnetic moment. This magnetic moment is called **electron spin**. This is a property with no classical analog (the electron is NOT rotating) and it does not depend on spatial coordinates (x, y, z) to describe it.



Figure 3.4.2: Electron Spin. In a magnetic field, an electron has two possible orientations with different energies, one aligned with the magnetic field (+½), and one aligned against it (−½). All other orientations are forbidden.

In an external magnetic field, the electron has two possible orientations (Figure Figure 3.4.2). These are described by a fourth quantum number (m_s), which for any electron can have only two possible values, designated +½ (up) and −½ (down) to indicate that the two orientations are opposites; the subscript *s* is for spin. An electron behaves like a magnet that has one of two possible orientations, aligned either with the magnetic field or against it.

The Pauli Exclusion Principle

The implications of electron spin for chemistry were recognized almost immediately by an Austrian physicist, Wolfgang Pauli (1900–1958; Nobel Prize in Physics, 1945), who determined that each orbital can contain no more than two electrons. He developed the Pauli exclusion principle: *No two electrons in an atom can have the same values of all four quantum numbers (n, l, m_l, m_s).*

By giving the values of n, l, and m_l, we also specify a particular orbital (e.g., 1*s* with $n = 1$, $l = 0$, $m_l = 0$). Because m_s has only two possible values (+½ or −½), two electrons, *and only two electrons*, can occupy any given orbital, one with spin up and one with

spin down. With this information, we can proceed to construct the entire periodic table, which was originally based on the physical and chemical properties of the known elements.

Example 3.4.1

List all the allowed combinations of the four quantum numbers (n, l, m_l, m_s) for electrons in a 2p orbital and predict the maximum number of electrons the 2p subshell can accommodate.

Given: orbital

Asked for: allowed quantum numbers and maximum number of electrons in orbital

Strategy:

A. List the quantum numbers (n, l, m_l) that correspond to an n = 2p orbital. List all allowed combinations of (n, l, m_l).
B. Build on these combinations to list all the allowed combinations of (n, l, m_l, m_s).
C. Add together the number of combinations to predict the maximum number of electrons the 2p subshell can accommodate.

Solution:

A For a 2p orbital, we know that n = 2, $l = n - 1 = 1$, and $m_l = -l, (-l + 1), \ldots, (l - 1), l$. There are only three possible combinations of (n, l, m_l): (2, 1, 1), (2, 1, 0), and (2, 1, −1).

B Because m_s is independent of the other quantum numbers and can have values of only +½ and −½, there are six possible combinations of (n, l, m_l, m_s): (2, 1, 1, +½), (2, 1, 1, −½), (2, 1, 0, +½), (2, 1, 0, −½), (2, 1, −1, +½), and (2, 1, −1, −½).

C Hence the 2p subshell, which consists of three 2p orbitals (2p_x, 2p_y, and 2p_z), can contain a total of six electrons, two in each orbital.

Exercise 3.4.1

List all the allowed combinations of the four quantum numbers (n, l, m_l, m_s) for a 6s orbital, and predict the total number of electrons it can contain.

Answer

(6, 0, 0, +½), (6, 0, 0, −½); two electrons

Summary

The arrangement of atoms in the periodic table arises from the lowest energy arrangement of electrons in the valence shell. In addition to the three quantum numbers (n, l, m_l) dictated by quantum mechanics, a fourth quantum number is required to explain certain properties of atoms. This is the **electron spin** quantum number (m_s), which can have values of +½ or −½ for any electron, corresponding to the two possible orientations of an electron in a magnetic field. The concept of electron spin has important consequences for chemistry because the **Pauli exclusion principle** implies that no orbital can contain more than two electrons (with opposite spin).

Contributions and Attributions

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3.5: Electron Configurations

Learning Objectives

- To understand the basics of adding electrons to atomic orbitals
- To understand the basics of the Aufbau principle

The electron configuration of an element is the arrangement of its electrons in its atomic orbitals. By knowing the electron configuration of an element, we can predict and explain a great deal of its chemistry.

The Aufbau Principle

We construct the periodic table by following the aufbau principle (from German, meaning "building up"). First we determine the number of electrons in the atom; then we add electrons one at a time to the lowest-energy orbital available *without violating the Pauli principle*. We use the orbital energy diagram of Figure 3.5.1, recognizing that each orbital can hold two electrons, one with spin up ↑, corresponding to $m_s = +½$, which is arbitrarily written first, and one with spin down ↓, corresponding to $m_s = −½$. A filled orbital is indicated by ↑↓, in which the electron spins are said to be *paired*. Here is a schematic orbital diagram for a hydrogen atom in its ground state:

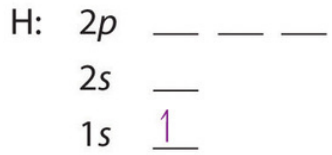
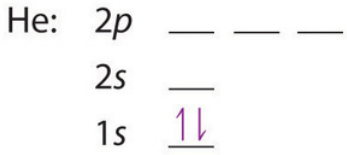


Figure 3.5.1: One electron in.

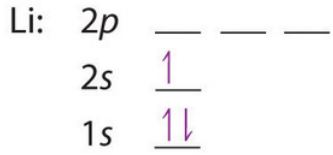
From the orbital diagram, we can write the electron configuration in an abbreviated form in which the occupied orbitals are identified by their principal quantum number *n* and their value of *l* (*s*, *p*, *d*, or *f*), with the number of electrons in the subshell indicated by a superscript. For hydrogen, therefore, the single electron is placed in the 1*s* orbital, which is the orbital lowest in energy (Figure 3.5.1), and the electron configuration is written as $1s^1$ and read as "one-s-one."

A neutral helium atom, with an atomic number of 2 ($Z = 2$), has two electrons. We place one electron in the orbital that is lowest in energy, the 1*s* orbital. From the Pauli exclusion principle, we know that an orbital can contain two electrons with opposite spin, so we place the second electron in the same orbital as the first but pointing down, so that the electrons are paired. The orbital diagram for the helium atom is therefore



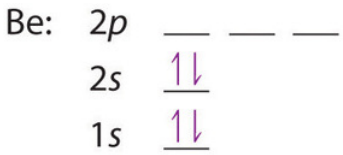
written as $1s^2$, where the superscript 2 implies the pairing of spins. Otherwise, our configuration would violate the Pauli principle.

The next element is lithium, with $Z = 3$ and three electrons in the neutral atom. We know that the 1*s* orbital can hold two of the electrons with their spins paired; the third electron must enter a higher energy orbital. Figure 6.29 tells us that the next lowest energy orbital is 2*s*, so the orbital diagram for lithium is

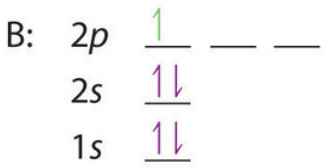


This electron configuration is written as $1s^22s^1$.

The next element is beryllium, with $Z = 4$ and four electrons. We fill both the 1*s* and 2*s* orbitals to achieve a $1s^22s^2$ electron configuration:

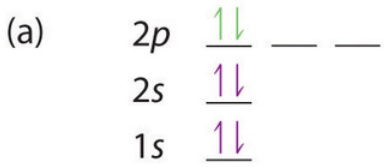


When we reach boron, with $Z = 5$ and five electrons, we must place the fifth electron in one of the 2*p* orbitals. Because all three 2*p* orbitals are degenerate, it doesn't matter which one we select. The electron configuration of boron is $1s^2 2s^2 2p^1$:

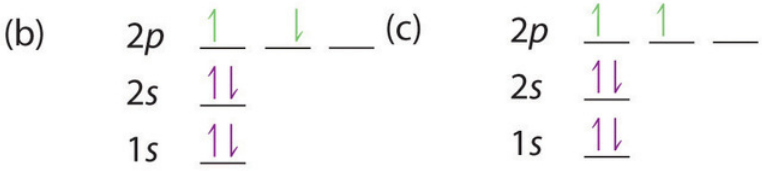


Boron has one electron pair in the 1 s orbital, one electron pair in the 2 s orbital, and one electron in the 2 p orbital.

At carbon, with $Z = 6$ and six electrons, we are faced with a choice. Should the sixth electron be placed in the same 2*p* orbital that already has an electron, or should it go in one of the empty 2*p* orbitals? If it goes in an empty 2*p* orbital, will the sixth electron have its spin aligned with or be opposite to the spin of the fifth? In short, which of the following three orbital diagrams is correct for carbon, remembering that the 2*p* orbitals are degenerate?



Three diagrams on where the sixth electron should go, a) paired with the lone electron in the 2 p orbital, b) unpaired with the lone electron and pointing downward, and c) unpaired with the lone electron



Because of electron-electron interactions, it is more favorable energetically for an electron to be in an unoccupied orbital than in one that is already occupied; hence we can eliminate choice a. Similarly, experiments have shown that choice b is slightly higher in energy (less stable) than choice c because electrons in degenerate orbitals prefer to line up with their spins parallel; thus, we can eliminate choice b. Choice c illustrates **Hund's rule** (named after the German physicist Friedrich H. Hund, 1896–1997), which today says that the lowest-energy electron configuration for an atom is the one that has the maximum number of electrons with parallel spins in degenerate orbitals. By Hund's rule, the electron configuration of carbon, which is $1s^2 2s^2 2p^2$, is understood to correspond to the orbital diagram shown in c. Experimentally, it is found that the ground state of a neutral carbon atom does indeed contain two unpaired electrons.

When we get to nitrogen ($Z = 7$, with seven electrons), Hund's rule tells us that the lowest-energy arrangement is

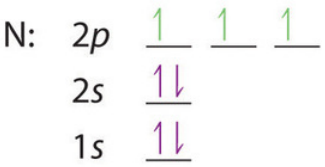
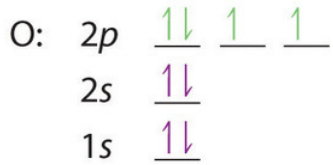


Figure 3.5.1: Copy and Paste Caption here. (Copyright; author via source)

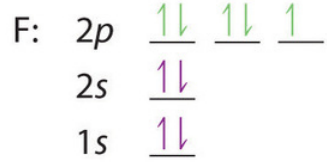
with three unpaired electrons. The electron configuration of nitrogen is thus $1s^2 2s^2 2p^3$.

At oxygen, with $Z = 8$ and eight electrons, we have no choice. One electron must be paired with another in one of the 2*p* orbitals, which gives us two unpaired electrons and a $1s^2 2s^2 2p^4$ electron configuration. Because all the 2*p* orbitals are degenerate, it doesn't matter which one has the pair of electrons.



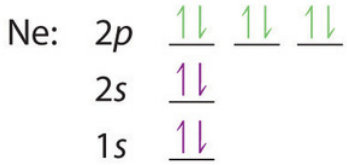
Oxygen has one electron pair in the 1 s orbital, one electron pair in the 2 s pair, and one electron pair, and 2 unpaired electrons in the 2 p orbitals.

Similarly, fluorine has the electron configuration $1s^2 2s^2 2p^5$:



Fluorine has one electron pair in the 1 s orbital, one electron pair in the 2 s orbital, and 2 electrons pairs with one unpaired electron in the 2 p orbital.

When we reach neon, with $Z = 10$, we have filled the $2p$ subshell, giving a $1s^2 2s^2 2p^6$ electron configuration:



Neon has one electron pair in the 1 s orbital, one electron pair in the 2 s orbital, and 3 electron pairs in the 2 p orbital.

Notice that for neon, as for helium, all the orbitals through the $2p$ level are completely filled. This fact is very important in dictating both the chemical reactivity and the bonding of helium and neon, as you will see.



Electron Configuration of Atoms: Electron Configuration of Atoms, YouTube(opens in new window) [youtu.be]

Valence Electrons

As we continue through the periodic table in this way, writing the electron configurations of larger and larger atoms, it becomes tedious to keep copying the configurations of the filled inner subshells. In practice, chemists simplify the notation by using a bracketed noble gas symbol to represent the configuration of the noble gas from the preceding row because all the orbitals in a noble gas are filled. For example, [Ne] represents the $1s^2 2s^2 2p^6$ electron configuration of neon ($Z = 10$), so the electron configuration of sodium, with $Z = 11$, which is $1s^2 2s^2 2p^6 3s^1$, is written as [Ne]$3s^1$:

Electron Configuration of Neon and Sodium

Neon	Z = 10	$1s^2 2s^2 2p^6$

Neon	Z = 10	$1s^2 2s^2 2p^6$
Sodium	Z = 11	$1s^2 2s^2 2p^6 \mathbf{3}s^1 = [Ne]\mathbf{3}s^1$

Because electrons in filled inner orbitals are closer to the nucleus and more tightly bound to it, they are rarely involved in chemical reactions. This means that the chemistry of an atom depends mostly on the electrons in its outermost shell, which are called the **valence electrons**. The simplified notation allows us to see the valence-electron configuration more easily. Using this notation to compare the electron configurations of sodium and lithium, we have:

Electron Configuration of Sodium and Lithium

Sodium	$1s^2 2s^2 2p^6 3s^1 = [Ne]3s^1$
Lithium	$1s^2 2s^1 = [He]2s^1$

It is readily apparent that both sodium and lithium have one *s* electron in their valence shell. We would therefore predict that sodium and lithium have very similar chemistry, which is indeed the case.

As we continue to build the eight elements of period 3, the 3*s* and 3*p* orbitals are filled, one electron at a time. This row concludes with the noble gas argon, which has the electron configuration $[Ne]3s^2 3p^6$, corresponding to a filled valence shell.

Example 3.5.1: Electronic Configuration of Phosphorus

Draw an orbital diagram and use it to derive the electron configuration of phosphorus, $Z = 15$. What is its valence electron configuration?

Given: atomic number

Asked for: orbital diagram and valence electron configuration for phosphorus

Strategy:

A. Locate the nearest noble gas preceding phosphorus in the periodic table. Then subtract its number of electrons from those in phosphorus to obtain the number of valence electrons in phosphorus.

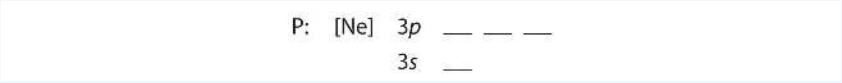
B. Referring to Figure 3.5.1, draw an orbital diagram to represent those valence orbitals. Following Hund's rule, place the valence electrons in the available orbitals, beginning with the orbital that is lowest in energy. Write the electron configuration from your orbital diagram.

C. Ignore the inner orbitals (those that correspond to the electron configuration of the nearest noble gas) and write the valence electron configuration for phosphorus.

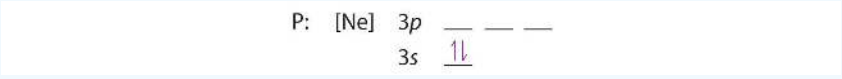
Solution:

A Because phosphorus is in the third row of the periodic table, we know that it has a [Ne] closed shell with 10 electrons. We begin by subtracting 10 electrons from the 15 in phosphorus.

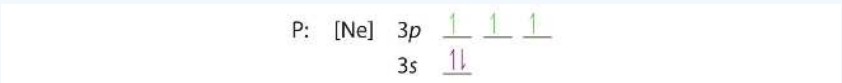
B The additional five electrons are placed in the next available orbitals, which Figure 3.5.1 tells us are the 3*s* and 3*p* orbitals:



Because the 3*s* orbital is lower in energy than the 3*p* orbitals, we fill it first:



Hund's rule tells us that the remaining three electrons will occupy the degenerate 3*p* orbitals separately but with their spins aligned:



The electron configuration is $[Ne]3s^2 3p^3$.

C We obtain the valence electron configuration by ignoring the inner orbitals, which for phosphorus means that we ignore the [Ne] closed shell. This gives a valence-electron configuration of $3s^2 3p^3$.

? Exercise 3.5.1

Draw an orbital diagram and use it to derive the electron configuration of chlorine, $Z = 17$. What is its valence electron configuration?

Answer

$[Ne]3s^2 3p^5$; $3s^2 3p^5$



Definition of Valence Electrons: Definition of Valence Electrons, YouTube(opens in new window) [youtu.be]

The general order in which orbitals are filled is depicted in Figure 3.5.2. Subshells corresponding to each value of n are written from left to right on successive horizontal lines, where each row represents a row in the periodic table. The order in which the orbitals are filled is indicated by the diagonal lines running from the upper right to the lower left. Accordingly, the 4*s* orbital is filled prior to the 3*d* orbital because of shielding and penetration effects. Consequently, the electron configuration of potassium, which begins the fourth period, is $[Ar]4s^1$, and the configuration of calcium is $[Ar]4s^2$. Five 3*d* orbitals are filled by the next 10 elements, the transition metals, followed by three 4*p* orbitals. Notice that the last member of this row is the noble gas krypton ($Z = 36$), $[Ar]4s^2 3d^{10} 4p^6 = [Kr]$, which has filled 4*s*, 3*d*, and 4*p* orbitals. The fifth row of the periodic table is essentially the same as the fourth, except that the 5*s*, 4*d*, and 5*p* orbitals are filled sequentially.

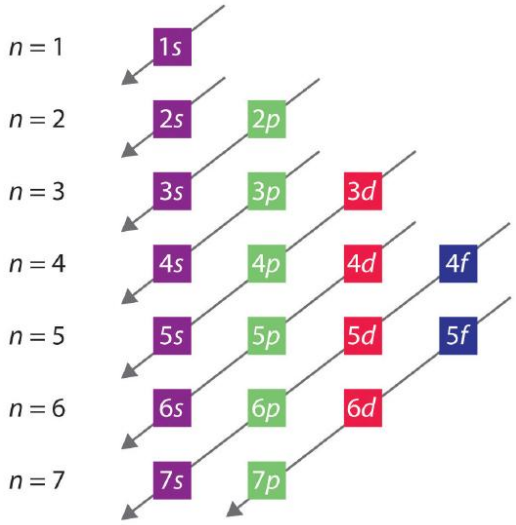


Figure 3.5.2: Predicting the Order in Which Orbitals Are Filled in Multielectron Atoms. If you write the subshells for each value of the principal quantum number on successive lines, the observed order in which they are filled is indicated by a series of diagonal lines running from the upper right to the lower left.

The sixth row of the periodic table will be different from the preceding two because the 4*f* orbitals, which can hold 14 electrons, are filled between the 6*s* and the 5*d* orbitals. The elements that contain 4*f* orbitals in their valence shell are the lanthanides. When the 6*p* orbitals are finally filled, we have reached the next noble gas, radon (Z = 86), [Xe]$6s^2 4f^{14} 5d^{10} 6p^6$ = [Rn]. In the last row, the 5*f* orbitals are filled between the 7*s* and the 6*d* orbitals, which gives the 14 actinide elements. Because the large number of protons makes their nuclei unstable, all the actinides are radioactive.

Example 3.5.2: Electron Configuration of Mercury

Write the electron configuration of mercury (Z = 80), showing all the inner orbitals.

Given: atomic number

Asked for: complete electron configuration

Strategy:

Using the orbital diagram in Figure 3.5.1 and the periodic table as a guide, fill the orbitals until all 80 electrons have been placed.

Solution:

By placing the electrons in orbitals following the order shown in Figure 3.5.2 and using the periodic table as a guide, we obtain

Solution to Example 6.8.2

$1s^2$	row 1	2 electrons
$2s^2 2p^6$	row 2	8 electrons
$3s^2 3p^6$	row 3	8 electrons
$4s^2 3d^{10} 4p^6$	row 4	18 electrons
$5s^2 4d^{10} 5p^6$	row 5	18 electrons
	row 1–5	54 electrons

After filling the first five rows, we still have 80 − 54 = 26 more electrons to accommodate. According to Figure 3.5.2, we need to fill the 6*s* (2 electrons), 4*f* (14 electrons), and 5*d* (10 electrons) orbitals. The result is mercury's electron configuration:

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} = \text{Hg} = [\text{Xe}]6s^2 4f^{14} 5d^{10}$$

with a filled 5*d* subshell, a $6s^2 4f^{14} 5d^{10}$ valence shell configuration, and a total of 80 electrons. (You should always check to be sure that the total number of electrons equals the atomic number.)

? Exercise 3.5.2: Electron Configuration of Flerovium

Although element 114 is not stable enough to occur in nature, atoms of element 114 were created for the first time in a nuclear reactor in 1998 by a team of Russian and American scientists. The element is named after the Flerov Laboratory of Nuclear Reactions of the Joint Institute for Nuclear Research in Dubna, Russia, where the element was discovered. The name of the laboratory, in turn, honors the Russian physicist Georgy Flyorov. Write the complete electron configuration for element 114.

Answer

$s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2 5f^{14} 6d^{10} 7p^2$

The electron configurations of the elements are presented in Figure 3.5.2, which lists the orbitals in the order in which they are filled. In several cases, the ground state electron configurations are different from those predicted by Figure 3.5.1. Some of these anomalies occur as the 3*d* orbitals are filled. For example, the observed ground state electron configuration of chromium is $[Ar]4s^1 3d^5$ rather than the predicted $[Ar]4s^2 3d^4$. Similarly, the observed electron configuration of copper is $[Ar]4s^1 3d^{10}$ instead of $[Ar]s^2 3d^9$. The actual electron configuration may be rationalized in terms of an added stability associated with a half-filled (ns^1, np^3, nd^5, nf^7) or filled (ns^2, np^6, nd^{10}, nf^{14}) subshell. (In fact, this "special stability" is really another consequence of the *instability* caused by pairing an electron with another in the same orbital, as illustrated by Hund's rule.) Given the small differences between higher energy levels, this added stability is enough to shift an electron from one orbital to another. In heavier elements, other more complex effects can also be important, leading to many additional anomalies. For example, cerium has an electron configuration of $[Xe]6s^2 4f^1 5d^1$, which is impossible to rationalize in simple terms. In most cases, however, these apparent anomalies do not have important chemical consequences.

> *Additional stability is associated with half-filled or filled subshells.*



Electron Configuration of Transition Metals: Electron Configuration of Transition Metals, YouTube(opens in new window) [youtu.be]

Summary

Based on the Pauli principle and a knowledge of orbital energies obtained using hydrogen-like orbitals, it is possible to construct the periodic table by filling up the available orbitals beginning with the lowest-energy orbitals (the **aufbau principle**), which gives rise to a particular arrangement of electrons for each element (its **electron configuration**). **Hund's rule** says that the lowest-energy arrangement of electrons is the one that places them in degenerate orbitals with their spins parallel. For chemical purposes, the most important electrons are those in the outermost principal shell, the **valence electrons**.

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3.6: Electron Configurations and the Periodic Table

Learning Objectives

- To correlate the arrangement of atoms in the periodic table results in blocks corresponding to filling of the *ns*, *np*, *nd*, and *nf* orbitals

As you have learned, the electron configurations of the elements explain the otherwise peculiar shape of the periodic table. Although the table was originally organized on the basis of physical and chemical similarities between the elements within groups, these similarities are ultimately attributable to orbital energy levels and the Pauli principle, which cause the individual subshells to be filled in a particular order. As a result, the periodic table can be divided into "blocks" corresponding to the type of subshell that is being filled, as illustrated in Figure 3.6.1. For example, the two columns on the left, known as the *s* block, consist of elements in which the *ns* orbitals are being filled. The six columns on the right, elements in which the *np* orbitals are being filled, constitute the *p* block. In between are the 10 columns of the *d* block, elements in which the $(n - 1)d$ orbitals are filled. At the bottom lie the 14 columns of the *f* block, elements in which the $(n - 2)f$ orbitals are filled. Because two electrons can be accommodated per orbital, the number of columns in each block is the same as the maximum electron capacity of the subshell: 2 for *ns*, 6 for *np*, 10 for $(n - 1)d$, and 14 for $(n - 2)f$. Within each column, each element has the same valence electron configuration—for example, ns^1 (group 1) or ns^2np^1 (group 13). As you will see, this is reflected in important similarities in the chemical reactivity and the bonding for the elements in each column.

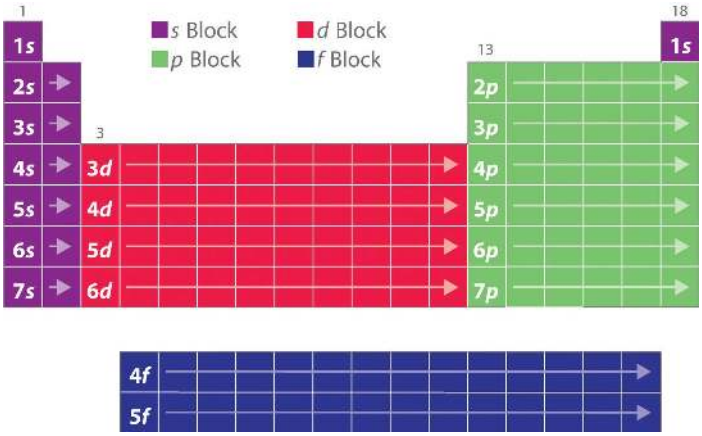


Figure 3.6.1: The Periodic Table, Showing How the Elements Are Grouped According to the Kind of Subshell (*s*, *p*, *d*, *f*) Being Filled with Electrons in the Valence Shell of Each Element. The electron configurations of the elements are in Figure 6.9.2.

Because each orbital can have a maximum of 2 electrons, there are 2 columns in the *s* block, 6 columns in the *p* block, 10 columns in the *d* block, and 14 columns in the *f* block.

Hydrogen and helium are placed somewhat arbitrarily. Although hydrogen is not an alkali metal, its $1s^1$ electron configuration suggests a similarity to lithium ($[He]2s^1$) and the other elements in the first column. Although helium, with a filled *ns* subshell, should be similar chemically to other elements with an ns^2 electron configuration, the closed principal shell dominates its chemistry, justifying its placement above neon on the right.

Atomic number	Symbol	Electron configuration	Atomic number	Symbol	Electron configuration	Atomic number	Symbol	Electron configuration
1	H	$1s^1$	37	Rb	[Kr]$5s^1$	73	Ta	[Xe]$6s^2 4f^{14} 5d^3$
2	He	$1s^2$	38	Sr	[Kr]$5s^2$	74	W	[Xe]$6s^2 4f^{14} 5d^4$
3	Li	[He]$2s^1$	39	Y	[Kr]$5s^2 4d^1$	75	Re	[Xe]$6s^2 4f^{14} 5d^5$
4	Be	[He]$2s^2$	40	Zr	[Kr]$5s^2 4d^2$	76	Os	[Xe]$6s^2 4f^{14} 5d^6$
5	B	[He]$2s^2 2p^1$	41	Nb	[Kr]$5s^1 4d^4$	77	Ir	[Xe]$6s^2 4f^{14} 5d^7$
6	C	[He]$2s^2 2p^2$	42	Mo	[Kr]$5s^1 4d^5$	78	Pt	[Xe]$6s^1 4f^{14} 5d^9$
7	N	[He]$2s^2 2p^3$	43	Tc	[Kr]$5s^2 4d^5$	79	Au	[Xe]$6s^1 4f^{14} 5d^{10}$
8	O	[He]$2s^2 2p^4$	44	Ru	[Kr]$5s^1 4d^7$	80	Hg	[Xe]$6s^2 4f^{14} 5d^{10}$
9	F	[He]$2s^2 2p^5$	45	Rh	[Kr]$5s^1 4d^8$	81	Tl	[Xe]$6s^2 4f^{14} 5d^{10} 6p^1$
10	Ne	[He]$2s^2 2p^6$	46	Pd	[Kr]$4d^{10}$	82	Pb	[Xe]$6s^2 4f^{14} 5d^{10} 6p^2$
11	Na	[Ne]$3s^1$	47	Ag	[Kr]$5s^1 4d^{10}$	83	Bi	[Xe]$6s^2 4f^{14} 5d^{10} 6p^3$
12	Mg	[Ne]$3s^2$	48	Cd	[Kr]$5s^2 4d^{10}$	84	Po	[Xe]$6s^2 4f^{14} 5d^{10} 6p^4$
13	Al	[Ne]$3s^2 3p^1$	49	In	[Kr]$5s^2 4d^{10} 5p^1$	85	At	[Xe]$6s^2 4f^{14} 5d^{10} 6p^5$
14	Si	[Ne]$3s^2 3p^2$	50	Sn	[Kr]$5s^2 4d^{10} 5p^2$	86	Rn	[Xe]$6s^2 4f^{14} 5d^{10} 6p^6$
15	P	[Ne]$3s^2 3p^3$	51	Sb	[Kr]$5s^2 4d^{10} 5p^3$	87	Fr	[Rn]$7s^1$
16	S	[Ne]$3s^2 3p^4$	52	Te	[Kr]$5s^2 4d^{10} 5p^4$	88	Ra	[Rn]$7s^2$
17	Cl	[Ne]$3s^2 3p^5$	53	I	[Kr]$5s^2 4d^{10} 5p^5$	89	Ac	[Rn]$7s^2 6d^1$
18	Ar	[Ne]$3s^2 3p^6$	54	Xe	[Kr]$5s^2 4d^{10} 5p^6$	90	Th	[Rn]$7s^2 6d^2$
19	K	[Ar]$4s^1$	55	Cs	[Xe]$6s^1$	91	Pa	[Rn]$7s^2 5f^2 6d^1$
20	Ca	[Ar]$4s^2$	56	Ba	[Xe]$6s^2$	92	U	[Rn]$7s^2 5f^3 6d^1$
21	Sc	[Ar]$4s^2 3d^1$	57	La	[Xe]$6s^2 5d^1$	93	Np	[Rn]$7s^2 5f^4 6d^1$
22	Ti	[Ar]$4s^2 3d^2$	58	Ce	[Xe]$6s^2 4f^1 5d^1$	94	Pu	[Rn]$7s^2 5f^6$
23	V	[Ar]$4s^2 3d^3$	59	Pr	[Xe]$6s^2 4f^3$	95	Am	[Rn]$7s^2 5f^7$
24	Cr	[Ar]$4s^1 3d^5$	60	Nd	[Xe]$6s^2 4f^4$	96	Cm	[Rn]$7s^2 5f^7 6d^1$
25	Mn	[Ar]$4s^2 3d^5$	61	Pm	[Xe]$6s^2 4f^5$	97	Bk	[Rn]$7s^2 5f^9$
26	Fe	[Ar]$4s^2 3d^6$	62	Sm	[Xe]$6s^2 4f^6$	98	Cf	[Rn]$7s^2 5f^{10}$
27	Co	[Ar]$4s^2 3d^7$	63	Eu	[Xe]$6s^2 4f^7$	99	Es	[Rn]$7s^2 5f^{11}$
28	Ni	[Ar]$4s^2 3d^8$	64	Gd	[Xe]$6s^2 4f^7 5d^1$	100	Fm	[Rn]$7s^2 5f^{12}$
29	Cu	[Ar]$4s^1 3d^{10}$	65	Tb	[Xe]$6s^2 4f^9$	101	Md	[Rn]$7s^2 5f^{13}$
30	Zn	[Ar]$4s^2 3d^{10}$	66	Dy	[Xe]$6s^2 4f^{10}$	102	No	[Rn]$7s^2 5f^{14}$
31	Ga	[Ar]$4s^2 3d^{10} 4p^1$	67	Ho	[Xe]$6s^2 4f^{11}$	103	Lr	[Rn]$7s^2 5f^{14} 6d^1$
32	Ge	[Ar]$4s^2 3d^{10} 4p^2$	68	Er	[Xe]$6s^2 4f^{12}$	104	Rf	[Rn]$7s^2 5f^{14} 6d^2$
33	As	[Ar]$4s^2 3d^{10} 4p^3$	69	Tm	[Xe]$6s^2 4f^{13}$	105	Db	[Rn]$7s^2 5f^{14} 6d^3$
34	Se	[Ar]$4s^2 3d^{10} 4p^4$	70	Yb	[Xe]$6s^2 4f^{14}$	106	Sg	[Rn]$7s^2 5f^{14} 6d^4$
35	Br	[Ar]$4s^2 3d^{10} 4p^5$	71	Lu	[Xe]$6s^2 4f^{14} 5d^1$	107	Bh	[Rn]$7s^2 5f^{14} 6d^5$
36	Kr	[Ar]$4s^2 3d^{10} 4p^6$	72	Hf	[Xe]$6s^2 4f^{14} 5d^2$	108	Hs	[Rn]$7s^2 5f^{14} 6d^6$
						109	Mt	[Rn]$7s^2 5f^{14} 6d^7$
						110	Ds	[Rn]$7s^1 5f^{14} 6d^9$
						111	Rg	[Rn]$7s^1 5f^{14} 6d^{10}$

Figure 3.6.2: Electron Configurations of the Elements. The electron configurations of elements indicated in red are exceptions due to the added stability associated with half-filled and filled subshells. The electron configurations of the elements indicated in blue are also anomalous, but the reasons for the observed configurations are more complex. For elements after No, the electron configurations are tentative.

Example 3.6.1

Use the periodic table to predict the valence electron configuration of all the elements of group 2 (beryllium, magnesium, calcium, strontium, barium, and radium).

Given: series of elements

Asked for: valence electron configurations

Strategy:

A. Identify the block in the periodic table to which the group 2 elements belong. Locate the nearest noble gas preceding each element and identify the principal quantum number of the valence shell of each element.

B. Write the valence electron configuration of each element by first indicating the filled inner shells using the symbol for the nearest preceding noble gas and then listing the principal quantum number of its valence shell, its valence orbitals, and the number of valence electrons in each orbital as superscripts.

Solution:

A The group 2 elements are in the *s* block of the periodic table, and as group 2 elements, they all have two valence electrons. Beginning with beryllium, we see that its nearest preceding noble gas is helium and that the principal quantum number of its

valence shell is $n = 2$.

B Thus beryllium has an [He]s^2 electron configuration. The next element down, magnesium, is expected to have exactly the same arrangement of electrons in the $n = 3$ principal shell: [Ne]s^2. By extrapolation, we expect all the group 2 elements to have an ns^2 electron configuration.

? Exercise 3.6.1

Use the periodic table to predict the characteristic valence electron configuration of the halogens in group 17.

Answer

All have an ns^2np^5 electron configuration, one electron short of a noble gas electron configuration. (Note that the heavier halogens also have filled $(n - 1)d^{10}$ subshells, as well as an $(n - 2)f^{14}$ subshell for Rn; these do not, however, affect their chemistry in any significant way.

Summary

The arrangement of atoms in the periodic table results in blocks corresponding to filling of the *ns*, *np*, *nd*, and *nf* orbitals to produce the distinctive chemical properties of the elements in the ***s* block**, ***p* block**, ***d* block**, and ***f* block**, respectively.

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CHAPTER OVERVIEW

4: Periodic Trends in Elements and Compounds

4.1: Development of the Periodic Table
4.2: Electronic Structure
4.3: Sizes of Atoms and Ions
4.4: Ionization Energy
4.5: Electron Affinity
4.6: Electronegativity

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4.1: Development of the Periodic Table

Learning Objectives

- To become familiar with the history of the periodic table.

The modern periodic table has evolved through a long history of attempts by chemists to arrange the elements according to their properties as an aid in predicting chemical behavior. One of the first to suggest such an arrangement was the German chemist Johannes Dobereiner (1780–1849), who noticed that many of the known elements could be grouped in triads (a set of three elements that have similar properties)—for example, chlorine, bromine, and iodine; or copper, silver, and gold. Dobereiner proposed that all elements could be grouped in such triads, but subsequent attempts to expand his concept were unsuccessful. We now know that portions of the periodic table—the *d* block in particular—contain triads of elements with substantial similarities. The middle three members of most of the other columns, such as sulfur, selenium, and tellurium in group 16 or aluminum, gallium, and indium in Group 13, also have remarkably similar chemistry.

No.	No.	No.	No.	No.	No.	No.	No.
H 1	F 8	Cl 15	Co & Ni 22	Br 29	Pd 36	I 42	Pt & Ir 50
Li 2	Na 9	K 16	Cu 23	Rb 30	Ag 37	Cs 44	Tl 51
G 3	Mg 10	Ca 17	Zn 25	Sr 31	Bd [sic-Cd] 38	Ba & V 45	Pb 54
Bo 4	Al 11	Cr 19	Y 24	Ce & La 33	U 40	Ta 46	Th 56
C 5	Si 12	Ti 18	In 26	Zr 32	Sn 39	W 47	Hg 52
N 6	P 13	Mn 20	As 27	Di & Mo 34	Sb 41	Nb 48	Bi 55
O 7	S 14	Fe 21	Se 28	Ro & Ru 35	Te 43	Au 49	Os 51

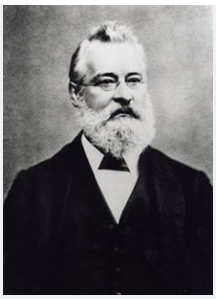
NOTE. Where two elements happen to have the same equivalent, both are designated by the same number.

Figure 4.1.1: The Arrangement of the Elements into Octaves as Proposed by Newlands. The table shown here accompanied a letter from a 27-year-old Newlands to the editor of the journal *Chemical News* in which he wrote: "If the elements are arranged in the order of their equivalents, with a few slight transpositions, as in the accompanying table, it will be observed that elements belonging to the same group usually appear on the same horizontal line. It will also be seen that the numbers of analogous elements generally differ either by 7 or by some multiple of seven; in other words, members of the same group stand to each other in the same relation as the extremities of one or more octaves in music. Thus, in the nitrogen group, between nitrogen and phosphorus there are 7 elements; between phosphorus and arsenic, 14; between arsenic and antimony, 14; and lastly, between antimony and bismuth, 14 also. This peculiar relationship I propose to provisionally term the *Law of Octaves*. I am, &c. John A. R. Newlands, F.C.S. Laboratory, 19, Great St. Helen's, E.C., August 8, 1865."

By the mid-19th century, the atomic masses of many of the elements had been determined. The English chemist John Newlands (1838–1898), hypothesizing that the chemistry of the elements might be related to their masses, arranged the known elements in order of increasing atomic mass and discovered that every seventh element had similar properties (Figure 4.1.1). Newlands therefore suggested that the elements could be classified into octaves. He described octaves as a group of seven elements which correspond to the horizontal rows in the main groups of today's periodic table. There were seven elements because the noble gases were not known at the time. Unfortunately, Newlands's "law of octaves" did not seem to work for elements heavier than calcium, and his idea was publicly ridiculed. At one scientific meeting, Newlands was asked why he didn't arrange the elements in alphabetical order instead of by atomic mass, since that would make just as much sense! Actually, Newlands was on the right track—with only a few exceptions, atomic mass does increase with atomic number, and similar properties occur every time a set of ns^2np^6 subshells is filled. Despite the fact that Newlands's table had no logical place for the *d*-block elements, he was honored for his idea by the Royal Society of London in 1887.

John Newlands (1838–1898)

John Alexander Reina Newlands was an English chemist who worked on the development of the periodic table. He noticed that elemental properties repeated every seventh (or multiple of seven) element, as musical notes repeat every eighth note.



The periodic table achieved its modern form through the work of the German chemist Julius Lothar Meyer (1830–1895) and the Russian chemist Dimitri Mendeleev (1834–1907), both of whom focused on the relationships between atomic mass and various physical and chemical properties. In 1869, they independently proposed essentially identical arrangements of the elements. Meyer aligned the elements in his table according to periodic variations in simple atomic properties, such as “atomic volume” (Figure 4.1.2), which he obtained by dividing the atomic mass (molar mass) in grams per mole by the density (ρ) of the element in grams per cubic centimeter. This property is equivalent to what is today defined as molar volume, the molar mass of an element divided by its density, (measured in cubic centimeters per mole):

$$\frac{molar\ mass\left(g/mol\right)}{density\left(g/cm^3\right)} = molar\ volume\left(cm^3/mol\right) \tag{4.1.1}$$

As shown in Figure 4.1.2, the alkali metals have the highest molar volumes of the solid elements. In Meyer’s plot of atomic volume versus atomic mass, the nonmetals occur on the rising portion of the graph, and metals occur at the peaks, in the valleys, and on the downslopes.

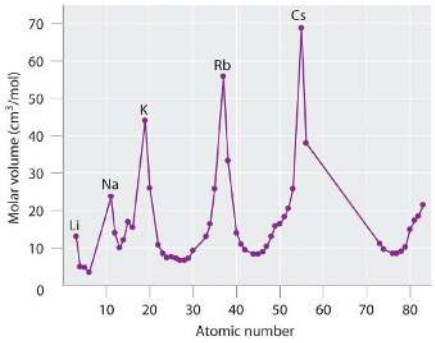
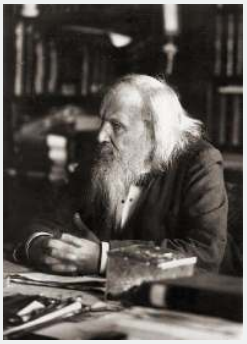


Figure 4.1.2: Variation of Atomic Volume with Atomic Number, Adapted from Meyer’s Plot of 1870. Note the periodic increase and decrease in atomic volume. Because the noble gases had not yet been discovered at the time this graph was formulated, the peaks correspond to the alkali metals (Group 1).

Dimitri Mendeleev (1834–1907)

When his family’s glass factory was destroyed by fire, Mendeleev moved to St. Petersburg, Russia, to study science. He became ill and was not expected to recover, but he finished his PhD with the help of his professors and fellow students.



In addition to the periodic table, another of Mendeleev's contributions to science was an outstanding textbook, *The Principles of Chemistry*, which was used for many years.

Mendeleev's Periodic Table

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4.2: Electronic Structure

Skills to Develop

- To understand the basics of electron shielding and penetration

For an atom or an ion with only a single electron, we can calculate the potential energy by considering only the electrostatic attraction between the positively charged nucleus and the negatively charged electron. When more than one electron is present, however, the total energy of the atom or the ion depends not only on attractive electron-nucleus interactions but also on repulsive electron-electron interactions. When there are two electrons, the repulsive interactions depend on the positions of *both* electrons at a given instant, but because we cannot specify the exact positions of the electrons, it is impossible to exactly calculate the repulsive interactions. Consequently, we must use approximate methods to deal with the effect of electron-electron repulsions on orbital energies. These effects are the underlying basis for the periodic trends in elemental properties that we will explore in this chapter.

Electron Shielding and Effective Nuclear Charge

If an electron is far from the nucleus (i.e., if the distance r between the nucleus and the electron is large), then at any given moment, many of the other electrons will be *between* that electron and the nucleus (Figure $4.2.1$). Hence the electrons will cancel a portion of the positive charge of the nucleus and thereby decrease the attractive interaction between it and the electron farther away. As a result, the electron farther away experiences an effective nuclear charge (Z_{eff}) that is less than the actual nuclear charge Z. This effect is called electron shielding.

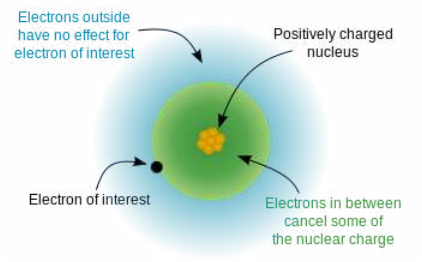


Figure* $4.2.1$*: *This image shows how inner electrons can shield outer electrons from the nuclear charge. Image used with permission (CC BY-SA 3.0; from NikNaks).*

Shielding

Shielding refers to the core electrons repelling the outer electrons, which lowers the effective charge of the nucleus on the outer electrons. Hence, the nucleus has "less grip" on the outer electrons insofar as it is shielded from them.

As the distance between an electron and the nucleus approaches infinity, Z_{eff} approaches a value of 1 because all the other ($Z-1$) electrons in the neutral atom are, on the average, between it and the nucleus. If, on the other hand, an electron is very close to the nucleus, then at any given moment most of the other electrons are farther from the nucleus and do not shield the nuclear charge. At $r \approx 0$, the positive charge experienced by an electron is approximately the full nuclear charge, or $Z_{eff} \approx Z$. At intermediate values of r, the effective nuclear charge is somewhere between 1 and Z:

$$1 \leq Z_{eff} \leq Z. \tag{4.2.1}$$

Notice that $Z_{eff} = Z$ only for hydrogen. Only for helium are Z_{eff} and Z comparable in magnitude − for most atoms, Z_{eff} for the valence (outermost) electrons is significantly less than Z (Figure $4.2.2$). In general, the effective nuclear charge of an atom increases as the number of protons in an atom increases, as long as the valence electrons occupy the same shell (Figure $4.2.2$). Therefore as we go from left to right on the periodic table the effective nuclear charge of an atom increases in strength and holds the outer electrons closer and tighter to the nucleus.

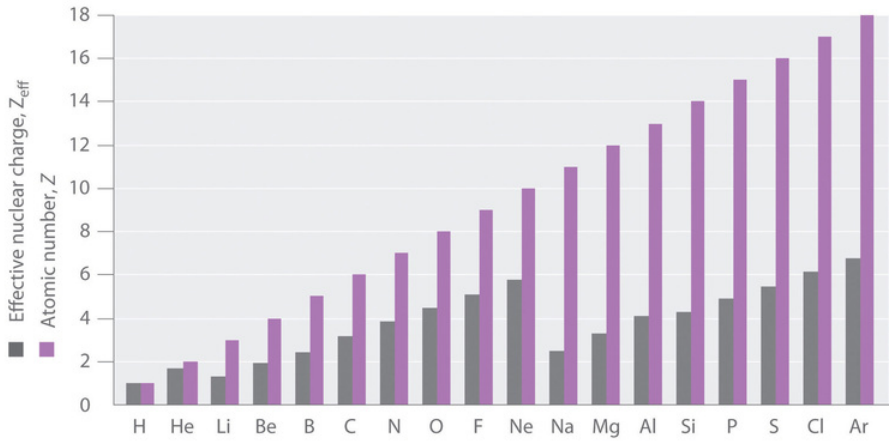


Figure* 4.2.2*: *Relationship between the Effective Nuclear Charge Z_{eff} and the Atomic Number Z for the Outer Electrons of the Elements of the First Three Rows of the Periodic Table. Except for hydrogen, (Z_{eff} is always less than Z, and (Z_{eff} increases from left to right as you go across a row.*

Example 4.2.1: Fluorine, Neon, and Sodium

Rank the effective attraction Z_{eff} experienced by the valence electrons in the three isoelectronic species: the fluorine anion, the neutral neon atom, and sodium cation.

Solution

Each species has 10 electrons, and the number of nonvalence electrons is 2 (10 total electrons - 8 valence), but the effective nuclear charge varies because each has a different atomic number A. According to the general principle, the more protons in the nucleus, the higher the effective nuclear charge, as long as the valence electrons are in the same shell (in this case, the n=2 shell).

The charge Z of the nucleus of a fluorine atom is 9, but the valence electrons are screened appreciably by the core electrons (four electrons from the 1s and 2s orbitals) and partially by the 7 electrons in the 2p orbitals. The same holds true for neon, but with Z = 10, and the sodium cation, but with Z = 11.

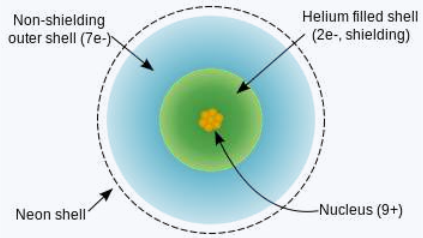


Diagram of a fluorine atom showing the extent of effective nuclear charge. Image used with permission (CC BY-SA- 3.0; from NikNaks).

The sodium cation, with the highest nuclear charge, also has the greatest effective nuclear charge. Z_{eff} : Na^+ > Ne > F^-. This also suggests that Na^+ has the smallest size among these species and that is correct.

Exercise 4.2.1: Sodium Species

Rank the effective attraction Z_{eff} experienced by the valence electrons in the sodium anion, the neutral sodium atom, and sodium cation.

Answer

In this case, all three species have the same nuclear charge, but going from the cation to the anion, electrons are added, which would increase the shielding of the other electrons. More shielding would mean a lower effective nuclear charge in the species with more electrons.

Z_{eff} : $Na^+ > Na > Na^-$

Electron Penetration

The actual Z_{eff} experienced by an electron in a given orbital depends not only on the spatial distribution of the electron in that orbital but also on the distribution of all the other electrons present. This leads to large differences in Z_{eff} for different elements, as shown in Figure 4.2.2 for the elements of the first three rows of the periodic table.

Penetration describes the proximity to which an electron can approach to the nucleus. In a multi-electron system, electron penetration is defined by an electron's relative electron density (probability density) near the nucleus of an atom (Figure 4.2.3). Electrons in different orbitals have different electron densities around the nucleus. In other words, penetration depends on the shell (n) and subshell (l).

For example, a 1s electron (Figure 4.2.3; purple curve) has greater electron density near the nucleus than a 2p electron (Figure 4.2.3; red curve) and has a greater penetration. This related to the amount of shielding since the 1s electrons are closer to the nucleus than a 2p electron, hence the 1s screens a 2p electron almost perfectly. However, the 2s electron has a lesser amount of shielding because it can penetrate close to the nucleus in the small area of electron density within the first spherical node (Figure 4.2.3; green curve). In this way the 2s electron can "avoid" some of the shielding effect of the inner 1s electron.

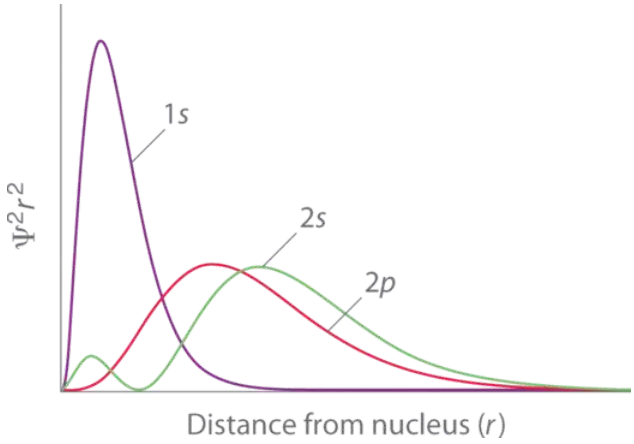


Figure 4.2.3: *Orbital Penetration. A comparison of the radial probability distribution of the 2s and 2p orbitals for various states of the hydrogen atom shows that the 2s orbital penetrates inside the 1s orbital more than the 2p orbital does. Consequently, when an electron is in the small inner lobe of the 2s orbital, it experiences a relatively large value of Z_{eff}, which causes the energy of the 2s orbital to be lower than the energy of the 2p orbital.*

For the same shell value (n) the penetrating power of an electron follows this trend in subshells (Figure 4.2.3):

$$s > p > d \approx f. \tag{4.2.2}$$

for different values of shell (n) and subshell (l), penetrating power of an electron follows this trend:

$$1\,\mathrm{s} > 2\,\mathrm{s} > 2\,\mathrm{p} > 3\,\mathrm{s} > 3\,\mathrm{p} > 4\,\mathrm{s} > 3\,\mathrm{d} > 4\,\mathrm{p} > 5\,\mathrm{s} > 4\,\mathrm{d} > 5\,\mathrm{p} > 6\,\mathrm{s} > 4\,\mathrm{f} \cdots \tag{4.2.3}$$

Penetration

Penetration describes the proximity of electrons in an orbital to the nucleus. Electrons that have greater penetration can get closer to the nucleus and effectively block out the charge from electrons that have less proximity.

Table 4.2.1: Effective Nuclear Charges for Selected Atoms

Atom	Sublevel	Z	Z_{eff}
H	1s	1	1
He	1s	2	1.69
Li	1s, 2s	3	2.69, 1.28

Atom	Sublevel	Z	Z_{eff}
Be	1s, 2s	4	3.68, 1.91
B	1s, 2s, 2p	5	4.68, 2.58, 2.42
F	1s, 2s, 2p	9	8.65, 5.13, 5.10
Na	1s, 2s, 2p, 3s	11	10.63, 6.57, 6.80, 2.51

Data from E. Clementi and D. L. Raimondi; The Journal of Chemical Physics 38, 2686 (1963).

Because of the effects of shielding and the different radial distributions of orbitals with the same value of *n* but different values of *l*, the different subshells are not degenerate in a multielectron atom. For a given value of *n*, the *ns* orbital is always lower in energy than the *np* orbitals, which are lower in energy than the *nd* orbitals, and so forth. As a result, some subshells with higher principal quantum numbers are actually lower in energy than subshells with a lower value of *n*; for example, the 4*s* orbital is lower in energy than the 3*d* orbitals for most atoms.

A Better Estimation of Shielding: Slater's Rules

The concepts of electron shielding, orbital penetration and effective nuclear charge were introduced above, but in a qualitative manner. A more accurate model for estimating electron shielding and corresponding effective nuclear charge quantitatively is Slater's Rules. However, the application of these rules is outside the scope of this text.

Summary

The calculation of orbital energies in atoms or ions with more than one electron (multielectron atoms or ions) is complicated by repulsive interactions between the electrons. The concept of **electron shielding**, in which intervening electrons act to reduce the positive nuclear charge experienced by an electron, allows the use of hydrogen-like orbitals and an **effective nuclear charge** (Z_{eff}) to describe electron distributions in more complex atoms or ions. The degree to which orbitals with different values of *l* and the same value of *n* overlap or penetrate filled inner shells results in slightly different energies for different subshells in the same principal shell in most atoms.

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4.3: Sizes of Atoms and Ions

Learning Objectives

- To understand periodic trends in atomic radii.
- To predict relative ionic sizes within an isoelectronic series.

Although some people fall into the trap of visualizing atoms and ions as small, hard spheres similar to miniature table-tennis balls or marbles, the quantum mechanical model tells us that their shapes and boundaries are much less definite than those images suggest. As a result, atoms and ions cannot be said to have exact sizes; however, some atoms are larger or smaller than others, and this influences their chemistry. In this section, we discuss how atomic and ion "sizes" are defined and obtained.

Atomic Radii

Recall that the probability of finding an electron in the various available orbitals falls off slowly as the distance from the nucleus increases. This point is illustrated in Figure 4.3.1 which shows a plot of total electron density for all occupied orbitals for three noble gases as a function of their distance from the nucleus. Electron density diminishes gradually with increasing distance, which makes it impossible to draw a sharp line marking the boundary of an atom.

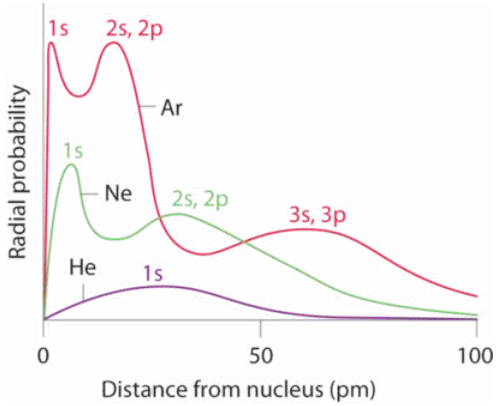


Figure 4.3.1: Plots of Radial Probability as a Function of Distance from the Nucleus for He, Ne, and Ar. In He, the 1*s* electrons have a maximum radial probability at ≈30 pm from the nucleus. In Ne, the 1*s* electrons have a maximum at ≈8 pm, and the 2*s* and 2*p* electrons combine to form another maximum at ≈35 pm (the $n = 2$ shell). In Ar, the 1*s* electrons have a maximum at ≈2 pm, the 2*s* and 2*p* electrons combine to form a maximum at ≈18 pm, and the 3*s* and 3*p* electrons combine to form a maximum at ≈70 pm.

Figure 4.3.1 also shows that there are distinct peaks in the total electron density at particular distances and that these peaks occur at different distances from the nucleus for each element. Each peak in a given plot corresponds to the electron density in a given principal shell. Because helium has only one filled shell ($n = 1$), it shows only a single peak. In contrast, neon, with filled $n = 1$ and 2 principal shells, has two peaks. Argon, with filled $n = 1$, 2, and 3 principal shells, has three peaks. The peak for the filled $n = 1$ shell occurs at successively shorter distances for neon ($Z = 10$) and argon ($Z = 18$) because, with a greater number of protons, their nuclei are more positively charged than that of helium. Because the $1s^2$ shell is closest to the nucleus, its electrons are very poorly shielded by electrons in filled shells with larger values of n. Consequently, the two electrons in the $n = 1$ shell experience nearly the full nuclear charge, resulting in a strong electrostatic interaction between the electrons and the nucleus. The energy of the $n = 1$ shell also decreases tremendously (the filled 1*s* orbital becomes more stable) as the nuclear charge increases. For similar reasons, the filled $n = 2$ shell in argon is located closer to the nucleus and has a lower energy than the $n = 2$ shell in neon.

Figure 4.3.1 illustrates the difficulty of measuring the dimensions of an individual atom. Because distances between the nuclei in pairs of covalently bonded atoms can be measured quite precisely, however, chemists use these distances as a basis for describing the approximate sizes of atoms. For example, the internuclear distance in the diatomic Cl_2 molecule is known to be 198 pm. We assign half of this distance to each chlorine atom, giving chlorine a **covalent atomic radius** (r_{cov}), which is half the distance between the nuclei of two like atoms joined by a covalent bond in the same molecule, of 99 pm or 0.99 Å (Figure 4.3.2*a*). Atomic radii are often measured in angstroms (Å), a non-SI unit: $1 \text{ Å} = 1 \times 10^{-10} \text{ m} = 100 \text{ pm}$.

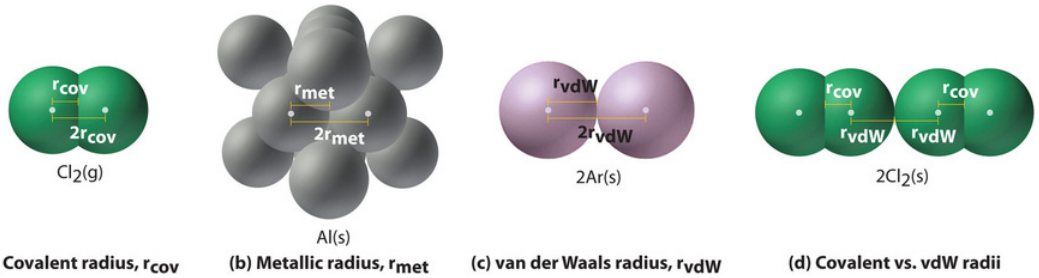


Figure 4.3.2: Definitions of the Atomic Radius. (a) The covalent atomic radius, r_{cov}, is half the distance between the nuclei of two like atoms joined by a covalent bond in the same molecule, such as Cl_2. (b) The metallic atomic radius, r_{met}, is half the distance between the nuclei of two adjacent atoms in a pure solid metal, such as aluminum. (c) The van der Waals atomic radius, r_{vdW}, is half the distance between the nuclei of two like atoms, such as argon, that are closely packed but not bonded. (d) This is a depiction of covalent versus van der Waals radii of chlorine. The covalent radius of Cl_2 is half the distance between the two chlorine atoms in a single molecule of Cl_2. The van der Waals radius is half the distance between chlorine nuclei in two different but touching Cl_2 molecules. Which do you think is larger? Why?

In a similar approach, we can use the lengths of carbon–carbon single bonds in organic compounds, which are remarkably uniform at 154 pm, to assign a value of 77 pm as the covalent atomic radius for carbon. If these values do indeed reflect the actual sizes of the atoms, then we should be able to predict the lengths of covalent bonds formed between different elements by adding them. For example, we would predict a carbon–chlorine distance of 77 pm + 99 pm = 176 pm for a C–Cl bond, which is very close to the average value observed in many organochlorine compounds. A similar approach for measuring the size of ions is discussed later in this section.

Covalent atomic radii can be determined for most of the nonmetals, but how do chemists obtain atomic radii for elements that do not form covalent bonds? For these elements, a variety of other methods have been developed. With a metal, for example, the **metallic atomic radius** (r_{met}) is defined as half the distance between the nuclei of two adjacent metal atoms in the solid (Figure 4.3.2*b*). For elements such as the noble gases, most of which form no stable compounds, we can use what is called the **van der Waals atomic radius** (r_{vdW}), which is half the internuclear distance between two nonbonded atoms in the solid (Figure 4.3.2*c*). This is somewhat difficult for helium which does not form a solid at any temperature. An atom such as chlorine has both a covalent radius (the distance between the two atoms in a Cl_2 molecule) and a van der Waals radius (the distance between two Cl atoms in different molecules in, for example, $Cl_2(s)$ at low temperatures). These radii are generally not the same (Figure 4.3.2*d*).

Periodic Trends in Atomic Radii

Because it is impossible to measure the sizes of both metallic and nonmetallic elements using any one method, chemists have developed a self-consistent way of calculating atomic radii using the quantum mechanical functions. Although the radii values obtained by such calculations are not identical to any of the experimentally measured sets of values, they do provide a way to compare the intrinsic sizes of all the elements and clearly show that atomic size varies in a periodic fashion (Figure 4.3.3).

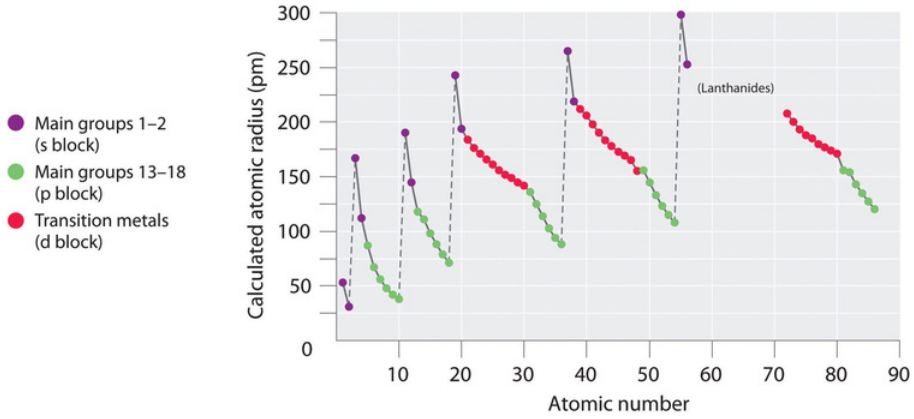


Figure 4.3.3: A Plot of Periodic Variation of Atomic Radius with Atomic Number for the First Six Rows of the Periodic Table

In the periodic table, atomic radii decrease from left to right across a row and increase from top to bottom down a column. Because of these two trends, the largest atoms are found in the lower left corner of the periodic table, and the smallest are found in the upper right corner (Figure 4.3.4).

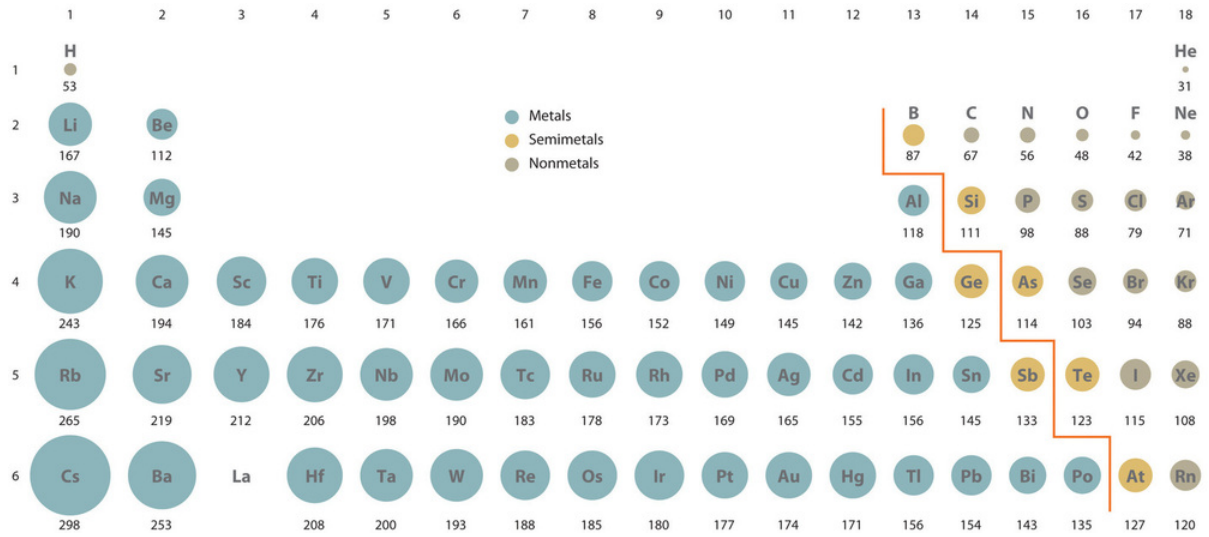


Figure 4.3.4 Calculated Atomic Radii (in Picometers) of the *s*-, *p*-, and *d*-Block Elements. The sizes of the circles illustrate the relative sizes of the atoms. The calculated values are based on quantum mechanical wave functions. Source: Web elements [www.webelements.com]. Web Elements is an excellent online source for looking up atomic properties.

Trends in atomic size result from differences in the **effective nuclear charges** (Z_{eff}) experienced by electrons in the outermost orbitals of the elements. For all elements except H, the effective nuclear charge is always *less* than the actual nuclear charge because of shielding effects. The greater the effective nuclear charge, the more strongly the outermost electrons are attracted to the nucleus and the smaller the atomic radius.

> *Atomic radii decrease from left to right across a row and increase from top to bottom down a column.*

The atoms in the second row of the periodic table (Li through Ne) illustrate the effect of electron shielding. All have a filled $1s^2$ inner shell, but as we go from left to right across the row, the nuclear charge increases from +3 to +10. Although electrons are being added to the 2*s* and 2*p* orbitals, *electrons in the same principal shell are not very effective at shielding one another from the nuclear charge*. Thus the single 2*s* electron in lithium experiences an effective nuclear charge of approximately +1 because the electrons in the filled $1s^2$ shell effectively neutralize two of the three positive charges in the nucleus. (More detailed calculations give a value of Z_{eff} = +1.26 for Li.) In contrast, the two 2*s* electrons in beryllium do not shield each other very well, although the filled $1s^2$ shell effectively neutralizes two of the four positive charges in the nucleus. This means that the effective nuclear charge experienced by the 2*s* electrons in beryllium is between +1 and +2 (the calculated value is +1.66). Consequently, beryllium is significantly smaller than lithium. Similarly, as we proceed across the row, the increasing nuclear charge is not effectively neutralized by the electrons being added to the 2*s* and 2*p* orbitals. The result is a steady increase in the effective nuclear charge and a steady decrease in atomic size (Figure 4.3.5).

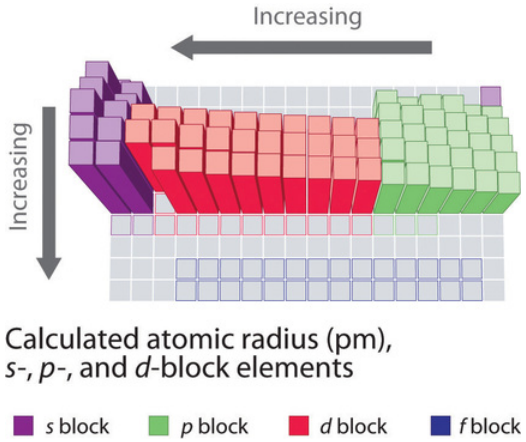


Figure 4.3.5: The Atomic Radius of the Elements. The atomic radius of the elements increases as we go from right to left across a period and as we go down the periods in a group.

The increase in atomic size going down a column is also due to electron shielding, but the situation is more complex because the principal quantum number *n* is not constant. As we saw in Chapter 2, the size of the orbitals increases as *n* increases, *provided the nuclear charge remains the same*. In group 1, for example, the size of the atoms increases substantially going down the column. It may at first seem reasonable to attribute this effect to the successive addition of electrons to *ns* orbitals with increasing values of *n*. However, it is important to remember that the radius of an orbital depends dramatically on the nuclear charge. As we go down the column of the group 1 elements, the principal quantum number *n* increases from 2 to 6, but the nuclear charge increases from +3 to +55!

As a consequence the radii of the **lower electron orbitals** in Cesium are much smaller than those in lithium and the electrons in those orbitals experience a much larger force of attraction to the nucleus. That force depends on the effective nuclear charge experienced by the the inner electrons. If the outermost electrons in cesium experienced the full nuclear charge of +55, a cesium atom would be very small indeed. In fact, the effective nuclear charge felt by the outermost electrons in cesium is much less than expected (6 rather than 55). This means that cesium, with a $6s^1$ valence electron configuration, is much larger than lithium, with a $2s^1$ valence electron configuration. The effective nuclear charge changes relatively little for electrons in the outermost, or valence shell, from lithium to cesium because *electrons in filled inner shells are highly effective at shielding electrons in outer shells from the nuclear charge*. Even though cesium has a nuclear charge of +55, it has 54 electrons in its filled $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6$ shells, abbreviated as $[Xe]5s^2 4d^{10} 5p^6$, which effectively neutralize most of the 55 positive charges in the nucleus. The same dynamic is responsible for the steady increase in size observed as we go down the other columns of the periodic table. Irregularities can usually be explained by variations in effective nuclear charge.

Not all Electrons shield equally

Electrons in the same principal shell are not very effective at shielding one another from the nuclear charge, whereas electrons in filled inner shells are highly effective at shielding electrons in outer shells from the nuclear charge.

Example 4.3.1

On the basis of their positions in the periodic table, arrange these elements in order of increasing atomic radius: aluminum, carbon, and silicon.

Given: three elements

Asked for: arrange in order of increasing atomic radius

Strategy:

A. Identify the location of the elements in the periodic table. Determine the relative sizes of elements located in the same column from their principal quantum number *n*. Then determine the order of elements in the same row from their effective nuclear charges. If the elements are not in the same column or row, use pairwise comparisons.

B. List the elements in order of increasing atomic radius.

Solution:

A These elements are not all in the same column or row, so we must use pairwise comparisons. Carbon and silicon are both in group 14 with carbon lying above, so carbon is smaller than silicon (C < Si). Aluminum and silicon are both in the third row with aluminum lying to the left, so silicon is smaller than aluminum (Si < Al) because its effective nuclear charge is greater.

B Combining the two inequalities gives the overall order: C < Si < Al.

Exercise 4.3.1

On the basis of their positions in the periodic table, arrange these elements in order of increasing size: oxygen, phosphorus, potassium, and sulfur.

Answer

O < S < P < K



Atomic Radius: Atomic Radius, YouTube(opens in new window) [youtu.be]

Ionic Radii and Isoelectronic Series

An ion is formed when either one or more electrons are removed from a neutral atom to form a positive ion (cation) or when additional electrons attach themselves to neutral atoms to form a negative one (anion). The designations cation or anion come from the early experiments with electricity which found that positively charged particles were attracted to the negative pole of a battery, the cathode, while negatively charged ones were attracted to the positive pole, the anode.

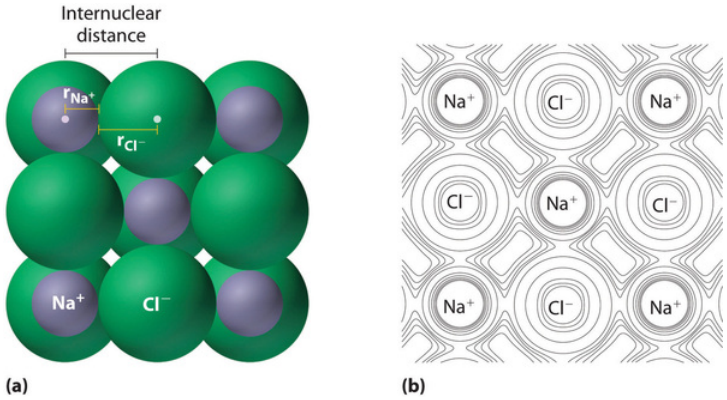


Figure 4.3.6: Definition of Ionic Radius. (a) The internuclear distance is apportioned between adjacent cations (positively charged ions) and anions (negatively charged ions) in the ionic structure, as shown here for Na^+ and Cl^- in sodium chloride. (b) This depiction of electron density contours for a single plane of atoms in the NaCl structure shows how the lines connect points of equal electron density. Note the relative sizes of the electron density contour lines around Cl^- and Na^+.

Ionic compounds consist of regular repeating arrays of alternating positively charged cations and negatively charges anions. Although it is not possible to measure an ionic radius directly for the same reason it is not possible to directly measure an atom's radius, it *is* possible to measure the distance between the nuclei of a cation and an adjacent anion in an ionic compound to determine the ionic radius (the radius of a cation or anion) of one or both. As illustrated in Figure 4.3.6, the internuclear distance corresponds to the *sum* of the radii of the cation and anion. A variety of methods have been developed to divide the experimentally measured distance proportionally between the smaller cation and larger anion. These methods produce sets of ionic radii that are internally consistent from one ionic compound to another, although each method gives slightly different values. For example, the radius of the Na^+ ion is essentially the same in NaCl and Na_2S, as long as the same method is used to measure it. Thus despite minor differences due to methodology, certain trends can be observed.

A comparison of ionic radii with atomic radii (Figure 4.3.7) shows that *a cation, having lost an electron, is always smaller than its parent neutral atom, and an anion, having gained an electron, is always larger than the parent neutral atom*. When one or more electrons is removed from a neutral atom, two things happen: (1) repulsions between electrons in the same principal shell decrease because fewer electrons are present, and (2) the effective nuclear charge felt by the remaining electrons increases because there are fewer electrons to shield one another from the nucleus. Consequently, the size of the region of space occupied by electrons decreases and the ion shrinks (compare Li at 167 pm with Li^+ at 76 pm). If different numbers of electrons can be removed to

produce ions with different charges, the ion with the greatest positive charge is the smallest (compare Fe^{2+} at 78 pm with Fe^{3+} at 64.5 pm). Conversely, adding one or more electrons to a neutral atom causes electron–electron repulsions to increase and the effective nuclear charge to decrease, so the size of the probability region increases and the ion expands (compare F at 42 pm with F^- at 133 pm).

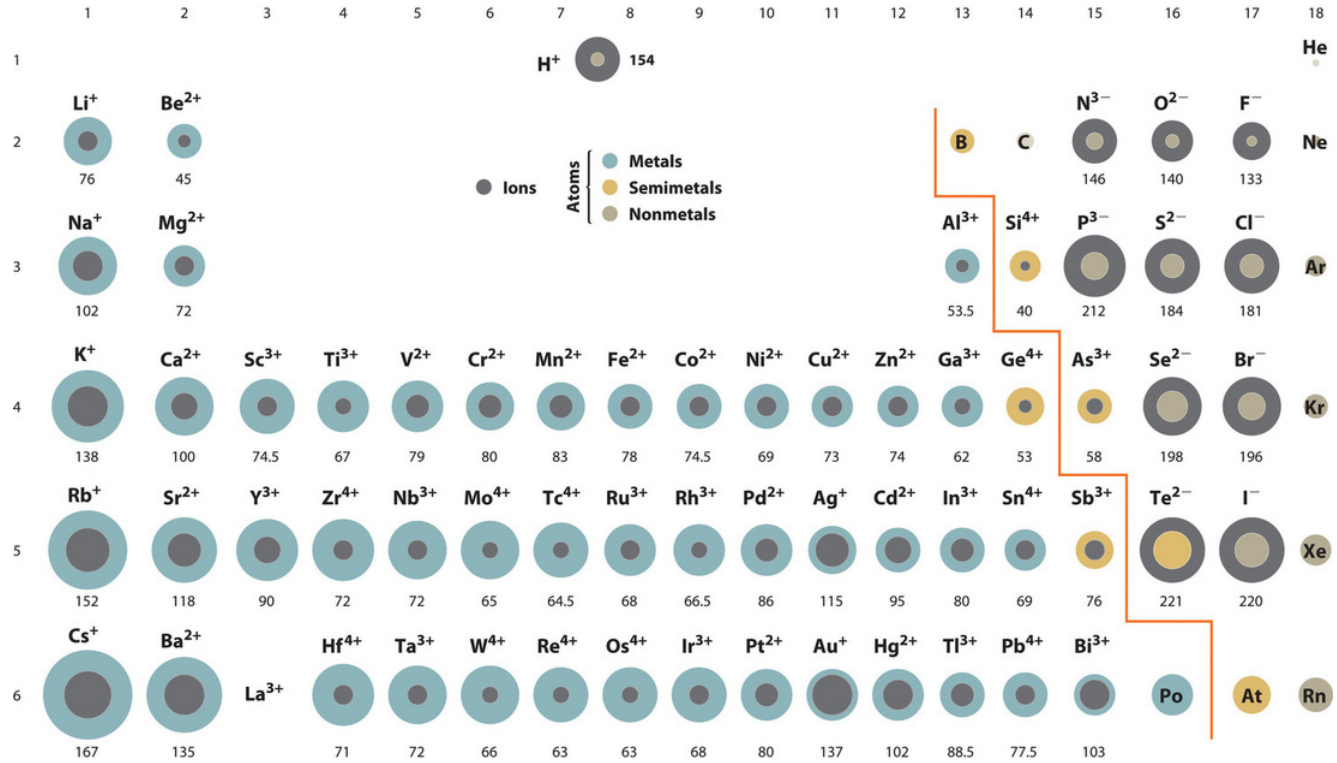


Figure 4.3.7: Ionic Radii (in Picometers) of the Most Common Ionic States of the *s*-, *p*-, and *d*-Block Elements.Gray circles indicate the sizes of the ions shown; colored circles indicate the sizes of the neutral atoms. Source: Ionic radius data from R. D. Shannon, "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides," *Acta Crystallographica* 32, no. 5 (1976): 751–767.

> *Cations are **always** smaller than the neutral atom and anions are **always** larger.*

Because most elements form either a cation or an anion but not both, there are few opportunities to compare the sizes of a cation and an anion derived from the same neutral atom. A few compounds of sodium, however, contain the Na^- ion, allowing comparison of its size with that of the far more familiar Na^+ ion, which is found in *many* compounds. The radius of sodium in each of its three known oxidation states is given in Table 4.3.1. All three species have a nuclear charge of +11, but they contain 10 (Na^+), 11 (Na^0), and 12 (Na^-) electrons. The Na^+ ion is significantly smaller than the neutral Na atom because the $3s^1$ electron has been removed to give a closed shell with $n = 2$. The Na^- ion is larger than the parent Na atom because the additional electron produces a $3s^2$ valence electron configuration, while the nuclear charge remains the same.

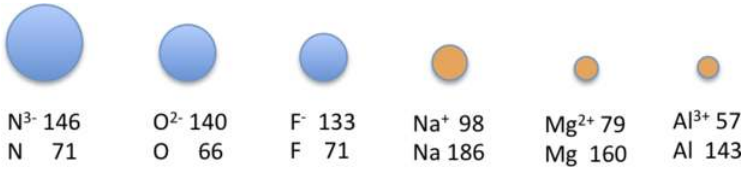
Table 4.3.1: Experimentally Measured Values for the Radius of Sodium in Its Three Known Oxidation States

	Na^+	Na^0	Na^-
Electron Configuration	$1s^2 2s^2 2p^6$	$1s^2 2s^2 2p^6 3s^1$	$1s^2 2s^2 2p^6 3s^2$
Radius (pm)	102	154*	202†

*The metallic radius measured for Na(s). †Source: M. J. Wagner and J. L. Dye, "Alkalides, Electrides, and Expanded Metals," Annual Review of Materials Science 23 (1993): 225–253.

Ionic radii follow the same vertical trend as atomic radii; that is, for ions with the same charge, the ionic radius increases going down a column. The reason is the same as for atomic radii: shielding by filled inner shells produces little change in the effective nuclear charge felt by the outermost electrons. Again, principal shells with larger values of *n* lie at successively greater distances from the nucleus.

Because elements in different columns tend to form ions with different charges, it is not possible to compare ions of the same charge across a row of the periodic table. Instead, elements that are next to each other tend to form ions with the same number of electrons but with different overall charges because of their different atomic numbers. Such a set of species is known as an **isoelectronic series**. For example, the isoelectronic series of species with the neon closed-shell configuration ($1s^2 2s^2 2p^6$) is shown in Table 4.3.3.



The sizes of the ions in this series decrease smoothly from N^{3-} to Al^{3+}. All six of the ions contain 10 electrons in the 1*s*, 2*s*, and 2*p* orbitals, but the nuclear charge varies from +7 (N) to +13 (Al). As the positive charge of the nucleus increases while the number of electrons remains the same, there is a greater electrostatic attraction between the electrons and the nucleus, which causes a decrease in radius. Consequently, the ion with the greatest nuclear charge (Al^{3+}) is the smallest, and the ion with the smallest nuclear charge (N^{3-}) is the largest. The neon atom in this isoelectronic series is not listed in Table 4.3.3, because neon forms no covalent or ionic compounds and hence its radius is difficult to measure.

Table 4.3.3: Radius of Ions with the Neon Closed-Shell Electron Configuration. Source: R. D. Shannon, "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides," Acta Crystallographica 32, no. 5 (1976): 751–767.

Ion	Radius (pm)	Atomic Number
N^{3-}	146	7
O^{2-}	140	8
F^-	133	9
Na^+	98	11
Mg^{2+}	79	12
Al^{3+}	57	13

Example 4.3.2

Based on their positions in the periodic table, arrange these ions in order of increasing radius: Cl^-, K^+, S^{2-}, and Se^{2-}.

Given: four ions

Asked for: order by increasing radius

Strategy:

A. Determine which ions form an isoelectronic series. Of those ions, predict their relative sizes based on their nuclear charges. For ions that do not form an isoelectronic series, locate their positions in the periodic table.

B. Determine the relative sizes of the ions based on their principal quantum numbers *n* and their locations within a row.

Solution:

A We see that S and Cl are at the right of the third row, while K and Se are at the far left and right ends of the fourth row, respectively. K^+, Cl^-, and S^{2-} form an isoelectronic series with the [Ar] closed-shell electron configuration; that is, all three ions contain 18 electrons but have different nuclear charges. Because K^+ has the greatest nuclear charge (Z = 19), its radius is smallest, and S^{2-} with Z = 16 has the largest radius. Because selenium is directly below sulfur, we expect the Se^{2-} ion to be even larger than S^{2-}.

B The order must therefore be $K^+ < Cl^- < S^{2-} < Se^{2-}$.

? Exercise 4.3.2

Based on their positions in the periodic table, arrange these ions in order of increasing size: Br^-, Ca^{2+}, Rb^+, and Sr^{2+}.

Answer

$Ca^{2+} < Sr^{2+} < Rb^+ < Br^-$

Summary

Ionic radii share the same vertical trend as atomic radii, but the horizontal trends differ due to differences in ionic charges. A variety of methods have been established to measure the size of a single atom or ion. The **covalent atomic radius (r_{cov})** is half the internuclear distance in a molecule with two identical atoms bonded to each other, whereas the **metallic atomic radius (r_{met})** is defined as half the distance between the nuclei of two adjacent atoms in a metallic element. The **van der Waals radius (r_{vdW})** of an element is half the internuclear distance between two nonbonded atoms in a solid. Atomic radii decrease from left to right across a row because of the increase in effective nuclear charge due to poor electron screening by other electrons in the same principal shell. Moreover, atomic radii increase from top to bottom down a column because the effective nuclear charge remains relatively constant as the principal quantum number increases. The **ionic radii** of cations and anions are always smaller or larger, respectively, than the parent atom due to changes in electron–electron repulsions, and the trends in ionic radius parallel those in atomic size. A comparison of the dimensions of atoms or ions that have the same number of electrons but different nuclear charges, called an **isoelectronic series**, shows a clear correlation between increasing nuclear charge and decreasing size.

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4.4: Ionization Energy

Learning Objectives

- To correlate ionization energies with the chemistry of the elements

We have seen that when elements react, they often gain or lose enough electrons to achieve the valence electron configuration of the nearest noble gas. Why is this so? In this section, we develop a more quantitative approach to predicting such reactions by examining periodic trends in the energy changes that accompany ion formation.

Ionization Energies

Because atoms do not spontaneously lose electrons, energy is required to remove an electron from an atom to form a cation. Chemists define the ionization energy (I) of an element as the amount of energy needed to remove an electron from the gaseous atom E in its ground state. I is therefore the energy required for the reaction

$$E_{(g)} \rightarrow E^+_{(g)} + e^- \qquad \text{energy required=I} \tag{4.4.1}$$

Because an input of energy is required, the ionization energy is always positive ($I > 0$) for the reaction as written in Equation 4.4.1. Larger values of *I* mean that the electron is more tightly bound to the atom and harder to remove. Typical units for ionization energies are kilojoules/mole (kJ/mol) or electron volts (eV):

$$1\ eV/atom = 96.49\ kJ/mol$$

If an atom possesses more than one electron, the amount of energy needed to remove successive electrons increases steadily. We can define a first ionization energy (I_1), a second ionization energy (I_2), and in general an nth ionization energy (I_n) according to the following reactions:

$$\mathrm{E(g) \rightarrow E^+(g) + e^-} \qquad I_1 = \text{1st ionization energy} \tag{4.4.2}$$

$$\mathrm{E^+(g) \rightarrow E^{2+}(g) + e^-} \qquad I_2 = \text{2nd ionization energy} \tag{4.4.3}$$

$$\mathrm{E^{2+}(g) \rightarrow E^{3+}(g) + e^-} \qquad I_3 = \text{3rd ionization energy} \tag{4.4.4}$$

Values for the ionization energies of Li and Be listed in Table 4.4.1 show that successive ionization energies for an element increase as they go; that is, it takes more energy to remove the second electron from an atom than the first, and so forth. There are two reasons for this trend. First, the second electron is being removed from a positively charged species rather than a neutral one, so in accordance with Coulomb's law, more energy is required. Second, removing the first electron reduces the repulsive forces among the remaining electrons, so the attraction of the remaining electrons to the nucleus is stronger.

> *Successive ionization energies for an element **increase**.*

Table 4.4.1: Ionization Energies (in kJ/mol) for Removing Successive Electrons from Li and Be. Source: Data from CRC Handbook of Chemistry and Physics (2004).

Reaction	Electronic Transition	I	Reaction	Electronic Transition	I
$\mathrm{Li(g) \rightarrow Li^+(g) + e^-}$	$1s^2 2s^1 \rightarrow 1s^2$	I_1 = 520.2	$\mathrm{Be(g) \rightarrow Be^+(g) + e^-}$	$1s^2 2s^2 \rightarrow 1s^2 2s^1$	I_1 = 899.5
$\mathrm{Li^+(g) \rightarrow Li^{2+}(g) + e^-}$	$1s^2 \rightarrow 1s^1$	I_2 = 7298.2	$\mathrm{Be^+(g) \rightarrow Be^{2+}(g) + e^-}$	$1s^2 2s^1 \rightarrow 1s^2$	I_2 = 1757.1
$\mathrm{Li^{2+}(g) \rightarrow Li^{3+}(g) + e^-}$	$1s^1 \rightarrow 1s^0$	I_3 = 11,815.0	$\mathrm{Be^{2+}(g) \rightarrow Be^{3+}(g) + e^-}$	$1s^2 \rightarrow 1s^1$	I_3 = 14,848.8
			$\mathrm{Be^{3+}(g) \rightarrow Be^{4+}(g) + e^-}$	$1s^1 \rightarrow 1s^0$	I_4 = 21,006.6

The increase in successive ionization energies, however, is not linear, but increases drastically when removing electrons in lower n orbitals closer to the nucleus. The most important consequence of the values listed in Table 4.4.1 is that the chemistry of Li is dominated by the $\mathrm{Li^+}$ ion, while the chemistry of Be is dominated by the +2 oxidation state. The energy required to remove the *second* electron from Li:

$$\mathrm{Li^+(g) \rightarrow Li^{2+}(g) + e^-} \tag{4.4.5}$$

is more than 10 times greater than the energy needed to remove the first electron. Similarly, the energy required to remove the *third* electron from Be:

$$\mathrm{Be^{2+}(g) \rightarrow Be^{3+}(g) + e^-} \tag{4.4.6}$$

is about 15 times greater than the energy needed to remove the first electron and around 8 times greater than the energy required to remove the second electron. Both $\mathrm{Li^+}$ and $\mathrm{Be^{2+}}$ have $1s^2$ closed-shell configurations, and much more energy is required to remove an electron from the $1s^2$ core than from the 2*s* valence orbital of the same element. The chemical consequences are enormous: lithium (and all the alkali metals) forms compounds with the 1+ ion but not the 2+ or 3+ ions. Similarly, beryllium (and all the alkaline earth metals) forms compounds with the 2+ ion but not the 3+ or 4+ ions. *The energy required to remove electrons from a filled core is prohibitively large and simply cannot be achieved in normal chemical reactions.*

> *The energy required to remove electrons from a filled core is prohibitively large under normal reaction conditions.*



Ionization Energy: Ionization Energy, YouTube(opens in new window) [youtu.be] (opens in new window)

Ionization Energies of *s*- and *p*-Block Elements

Ionization energies of the elements in the third row of the periodic table exhibit the same pattern as those of *Li* and *Be* (Table 4.4.2): successive ionization energies increase steadily as electrons are removed from the valence orbitals (3*s* or 3*p*, in this case), followed by an especially large increase in ionization energy when electrons are removed from filled core levels as indicated by the bold diagonal line in Table 4.4.2. Thus in the third row of the periodic table, the largest increase in ionization energy corresponds to removing the fourth electron from *Al*, the fifth electron from Si, and so forth—that is, removing an electron from an ion that has the valence electron configuration of the preceding noble gas. This pattern explains why the chemistry of the elements normally involves only valence electrons. Too much energy is required to either remove or share the inner electrons.

Table 4.4.2: Successive Ionization Energies (in kJ/mol) for the Elements in the Third Row of the Periodic Table.Source: Data from CRC Handbook of Chemistry and Physics (2004).

Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	495.8	**4562.4***	—	—	—	—	—
Mg	737.7	1450.7	**7732.7**	—	—	—	—
Al	577.4.4	1816.7	2744.8	**11,577.4.4**	—	—	—
Si	786.5	1577.1	3231.6	4355.5	**16,090.6**	—	—
P	1011.8	1907.4.4	2914.1	4963.6	6274.0	**21,267.4.3**	—

*Inner-shell electron

Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
S	999.6	2251.8	3357	4556.2	7004.3	8495.8	**27,107.4.3**
Cl	1251.2	2297.7	3822	5158.6	6540	9362	11,018.2
Ar	1520.6	2665.9	3931	5771	7238	8781.0	11,995.3

*Inner-shell electron

Example 4.4.1: Highest Fourth Ionization Energy

From their locations in the periodic table, predict which of these elements has the highest fourth ionization energy: B, C, or N.

Given: three elements

Asked for: element with highest fourth ionization energy

Strategy:

a. List the electron configuration of each element.

b. Determine whether electrons are being removed from a filled or partially filled valence shell. Predict which element has the highest fourth ionization energy, recognizing that the highest energy corresponds to the removal of electrons from a filled electron core.

Solution:

A These elements all lie in the second row of the periodic table and have the following electron configurations:

- B: [He]$2s^2 2p^1$
- C: [He]$2s^2 2p^2$
- N: [He]$2s^2 2p^3$

B The fourth ionization energy of an element (I_4) is defined as the energy required to remove the fourth electron:

$$E^{3+}_{(g)} \rightarrow E^{4+}_{(g)} + e^-$$

Because carbon and nitrogen have four and five valence electrons, respectively, their fourth ionization energies correspond to removing an electron from a partially filled valence shell. The fourth ionization energy for boron, however, corresponds to removing an electron from the filled $1s^2$ subshell. This should require much more energy. The actual values are as follows: B, 25,026 kJ/mol; C, 6223 kJ/mol; and N, 7475 kJ/mol.

Exercise 4.4.1: Lowest Second Ionization Energy

From their locations in the periodic table, predict which of these elements has the lowest second ionization energy: Sr, Rb, or Ar.

Answer

Sr

The first column of data in Table 4.4.2 shows that first ionization energies tend to increase across the third row of the periodic table. This is because the valence electrons do not screen each other very well, allowing the effective nuclear charge to increase steadily across the row. The valence electrons are therefore attracted more strongly to the nucleus, so atomic sizes decrease and ionization energies increase. These effects represent two sides of the same coin: stronger electrostatic interactions between the electrons and the nucleus further increase the energy required to remove the electrons.

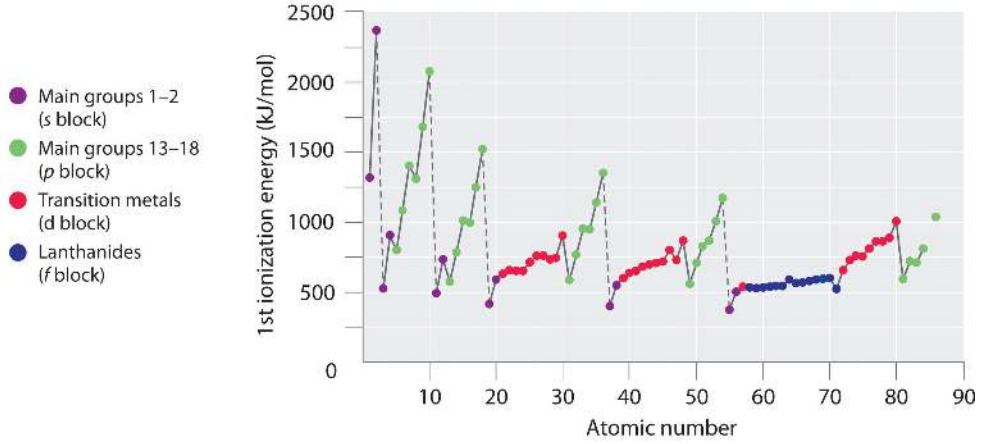


Figure 4.4.1: A Plot of Periodic Variation of First Ionization Energy with Atomic Number for the First Six Rows of the Periodic Table. There is a decrease in ionization energy within a group (most easily seen here for groups 1 and 18).

the main groups 1 and 2 are purple, the main groups 13 through 18 are green, the transition metals are red, and the lanthanides are blue.

However, the first ionization energy decreases at Al ([Ne]$3s^2 3p^1$) and at S ([Ne]$3s^2 3p^4$). The electron configurations of these "exceptions" provide the answer why. The electrons in aluminum's filled $3s^2$ subshell are better at screening the $3p^1$ electron than they are at screening each other from the nuclear charge, so the *s* electrons penetrate closer to the nucleus than the *p* electron does and the *p* electron is more easily removed. The decrease at S occurs because the two electrons in the same *p* orbital repel each other. This makes the S atom slightly less stable than would otherwise be expected, as is true of all the group 16 elements.

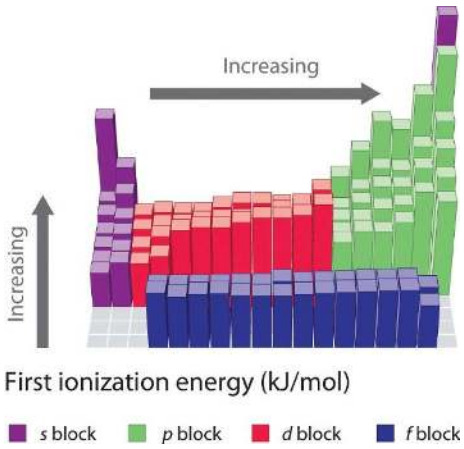


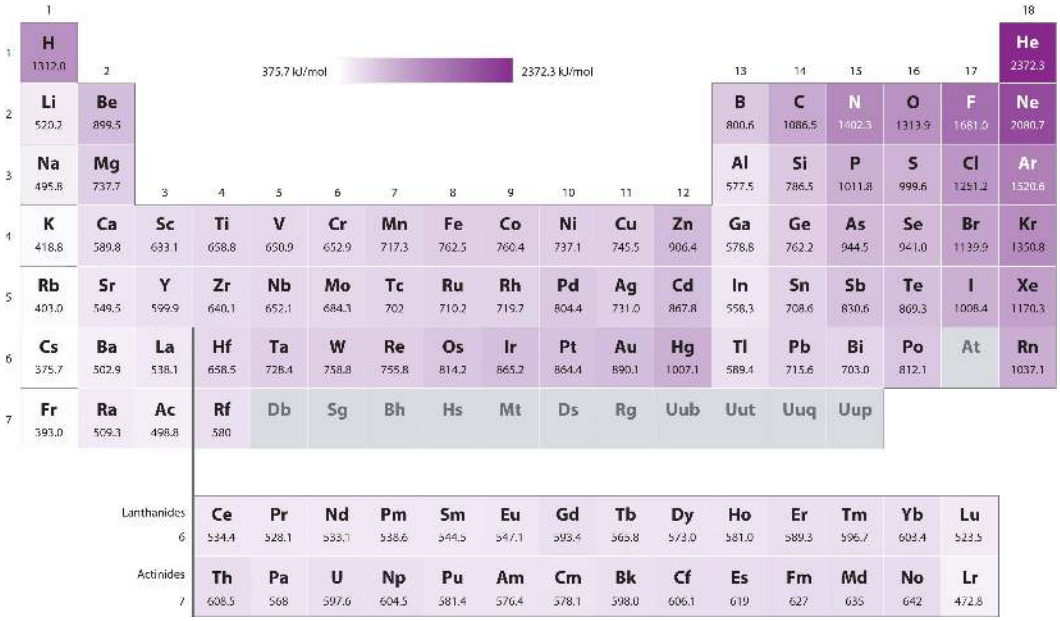
Figure 4.4.2: First Ionization Energies of the *s*-, *p*-, *d*-, and *f*-Block Elements

The s blocks are purple, the p blocks are green, the d blocks are red, and the f blocks are blue. First ionization energy increase from left to right and from bottom to top.

The first ionization energies of the elements in the first six rows of the periodic table are plotted in Figure 4.4.1 and are presented numerically and graphically in Figure 4.4.2. These figures illustrate three important trends:

1. The changes seen in the second (Li to Ne), fourth (K to Kr), fifth (Rb to Xe), and sixth (Cs to Rn) rows of the *s* and *p* blocks follow a pattern similar to the pattern described for the third row of the periodic table. The transition metals are included in the fourth, fifth, and sixth rows, however, and the lanthanides are included in the sixth row. The first ionization energies of the transition metals are somewhat similar to one another, as are those of the lanthanides. Ionization energies increase from left to right across each row, with discrepancies occurring at ns^2np^1 (group 13), ns^2np^4 (group 16), and $ns^2(n-1)d^{10}$ (group 12).
2. First ionization energies generally decrease down a column. Although the principal quantum number *n* increases down a column, filled inner shells are effective at screening the valence electrons, so there is a relatively small increase in the effective nuclear charge. Consequently, the atoms become larger as they acquire electrons. Valence electrons that are farther from the nucleus are less tightly bound, making them easier to remove, which causes ionization energies to decrease. *A larger radius typically corresponds to a lower ionization energy*.

3. Because of the first two trends, the elements that form positive ions most easily (have the lowest ionization energies) lie in the lower left corner of the periodic table, whereas those that are hardest to ionize lie in the upper right corner of the periodic table. Consequently, ionization energies generally increase diagonally from lower left (Cs) to upper right (He).



The darkness of the shading inside the cells of the table indicates the relative magnitudes of the ionization energies. Elements in gray have undetermined first ionization energies. Source: Data from *CRC Handbook of Chemistry and Physics* (2004).

> *Generally, I_1 increases diagonally from the lower left of the periodic table to the upper right.*

Gallium (Ga), which is the first element following the first row of transition metals, has the following electron configuration: $[Ar]4s^2 3d^{10} 4p^1$. Its first ionization energy is significantly lower than that of the immediately preceding element, zinc, because the filled $3d^{10}$ subshell of gallium lies inside the 4*p* subshell, shielding the single 4*p* electron from the nucleus. Experiments have revealed something of even greater interest: the second and third electrons that are removed when gallium is ionized come from the $4s^2$ orbital, *not* the $3d^{10}$ subshell. The chemistry of gallium is dominated by the resulting Ga^{3+} ion, with its $[Ar]3d^{10}$ electron configuration. This and similar electron configurations are particularly stable and are often encountered in the heavier *p*-block elements. They are sometimes referred to as *pseudo noble gas configurations*. In fact, for elements that exhibit these configurations, *no chemical compounds are known in which electrons are removed from the $(n - 1)d^{10}$ filled subshell*.

Ionization Energies of Transition Metals & Lanthanides

As we noted, the first ionization energies of the transition metals and the lanthanides change very little across each row. Differences in their second and third ionization energies are also rather small, in sharp contrast to the pattern seen with the *s*- and *p*-block elements. The reason for these similarities is that the transition metals and the lanthanides form cations by losing the *ns* electrons before the $(n - 1)d$ or $(n - 2)f$ electrons, respectively. This means that transition metal cations have $(n - 1)d^n$ valence electron configurations, and lanthanide cations have $(n - 2)f^n$ valence electron configurations. Because the $(n - 1)d$ and $(n - 2)f$ shells are closer to the nucleus than the *ns* shell, the $(n - 1)d$ and $(n - 2)f$ electrons screen the *ns* electrons quite effectively, reducing the effective nuclear charge felt by the *ns* electrons. As *Z* increases, the increasing positive charge is largely canceled by the electrons added to the $(n - 1)d$ or $(n - 2)f$ orbitals.

That the *ns* electrons are removed before the $(n - 1)d$ or $(n - 2)f$ electrons may surprise you because the orbitals were filled in the reverse order. In fact, the *ns*, the $(n - 1)d$, and the $(n - 2)f$ orbitals are so close to one another in energy, and interpenetrate one another so extensively, that very small changes in the effective nuclear charge can change the order of their energy levels. As the *d* orbitals are filled, the effective nuclear charge causes the 3*d* orbitals to be slightly lower in energy than the 4*s* orbitals. The $[Ar]3d^2$ electron configuration of Ti^{2+} tells us that the 4*s* electrons of titanium are lost before the 3*d* electrons; this is confirmed by experiment. A similar pattern is seen with the lanthanides, producing cations with an $(n - 2)f^n$ valence electron configuration.

Because their first, second, and third ionization energies change so little across a row, these elements have important *horizontal* similarities in chemical properties in addition to the expected vertical similarities. For example, all the first-row transition metals except scandium form stable compounds as M^{2+} ions, whereas the lanthanides primarily form compounds in which they exist as M^{3+} ions.

Example 4.4.2: Lowest First Ionization Energy

Use their locations in the periodic table to predict which element has the lowest first ionization energy: Ca, K, Mg, Na, Rb, or Sr.

Given: six elements

Asked for: element with lowest first ionization energy

Strategy:

Locate the elements in the periodic table. Based on trends in ionization energies across a row and down a column, identify the element with the lowest first ionization energy.

Solution:

These six elements form a rectangle in the two far-left columns of the periodic table. Because we know that ionization energies increase from left to right in a row and from bottom to top of a column, we can predict that the element at the bottom left of the rectangle will have the lowest first ionization energy: Rb.

Exercise 4.4.2: Highest First Ionization Energy

Use their locations in the periodic table to predict which element has the highest first ionization energy: As, Bi, Ge, Pb, Sb, or Sn.

Answer

As

Summary

The tendency of an element to lose electrons is one of the most important factors in determining the kind of compounds it forms. Periodic behavior is most evident for **ionization energy (*I*)**, the energy required to remove an electron from a gaseous atom. The energy required to remove successive electrons from an atom increases steadily, with a substantial increase occurring with the removal of an electron from a filled inner shell. Consequently, only valence electrons can be removed in chemical reactions, leaving the filled inner shell intact. Ionization energies explain the common oxidation states observed for the elements. Ionization energies increase diagonally from the lower left of the periodic table to the upper right. Minor deviations from this trend can be explained in terms of particularly stable electronic configurations, called **pseudo noble gas configurations**, in either the parent atom or the resulting ion.

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4.5: Electron Affinity

Learning Objectives

- To master the concept of electron affinity as a measure of the energy required to add an electron to an atom or ion.
- To recognize the inverse relationship of ionization energies and electron affinities

The electron affinity (EA) of an element E is defined as the energy change that occurs when an electron is added to a gaseous atom or ion:

$$E_{(g)} + e^- \rightarrow E^-_{(g)} \qquad \text{energy change} = EA \tag{4.5.1}$$

Unlike ionization energies, which are always positive for a neutral atom because energy is required to remove an electron, electron affinities can be negative (energy is released when an electron is added), positive (energy must be added to the system to produce an anion), or zero (the process is energetically neutral). This sign convention is consistent with a negative value corresponded to the energy change for an exothermic process, which is one in which heat is released (Figure 4.5.1).

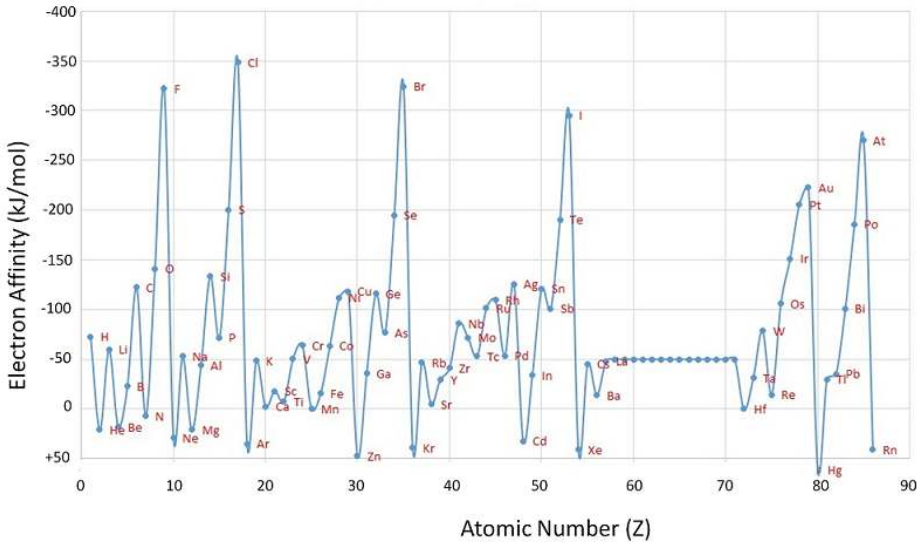


Figure 4.5.1: A Plot of Periodic Variation of Electron Affinity with Atomic Number for the First Six Rows of the Periodic Table. Notice that electron affinities can be both negative and positive. from Robert J. Lancashire (University of the West Indies).

The chlorine atom has the most negative electron affinity of any element, which means that more energy is released when an electron is added to a gaseous chlorine atom than to an atom of any other element:

\[\ce{ Cl(g) + e^- \rightarrow Cl^- (g)} \;\;\;\;\; EA=-346\; kJ/mol \label{7.5.2} \]

In contrast, beryllium does not form a stable anion, so its effective electron affinity is

$$\mathrm{Be(g) + e^- \rightarrow Be^-(g)} \qquad EA \geq 0 \tag{4.5.2}$$

Nitrogen is unique in that it has an electron affinity of approximately zero. Adding an electron neither releases nor requires a significant amount of energy:

$$\mathrm{N(g) + e^- \rightarrow N^-(g)} \qquad EA \approx 0 \tag{4.5.3}$$

> *Generally, electron affinities become more negative across a row of the periodic table.*

In general, electron affinities of the main-group elements become less negative as we proceed down a column. This is because as *n* increases, the extra electrons enter orbitals that are increasingly far from the nucleus.

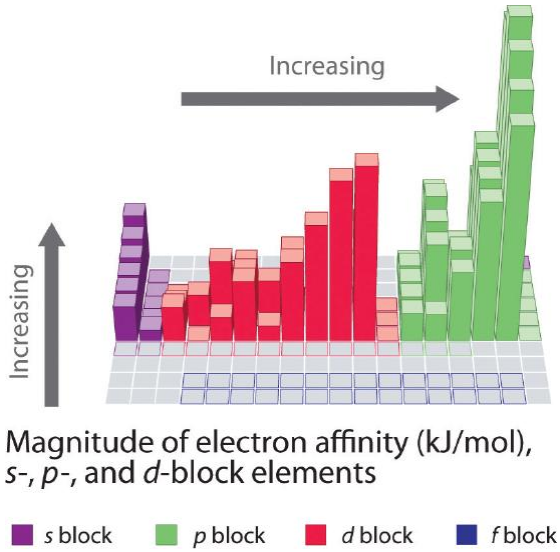


Figure 4.5.2: Electron Affinities (in kJ/mol) of the *s*-, *p*-, and *d*-Block Elements.

The s blocks are purple, the p blocks are green, the d blocks are red, and the f blocks are blue. Electron affinity increases from left to right and bottom to top.

Atoms with the largest radii, which have the lowest ionization energies (affinity for their own valence electrons), also have the lowest affinity for an added electron. There are, however, two major exceptions to this trend:

1. The electron affinities of elements B through F in the second row of the periodic table are *less* negative than those of the elements immediately below them in the third row. Apparently, the increased electron–electron repulsions experienced by electrons confined to the relatively small 2*p* orbitals overcome the increased electron–nucleus attraction at short nuclear distances. Fluorine, therefore, has a lower affinity for an added electron than does chlorine. Consequently, the elements of the *third* row ($n = 3$) have the most negative electron affinities. Farther down a column, the attraction for an added electron decreases because the electron is entering an orbital more distant from the nucleus. Electron–electron repulsions also decrease because the valence electrons occupy a greater volume of space. These effects tend to cancel one another, so the changes in electron affinity within a family are much smaller than the changes in ionization energy.
2. The electron affinities of the alkaline earth metals become more negative from Be to Ba. The energy separation between the filled ns^2 and the empty *np* subshells decreases with increasing *n*, so that formation of an anion from the heavier elements becomes energetically more favorable.

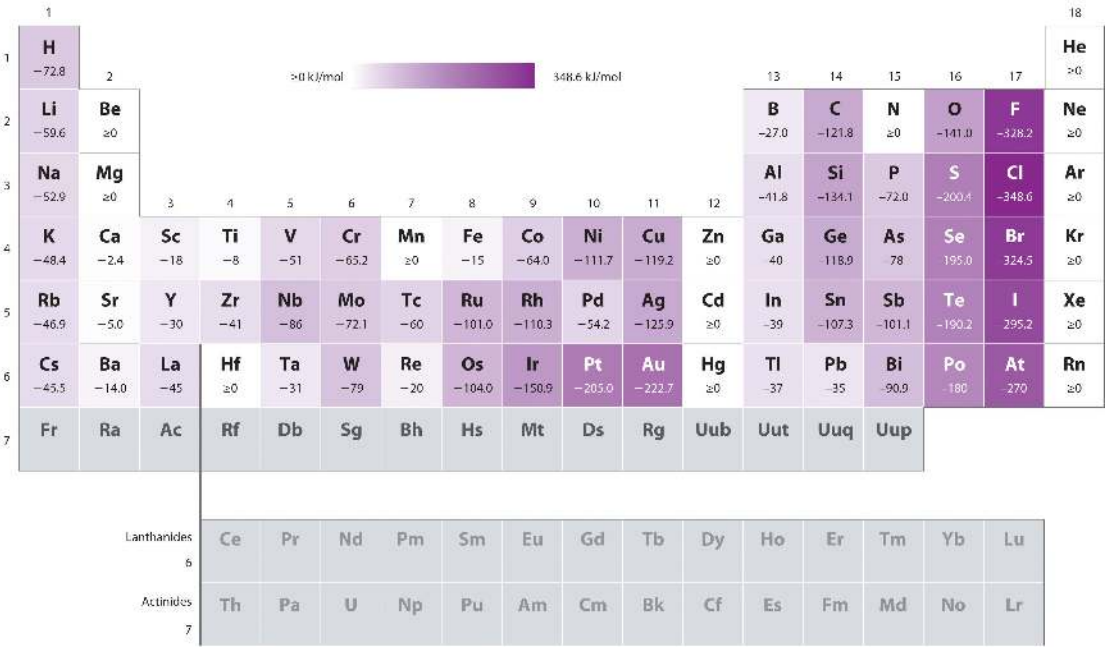


Figure 4.5.3: There are many more exceptions to the trends across rows and down columns than with first ionization energies. Elements that do not form stable ions, such as the noble gases, are assigned an effective electron affinity that is greater than or equal to zero. Elements for which no data are available are shown in gray. Source: Data from *Journal of Physical and Chemical Reference Data* 28, no. 6 (1999).

The equations for second and higher electron affinities are analogous to those for second and higher ionization energies:

$$E_{(g)} + e^- \rightarrow E^-_{(g)} \qquad \text{energy change} = EA_1 \tag{4.5.4}$$

$$E^-_{(g)} + e^- \rightarrow E^{2-}_{(g)} \qquad \text{energy change} = EA_2 \tag{4.5.5}$$

As we have seen, the first electron affinity can be greater than or equal to zero or negative, depending on the electron configuration of the atom. In contrast, the second electron affinity is *always* positive because the increased electron–electron repulsions in a dianion are far greater than the attraction of the nucleus for the extra electrons. For example, the first electron affinity of oxygen is −141 kJ/mol, but the second electron affinity is +744 kJ/mol:

$$O_{(g)} + e^- \rightarrow O^-_{(g)} \qquad EA_1 = -141\ kJ/mol \tag{4.5.6}$$

$$O^-_{(g)} + e^- \rightarrow O^{2-}_{(g)} \qquad EA_2 = +744\ kJ/mol \tag{4.5.7}$$

Thus the formation of a gaseous oxide (O^{2-}) ion is energetically quite *unfavorable* (estimated by adding both steps):

$$O_{(g)} + 2e^- \rightarrow O^{2-}_{(g)} \qquad EA = +603\ kJ/mol \tag{4.5.8}$$

Similarly, the formation of all common dianions (such as S^{2-}) or trianions (such as P^{3-}) is energetically unfavorable in the gas phase.

> *While first electron affinities can be negative, positive, or zero, second electron affinities are always positive.*



Electron Affinity: Electron Affinity, YouTube(opens in new window) [youtu.be] (opens in new window)

If energy is required to form both positively charged cations and monatomic polyanions, why do ionic compounds such as MgO, Na_2S, and Na_3P form at all? The key factor in the formation of stable ionic compounds is the favorable electrostatic interactions between the cations and the anions *in the crystalline salt*.

Example 4.5.1: Contrasting Electron Affinities of Sb, Se, and Te

Based on their positions in the periodic table, which of Sb, Se, or Te would you predict to have the most negative electron affinity?

Given: three elements

Asked for: element with most negative electron affinity

Strategy:

A. Locate the elements in the periodic table. Use the trends in electron affinities going down a column for elements in the same group. Similarly, use the trends in electron affinities from left to right for elements in the same row.

B. Place the elements in order, listing the element with the most negative electron affinity first.

Solution:

A We know that electron affinities become less negative going down a column (except for the anomalously low electron affinities of the elements of the second row), so we can predict that the electron affinity of Se is more negative than that of Te. We also know that electron affinities become more negative from left to right across a row, and that the group 15 elements tend to have values that are less negative than expected. Because Sb is located to the left of Te and belongs to group 15, we predict that the electron affinity of Te is more negative than that of Sb. The overall order is Se < Te < Sb, so Se has the most negative electron affinity among the three elements.

Exercise 4.5.1: Contrasting Electron Affinities of Rb, Sr, and Xe

Based on their positions in the periodic table, which of Rb, Sr, or Xe would you predict to most likely form a gaseous anion?

Answer

Rb

Summary

The **electron affinity** (*EA*) of an element is the energy change that occurs when an electron is added to a gaseous atom to give an anion. In general, elements with the most negative electron affinities (the highest affinity for an added electron) are those with the smallest size and highest ionization energies and are located in the upper right corner of the periodic table.

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4.6: Electronegativity

Skills to Develop

- To define electronegativity and bond polarity
- To recognize the periodic trend in electronegativities of the elements

Both ionization energy and electron affinity give us an idea of the tendency of different atoms to hold onto their electrons or attract new ones, respectively. This idea that different elements have different amounts of attraction for electrons is also the basis for the important property of **electronegativity**. Unlike ionization energy and electron affinity, however, electronegativity is not a property of atoms by themselves, but rather of atoms *when they participate in chemical bonds*. In chemical bonds, the electrons shared between two atoms *are not necessarily shared equally***.** For example, while an electron pair is shared equally in the covalent bond in Cl_2, in $NaCl$ the 3s electron is stripped from the Na atom and is incorporated into the electronic structure of the Cl atom - and the compound is most accurately described as consisting of individual Na^+ and Cl^- ions (ionic bonding). For most covalent substances, their bond character falls *between* these two extremes. Electronegativity values help us to make predictions about the **polarity** of chemical bonds in which the attraction for electrons between the two atoms is not equal.

Electronegativity

The elements with the highest ionization energies are generally those with the most negative electron affinities, which are located toward the upper right corner of the periodic table. Conversely, the elements with the lowest ionization energies are generally those with the least negative electron affinities and are located in the lower left corner of the periodic table.

Because the tendency of an element to gain or lose electrons is so important in determining its chemistry, various methods have been developed to quantitatively describe this tendency as a single number. The most important method is to use **electronegativity** (represented by the Greek letter *chi*, χ, pronounced “ky” as in “sky”), defined as the *relative* ability of an atom to attract electrons to itself *in a chemical compound*. Elements with high electronegativities tend to acquire electrons in chemical reactions and are found in the upper right corner of the periodic table. Elements with low electronegativities tend to lose electrons in chemical reactions and are found in the lower left corner of the periodic table.

Unlike ionization energy or electron affinity, the electronegativity of an atom is not a simple, fixed property that can be directly measured in a single experiment. In fact, an atom’s electronegativity should depend to some extent on its chemical environment because the properties of an atom are influenced by its neighbors in a chemical compound. Nevertheless, when different methods for measuring the electronegativity of an atom are compared, they all tend to assign similar relative values to a given element. For example, all scales predict that fluorine has the highest electronegativity and cesium the lowest of the stable elements, which suggests that all the methods are measuring the same fundamental property.

> *Electronegativity is defined as the ability of an atom in a particular molecule to attract electrons to itself. The greater the value, the greater the attractiveness for electrons.*

Electronegativity is a function of:

1. the atom's ***ionization energy*** (how strongly the atom holds on to its own electrons) and
2. the atom's ***electron affinity*** (how strongly the atom attracts other electrons).

Both of these are properties of the *isolated* atom. An element will be *highly electronegative* if it has a large (negative) electron affinity and a high ionization energy (always endothermic, or positive for neutral atoms). Thus, it will attract electrons from other atoms and resist having its own electrons attracted away.

The Pauling Electronegativity Scale

The original electronegativity scale, developed in the 1930s by Linus Pauling (1901– 1994) was based on measurements of the strengths of covalent bonds between different elements. Pauling arbitrarily set the electronegativity of fluorine at 4.0 (although today it has been refined to 3.98), thereby creating a scale in which all elements have values between 0 and 4.0.

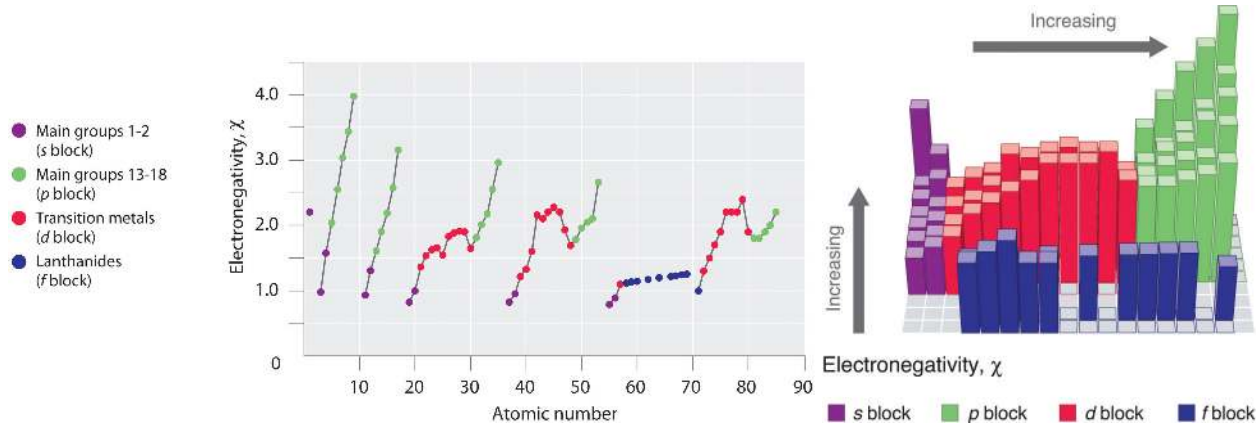


Figure* 4.6.1*: *Left: A Plot of Periodic Variation of Electronegativity with Atomic Number for the First Six Rows of the Periodic Table. Right: A Three-Dimensional Plot of the Trend in Electronegativity in the Periodic Table.*

Periodic variations in Pauling's electronegativity values are illustrated in Figures 4.6.1 and 4.6.2. If we ignore the inert gases and elements for which no stable isotopes are known, we see that fluorine ($\chi = 3.98$) is the most electronegative element and cesium is the least electronegative nonradioactive element ($\chi = 0.79$). Because electronegativities generally increase diagonally from the lower left to the upper right of the periodic table, elements lying on diagonal lines running from upper left to lower right tend to have comparable values (e.g., O and Cl and N, S, and Br).

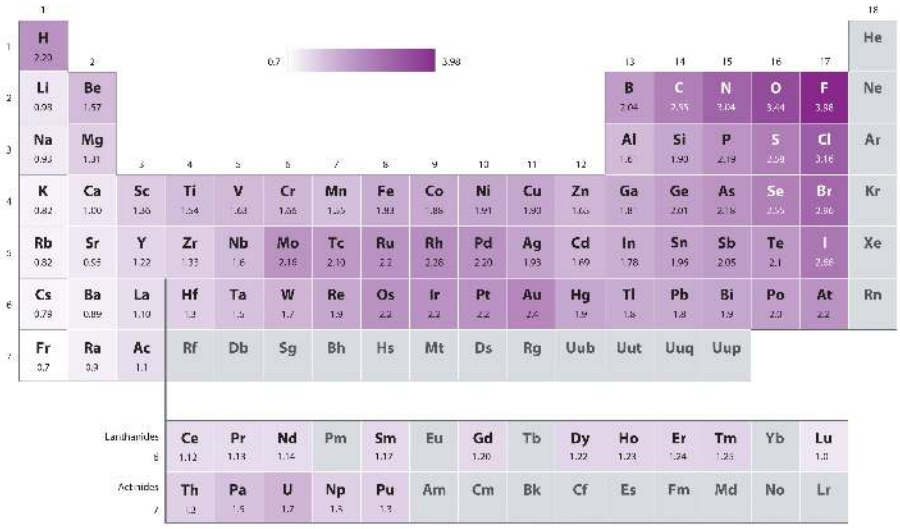


Figure* 4.6.2*: *Pauling Electronegativity Values of the s-, p-, d-, and f-Block Elements. Values for most of the actinides are approximate. Elements for which no data are available are shown in gray. Source: Data from L. Pauling, The Nature of the Chemical Bond, 3rd ed. (1960).*

Linus Pauling (1901-1994)

Linus Pauling 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.



Linus Pauling 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.

Pauling's method is limited by the fact that many elements do not form stable covalent compounds with other elements; hence their electronegativities cannot be measured by his method. Other definitions have since been developed that address this problem, e.g., the Mulliken, Allred-Rochow, and Allen electronegativity scales. The Mulliken electronegativity of an element is the average of its first ionization energy and the absolute value of its electron affinity, showing the relationship between electronegativity and these other periodic properties.

Electronegativity Differences between Metals and Nonmetals

An element's electronegativity provides us with a single value that we can use to characterize the chemistry of an element. Elements with a high electronegativity ($\chi \geq 2.2$ in Figure $4.6.2$) have very negative affinities and large ionization potentials, so they are generally nonmetals and electrical insulators that tend to gain electrons in chemical reactions (i.e., they are *oxidants*). In contrast, elements with a low electronegativity ($\chi \leq 1.8$) have electron affinities that have either positive or small negative values and small ionization potentials, so they are generally metals and good electrical conductors that tend to lose their valence electrons in chemical reactions (i.e., they are *reductants*). In between the metals and nonmetals, along the heavy diagonal line running from B to At is a group of elements with intermediate electronegativities ($\chi \sim 2.0$). These are the **metalloids** (or semimetals), elements that have some of the chemical properties of both nonmetals and metals. The distinction between metals and nonmetals is one of the most fundamental we can make in categorizing the elements and predicting their chemical behavior. Figure $4.6.3$ shows the strong correlation between electronegativity values, metallic versus nonmetallic character, and location in the periodic table.

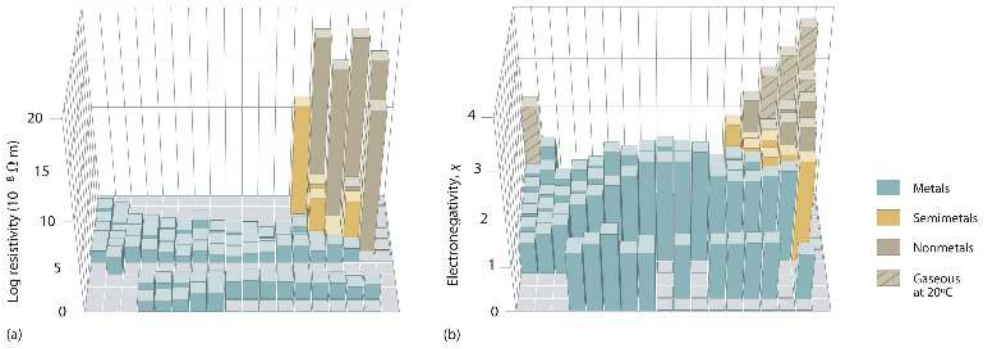


Figure* $4.6.3$*: *Three-Dimensional Plots Demonstrating the Relationship between Electronegativity and the Metallic/Nonmetallic Character of the Elements. (a) A plot of electrical resistivity (measured resistivity to electron flow) at or near room temperature shows that substances with high resistivity (little to no measured electron flow) are electrical insulators, whereas substances with low resistivity (high measured electron flow) are metals. (b) A plot of Pauling electronegativities for a like set of elements shows that high electronegativity values (≥ about 2.2) correlate with high electrical resistivities (insulators). Low electronegativity values (≤ about 2.2) correlate with low resistivities (metals). Because electrical resistivity is typically measured only for solids and liquids, the gaseous elements do not appear in part (a).*

Electronegativity values *increase* from lower left to upper right in the periodic table.

The rules for assigning oxidation states are based on the relative electronegativities of the elements; the more electronegative element in a binary compound is assigned a negative oxidation state. As we shall see, electronegativity values are also used to predict bond energies, bond polarities, and the kinds of reactions that compounds undergo.

Example 4.6.1: Increasing Electronegativity

On the basis of their positions in the periodic table, arrange Cl, Se, Si, and Sr in order of increasing electronegativity and classify each as a metal, a nonmetal, or a metalloid.

Given: four elements

Asked for: order by increasing electronegativity and classification

Strategy:

A. Locate the elements in the periodic table. From their diagonal positions from lower left to upper right, predict their relative electronegativities.
B. Arrange the elements in order of increasing electronegativity.
C. Classify each element as a metal, a nonmetal, or a metalloid according to its location about the diagonal belt of metalloids running from B to At.

Solution:

A Electronegativity increases from lower left to upper right in the periodic table (Figure 8.4.2). Because Sr lies far to the left of the other elements given, we can predict that it will have the lowest electronegativity. Because Cl lies above and to the right of Se, we can predict that $\chi_{Cl} > \chi_{Se}$. Because Si is located farther from the upper right corner than Se or Cl, its electronegativity should be lower than those of Se and Cl but greater than that of Sr. **B** The overall order is therefore $\chi_{Sr} < \chi_{Si} < \chi_{Se} < \chi_{Cl}$.

C To classify the elements, we note that Sr lies well to the left of the diagonal belt of metalloids running from B to At; while Se and Cl lie to the right and Si lies in the middle. We can predict that Sr is a metal, Si is a metalloid, and Se and Cl are nonmetals.

Exercise 4.6.1

On the basis of their positions in the periodic table, arrange Ge, N, O, Rb, and Zr in order of increasing electronegativity and classify each as a metal, a nonmetal, or a metalloid.

Answer

Rb < Zr < Ge < N < O; metals (Rb, Zr); metalloid (Ge); nonmetal (N, O)

Summary

Bond polarity and ionic character increase with an increasing difference in electronegativity. The **electronegativity (χ)** of an element is the relative ability of an atom to attract electrons to itself in a chemical compound and increases diagonally from the lower left of the periodic table to the upper right. The Pauling electronegativity scale is based on measurements of the strengths of covalent bonds between different atoms, whereas the Mulliken electronegativity of an element is the average of its first ionization energy and the absolute value of its electron affinity. Elements with a high electronegativity are generally nonmetals and electrical insulators and tend to behave as oxidants in chemical reactions. Conversely, elements with a low electronegativity are generally metals and good electrical conductors and tend to behave as reductants in chemical reactions.

Compounds with **polar covalent bonds** have electrons that are shared unequally between the bonded atoms. The polarity of such a bond is determined largely by the relative electronegativites of the bonded atoms. The asymmetrical charge distribution in a polar substance produces a **dipole moment**, which is the product of the partial charges on the bonded atoms and the distance between them.

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CHAPTER OVERVIEW

5: Molecular Structure and Geometry

5.1: Lewis Structures and the Octet Rule
5.2: Formal Charge and Resonance
5.3: Oxidation number
5.4: VSEPR Geometry
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5.5: Geometry and Molecular Polarity

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5.1: Lewis Structures and the Octet Rule

Skills to Develop

- Write Lewis symbols for neutral atoms and ions
- Draw Lewis structures depicting the bonding in simple molecules
- Understand the proper use of the octet rule to predict bonding in simple molecules

Thus far, 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 5.1.1 shows the Lewis symbols for the elements of the third period of the periodic table. Electron dots are typically arranged in four pairs located on the four "sides" of the atomic symbol.

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

Lewis symbols can 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 5.1.2 demonstrates the use of Lewis symbols to show the transfer of electrons during the formation of ionic compounds.

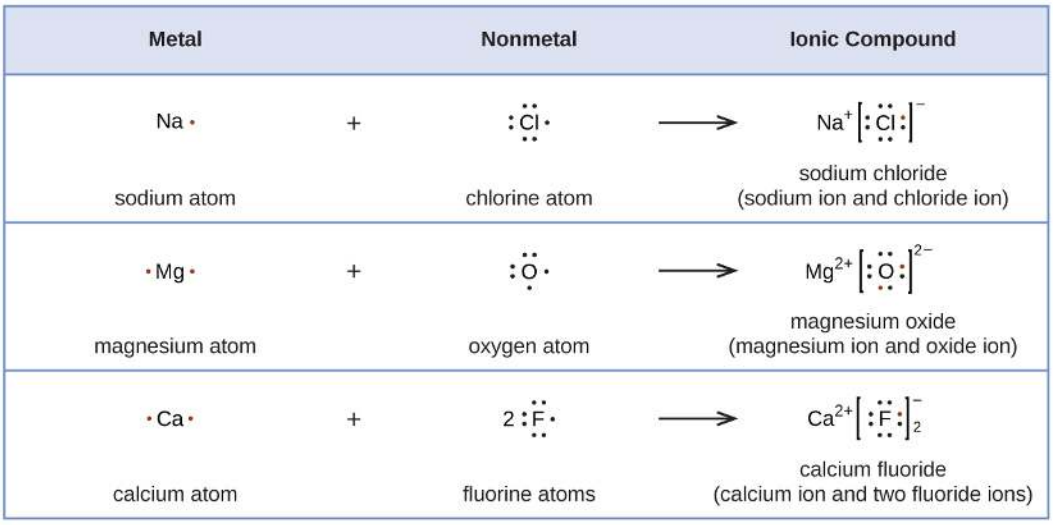
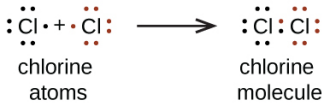


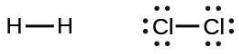
***Figure* 5.1.2**: *Cations are formed when atoms lose electrons, represented by fewer Lewis dots, whereas anions are formed by atoms gaining electrons. The total number of electrons does not change.*

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 usually used to indicate a shared pair of electrons:

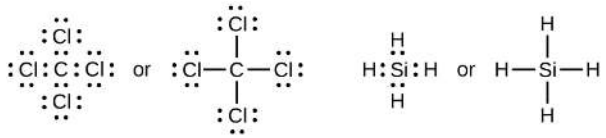


In the Lewis model, a single shared pair of electrons constitutes a **single bond**. Each Cl atom interacts with eight valence electrons total: the six in the lone pairs and the two in the single bond.

The Octet Rule

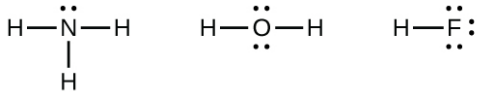
The other halogen molecules (F_2, Br_2, I_2, and At_2) form bonds like those in the chlorine molecule: one single bond between atoms and three lone pairs of electrons per atom. This allows each halogen atom to have a noble gas electron configuration, which corresponds to eight valence electrons. The 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 and only needs to form one bond. The transition elements and inner transition elements also do not follow the octet rule since they have d and f electrons involved in their valence shells.



carbon tetrachloride silane

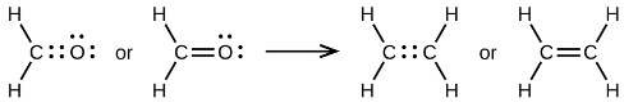
Group 15 elements such as nitrogen have five valence electrons in the atomic Lewis symbol: one lone pair and three unpaired electrons. To obtain an octet, these atoms form three covalent bonds, as in NH_3 (ammonia). Oxygen and other atoms in group 16 obtain an octet by forming two covalent bonds:



ammonia Water hydrogen fluoride

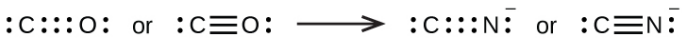
Multiple Bonds

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

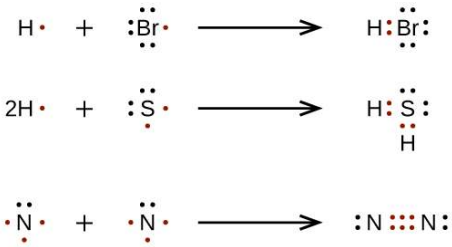
A **triple bond** forms when three electron pairs are shared by a pair of atoms, as in carbon monoxide (CO) and the cyanide ion (CN^-):



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:

1. Determine the total number of valence (outer shell) electrons among all the atoms. 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). Subtract the number of bonding electrons from the total.
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:

$$\begin{aligned} &SiH_4 && (5.1.1)\\ &\text{Si: } 4 \text{ valence electrons/atom} \times 1 \text{ atom} = 4 && (5.1.2)\\ &+\text{H: } 1 \text{ valence electron/atom} \times 4 \text{ atoms} = 4 && (5.1.3)\\ &\qquad\qquad = 8 \text{ valence electrons} && (5.1.4)\end{aligned}$$

- 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):

$$\begin{aligned} &CHO_2^-\\ &\text{C: } 4 \text{ valence electrons/atom} \times 1 \text{ atom} = 4\\ &\text{H: } 1 \text{ valence electron/atom} \times 1 \text{ atom} = 1\\ &\text{O: } 6 \text{ valence electrons/atom} \times 2 \text{ atoms} = 12\\ &+ \qquad\qquad 1 \text{ additional electron} = 1\\ &\qquad\qquad = 18 \text{ valence electrons}\end{aligned}$$

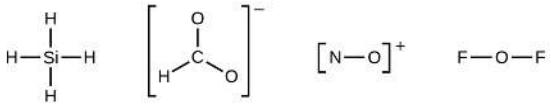
- For a *positive ion*, such as NO^+, we add the number of valence electrons on the atoms in the ion and then subtract the number of positive charges on the ion (one electron is lost for each single positive charge) from the total number of valence electrons:

$$\begin{aligned} &NO^+\\ &\text{N: } 5 \text{ valence electrons/atom} \times 1 \text{ atom} = 5\\ &\text{O: } 6 \text{ valence electron/atom} \times 1 \text{ atom} = 6\\ &+ -1 \text{ electron (positive charge)} = -1\\ &\qquad\qquad = 10 \text{ valence electrons}\end{aligned}$$

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

$$\begin{aligned} &OF_2\\ &\text{O: } 6 \text{ valence electrons/atom} \times 1 \text{ atom} = 6\\ &+\text{F: } 7 \text{ valence electrons/atom} \times 2 \text{ atoms} = 14\\ &\qquad\qquad = 20 \text{ valence electrons}\end{aligned}$$

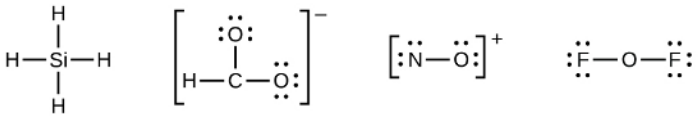
2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom and connecting each atom to the central atom with a single (one electron pair) bond. (Note that we denote ions with brackets around the structure, indicating the charge outside the brackets:)



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

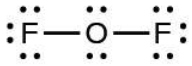
3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen) to complete their valence shells with an octet of electrons.

- There are no remaining electrons on SiH_4, so it is unchanged:



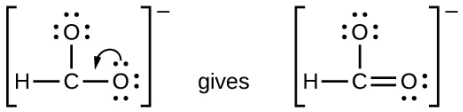
4. Place all remaining electrons on the central atom.

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

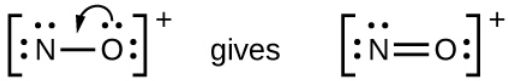


5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.

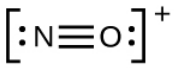
- SiH_4: Si already has an octet, so nothing needs to be done.
- CHO_2^-: We have distributed the valence electrons as lone pairs on the oxygen atoms, but the carbon atom lacks an octet:



- NO^+: For this ion, we added eight outer 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 5.1.1: Writing Lewis Structures

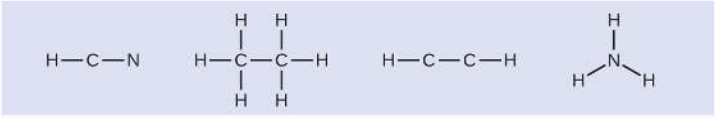
NASA's Cassini-Huygens mission detected a large cloud of toxic hydrogen cyanide (HCN) on Titan, one of Saturn's moons. Titan also contains ethane (H_3CCH_3), acetylene (HCCH), and ammonia (NH_3). What are the Lewis structures of these molecules?

Solution

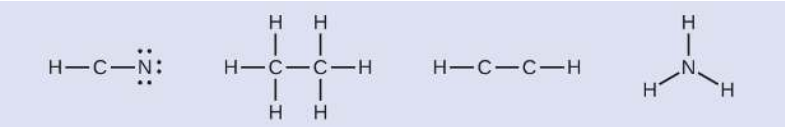
Calculate the number of valence electrons.

- 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

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

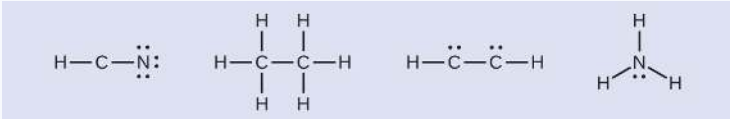


Where needed, distribute electrons to the terminal atoms:



- 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

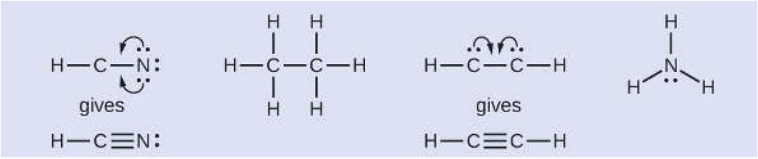
Where needed, place remaining electrons on the central atom:



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

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 5.1.1

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



Fullerene Chemistry

Carbon soot has been known to man since prehistoric times, but it was not until fairly recently that the molecular structure of the main component of soot was discovered. In 1996, the Nobel Prize in Chemistry was awarded to Richard Smalley, 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, consists of a complex network of single- and double-bonded carbon atoms arranged in such a way that each carbon atom obtains a full octet of electrons. 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.

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:

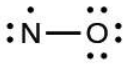
- Odd-electron molecules have an odd number of valence electrons, and therefore have an unpaired electron.
- Electron-deficient molecules have a central atom that has fewer electrons than needed for a noble gas configuration.
- Hypervalent molecules have a central atom that has more electrons than needed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

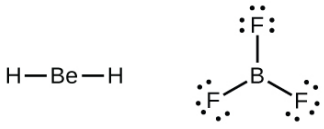


4. *Place all remaining electrons on the central atom*. Since there are no remaining electrons, this step does not apply.
5. *Rearrange the electrons to make multiple bonds with the central atom in order to obtain octets wherever possible.* We know that an odd-electron molecule cannot have an octet for 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:)

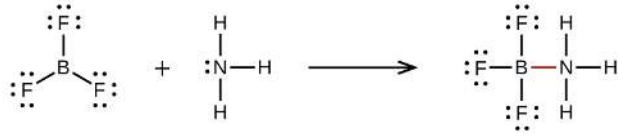


Electron-deficient Molecules

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 and 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. Elements in the third and higher periods ($n \geq 3$), however, can often share more than four pairs of electrons with other atoms. Molecules formed from these elements are sometimes called **hypervalent** molecules because they are able to *expand* the valence shell. Figure 5.1.3 shows the Lewis structures for two hypervalent molecules, PCl_5 and SF_6.

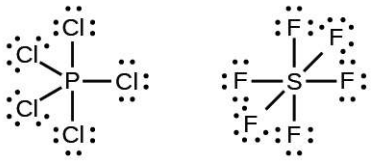
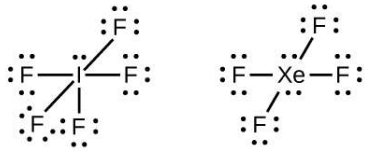


Figure 5.1.3: *In PCl_5, the central atom phosphorus shares five pairs of electrons. In SF_6, sulfur shares six pairs of electrons.*

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.

Why can atoms beyond the second row of the periodic table form hypervalent molecules? One explanation is that the presence of available *d* orbitals in larger atoms allows these atoms to make more bonds; however, more modern chemical calculations have shown that *d* orbitals are not significantly involved in hypervalent bonding. More important is simply the larger size of atoms beyond the second row, which allows more atoms to fit spatially around the central atom.

Example 5.1.2: 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

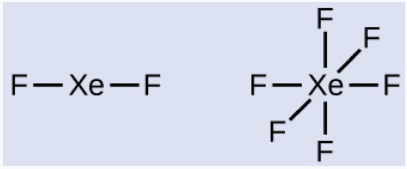
We can draw the Lewis structure of any covalent molecule by following the six steps discussed earlier. In this case, we can condense the last few steps, since not all of them apply.

Step 1: Calculate the number of valence electrons:

$$XeF_2: 8 + (2 \times 7) = 22$$

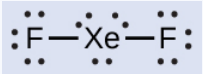
$$XeF_6: 8 + (6 \times 7) = 50$$

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

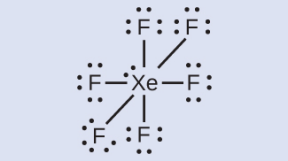


Step 3: Distribute the remaining electrons.

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:



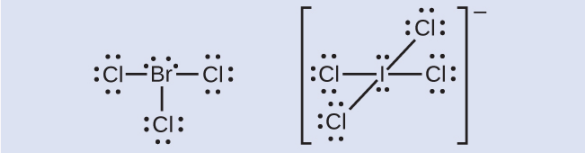
XeF_6: We place three lone pairs of electrons around each F atom, accounting for 36 electrons. Two electrons remain, and this lone pair is placed on the Xe atom:



Exercise 5.1.2

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



Summary

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

Contributors

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5.2: Formal Charge and Resonance

Learning Objectives

- 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

Previously, we discussed how to write Lewis structures for molecules and polyatomic ions. In some cases, however, 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.

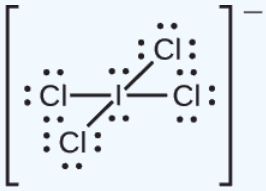
We must remember that the formal charge calculated for an atom is not the *actual* charge of the atom in the molecule. Formal charge is only a useful bookkeeping procedure; it does not indicate the presence of actual charges.

Example 5.2.1: Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in the interhalogen ion ICl_4^-.

Solution

We divide the bonding electron pairs equally for all I– Cl bonds:



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.

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 5.2.1

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



Answer

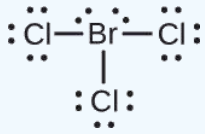
C −1, O +1

Example 5.2.2: Calculating Formal Charge from Lewis Structures

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

Solution

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



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

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

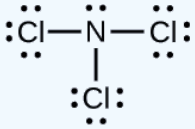
All atoms in $BrCl_3$ have a formal charge of zero, and the sum of the formal charges totals zero, as it must in a neutral molecule.

Exercise 5.2.2

Determine the formal charge for each atom in NCl_3.

Answer

N: 0; all three Cl atoms: 0



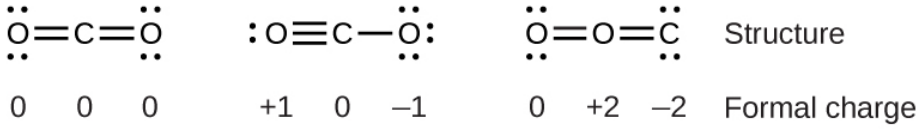
Using Formal Charge to Predict Molecular Structure

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.

Predicting Molecular Structure Guidelines

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.

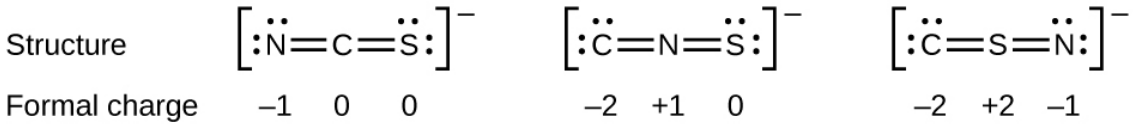
To see how these guidelines apply, let us consider some possible structures for carbon dioxide, CO_2. We know from our previous discussion that the less electronegative atom typically occupies the central position, but formal charges allow us to understand *why* this occurs. We can draw three possibilities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



Three Lewis structures are shown. The left and right structures show a carbon atom double bonded to two oxygen atoms, each of which has two lone pairs of electrons. The center structure shows a carbon atom that is triple bonded to an oxygen atom with one lone pair of electrons and single bonded to an oxygen atom with three lone pairs of electrons. The third structure shows an oxygen atom double bonded to another oxygen atom with to lone pairs of electrons. The first oxygen atom is also double bonded to a carbon atom with two lone pairs of electrons.

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

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

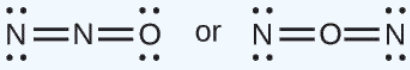


Two rows of structures and numbers are shown. The top row is labeled, “Structure” and depicts three Lewis structures and the bottom row is labeled, “Formal charge.” The left structure shows a carbon atom double bonded to a nitrogen atom with two lone electron pairs on one side and double bonded to a sulfur atom with two lone electron pairs on the other. The structure is surrounded by brackets and has a superscripted negative sign. Below this structure are the numbers negative one, zero, and zero. The middle structure shows a carbon atom with two lone pairs of electrons double bonded to a nitrogen atom that is double bonded to a sulfur atom with two lone electron pairs. The structure is surrounded by brackets and has a superscripted negative sign. Below this structure are the numbers negative two, positive one, and zero. The right structure shows a carbon atom with two lone electron pairs double bonded to a sulfur atom that is double bonded to a nitrogen atom with two lone electron pairs. The structure is surrounded by brackets and has a superscripted negative sign. Below this structure are the numbers negative two, positive two, and one.

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 5.2.3: Using Formal Charge to Determine Molecular Structure

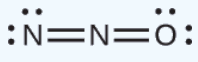
Nitrous oxide, N_2O, commonly known as laughing gas, is used as an anesthetic in minor surgeries, such as the routine extraction of wisdom teeth. Which is the likely structure for nitrous oxide?



Solution Determining formal charge yields the following:



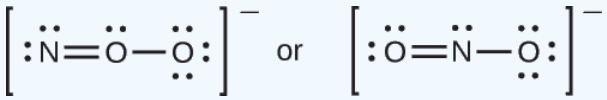
The structure with a terminal oxygen atom best satisfies the criteria for the most stable distribution of formal charge:



The number of atoms with formal charges are minimized (Guideline 2), and there is no formal charge larger than one (Guideline 2). This is again consistent with the preference for having the less electronegative atom in the central position.

? Exercise 5.2.3

Which is the most likely molecular structure for the nitrite (NO_2^-) ion?



Answer

ONO^-

Resonance

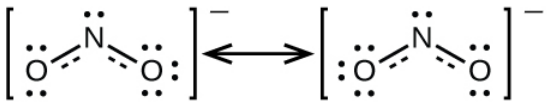
You may have noticed that the nitrite anion in Example 5.2.3 can have two possible structures with the atoms in the same positions. The electrons involved in the N–O double bond, however, are in different positions:



Two Lewis structures are shown. The left structure shows an oxygen atom with three lone pairs of electrons single bonded to a nitrogen atom with one lone pair of electrons that is double bonded to an oxygen with two lone pairs of electrons. Brackets surround this structure, and there is a superscripted negative sign. The right structure shows an oxygen atom with two lone pairs of electrons double bonded to a nitrogen atom with one lone pair of electrons that is single bonded to an oxygen atom with three lone pairs of electrons. Brackets surround this structure, and there is a superscripted negative sign.

If nitrite ions do indeed contain a single and a double bond, we would expect for the two bond lengths to be different. A double bond between two atoms is shorter (and stronger) than a single bond between the same two atoms. Experiments show, however, that both N–O bonds in NO_2^- have the same strength and length, and are identical in all other properties.

It is not possible to write a single Lewis structure for NO_2^- in which nitrogen has an octet and both bonds are equivalent. Instead, we use the concept of resonance: if two or more Lewis structures with the same arrangement of atoms can be written for a molecule or ion, the actual distribution of electrons is an *average* of that shown by the various Lewis structures. The actual distribution of electrons in each of the nitrogen-oxygen bonds in NO_2^- is the average of a double bond and a single bond. We call the individual Lewis structures resonance forms. The actual electronic structure of the molecule (the average of the resonance forms) is called a resonance hybrid of the individual resonance forms. A double-headed arrow between Lewis structures indicates that they are resonance forms. Thus, the electronic structure of the NO_2^- ion is shown as:

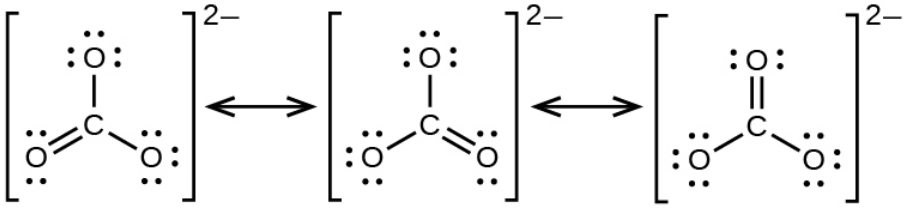


Two Lewis structures are shown with a double headed arrow drawn between them. The left structure shows an oxygen atom with two lone pairs of electrons double bonded to a nitrogen atom with one lone pair of electrons that is single bonded to an oxygen atom with three lone pairs of electrons. Brackets surround this structure, and there is a superscripted negative sign. The right structure shows an oxygen atom with three lone pairs of electrons single bonded to a nitrogen atom with one lone pair of electrons that is double bonded to an oxygen atom with two lone pairs of electrons. Brackets surround this structure, and there is a superscripted negative sign.

We should remember that a molecule described as a resonance hybrid *never* possesses an electronic structure described by either resonance form. It does not fluctuate between resonance forms; rather, the actual electronic structure is *always* the average of that shown by all resonance forms. George Wheland, one of the pioneers of resonance theory, used a historical analogy to describe the relationship between resonance forms and resonance hybrids. A medieval traveler, having never before seen a rhinoceros, described it as a hybrid of a dragon and a unicorn because it had many properties in common with both. Just as a rhinoceros is neither a

dragon sometimes nor a unicorn at other times, a resonance hybrid is neither of its resonance forms at any given time. Like a rhinoceros, it is a real entity that experimental evidence has shown to exist. It has some characteristics in common with its resonance forms, but the resonance forms themselves are convenient, imaginary images (like the unicorn and the dragon).

The carbonate anion, CO_3^{2-}, provides a second example of resonance:



Three Lewis structures are shown with double headed arrows in between. Each structure is surrounded by brackets, and each has a superscripted two negative sign. The left structure depicts a carbon atom bonded to three oxygen atoms. It is single bonded to two of these oxygen atoms, each of which has three lone pairs of electrons, and double bonded to the third, which has two lone pairs of electrons. The double bond is located between the lower left oxygen atom and the carbon atom. The central and right structures are the same as the first, but the position of the double bonded oxygen has moved to the lower right oxygen in the central structure and to the top oxygen in the right structure.

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.

Summary

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).

Key Equations

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

Glossary

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)

molecular structure

arrangement of atoms in a molecule or ion

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

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5.3: Oxidation number

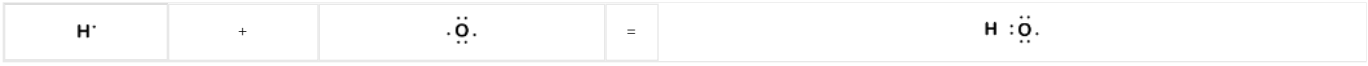
Redox reactions are all about electrons being transferred from one substance to another, so it would be useful if we had a system for keeping track of what gains and what loses electrons, and how many electrons are involved. We do - our record-keeping system is called **Oxidation Numbers.** You may remember from earlier chemistry classes something called **electronegativity.**

Electronegativity

The ability of a bonded atom to attract shared electrons towards itself

When two atoms of different elements are bonded together by a covalent bond (sharing electrons), the electrons are generally not shared equally between the two atoms due to differences in their electronegativity. Think of this as a tug-of-war for electrons. Sometimes both atoms pull with equal strength on shared electrons; other times there is a clearly stronger player who will pull the electrons closer to itself.

Consider the bond between a hydrogen atom (with one valence electron) and an oxygen atom (with its six valence electrons):



Because oxygen has a higher electronegativity than hydrogen, the shared electrons are closer to the oxygen atom than to the hydrogen atom. This is not the total transfer of electrons that would create an ion, but partial charges do form - the hydrogen end of the bond is partially positive (+1) because it has partially lost one electron, and the oxygen end of the H–O is partially negative (-1) because it has partially gained the one electron from hydrogen:



Our molecule is incomplete however, because there is a lone electron around oxygen. Let's add one more hydrogen to complete our water molecule:



We see that each of the two hydrogens has "lost" one electron to oxygen. Oxygen has "gained" two electrons - one from each hydrogen. Again, these are not true ions but it is useful to think of them in the same way.

Charges given to atoms in a molecule in this way are called **oxidation numbers**. We can use oxidation numbers to keep track of where electrons are in a molecule, and how they move during a reaction. In our water example, hydrogen is assigned an oxidation number of +1 because each individual hydrogen has "lost" one electron. Oxygen has an oxidation number of +2 because the single oxygen atom has "gained" a total of two electrons, one from each hydrogen.

Here is another molecule involving hydrogen and oxygen - hydrogen peroxide, H_2O_2:



In hydrogen peroxide, each hydrogen still has an oxidation number of +1 because each hydrogen "gives up" a single electron to oxygen. Oxygen, however, now has an oxidation number of -1 because each oxygen gains just one electron from its neighboring hydrogen. The electrons between the two identical oxygen atoms are shared equally, so there is no partial charge resulting from that bond.

Oxidation Numbers

A positive or negative number assigned to an atom in a molecule or ion that reflects a partial gain or loss of electrons

Knowing the oxidation number of each individual element in a molecule will be a key step in our understanding of redox reactions. Fortunately it will not usually involve drawing electron dot diagrams. Instead there are a series of rules that we can use to determine oxidation numbers. Here are the main rules:

1. The oxidation number of a pure element (by itself, and not an ion) is zero.

Element	Oxidation Number
Na	0
H_2	0
O_2	0
P_4	0

2. The oxidation number of a monatomic ion (by itself or as part of an ionic compound) is equal to its charge.
Alkali metals - elements in the first column of the periodic table - will always have an oxidation number of +1; Alkali metals (column 2) are almost always +2

Ionic Compound	Ions	Charge
NaCl	Na^+	+1
	Cl^-	-1
Mg_3N_2	Mg^{+2}	+2
	N^{-3}	-3

3. The oxidation number of hydrogen is almost always +1 when it is in a compound.

Compound	element	Ox N
HCl	H	
	Cl	
H_2S	H	
	S	

The oxidation number of oxygen is almost always -2 when it is in a compound

4. The exceptions:

- peroxides, such as hydrogen peroxide. In peroxides oxygen has an oxidation number of -1.
- when oxygen is combined with fluorine it's oxidation number is +2

Compound	element	Ox N
MgO magnesium oxide	Mg	
	O	
Na_2O sodium oxide	Na	
	O	
Na_2O_2 sodium peroxide	Na	
	O	

The sum of the oxidation numbers in a compound is zero.

To determine the oxidation number of Mn in Mn_2O_7 we must work backwards:

- We know each oxygen is -2 (Rule 4)
- 7 oxygen gives a total of:

-2 × 7 atoms = -14 total

5. Since the sum of oxidation numbers must be zero, the total oxidation number of Mn must be +14 to cancel out oxygen's -14, but since there are 2 Mn atoms, each **individual atom** will have an oxidation number of +7:

$$\frac{+14 \text{ total}}{2 \text{ Mn atoms}} = +7$$

Compound	element	Oxidation Number	Number atoms
Mg_3N_2	Mg	+2	3
	N	-3	2
			SUM
Mn_2O_7	Mn	+7	2
	O	-2	7
			SUM
Cl_2O_3	Cl	+3	2
	O	-2	3
			SUM

The sum of the oxidation numbers in a polyatomic ion is equal to the charge on that ion.

Again, work backwards to determine the oxidation number of any non-oxygen or non-hydrogen atom.

To determine the oxidation number of Cr in $Cr_2O_7^{2-}$:

- Oxygen will be -2 (Rule 4), for a total of:

-2 × 7 = -14

- Since the sum of the oxidation numbers will be -2 (the charge on the entire ion), the total for all Cr must be +12 because:

6. +**12** + (-14) = -2

- Since there is are two Cr, each Cr will have an oxidation number of +6

= +7

$$\frac{+12}{2} = +6$$

Compound	element	Oxidation Number	Number atoms
NO_3^-	N	+5	1
	O	-2	3
			SUM
$Cr_2O_7^{2-}$	Cr	+6	2
	O	-2	7
			SUM
SO_4^{2-}	S	+6	1
	O	-2	4
			SUM

It is important to note that oxidation number always refers to ***each individual atom*** in the compound, not to the total for that element.

For example in H_2O - the total positive "charge" for both hydrogen atoms will be +2 (which balances with the -2 from oxygen), but EACH HYDROGEN has an oxidation number of +1.

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5.4: VSEPR Geometry

Skills to Develop

- To use the VSEPR model to predict molecular geometries.
- To predict whether a molecule has a dipole moment.

The Lewis electron-pair approach can be used to predict the number and types of bonds between the atoms in a substance, and it indicates which atoms have lone pairs of electrons. This approach gives no information about the actual arrangement of atoms in space, however. We continue our discussion of structure and bonding by introducing the **valence-shell electron-pair repulsion** (VSEPR) model (pronounced “vesper”), which can be used to predict the shapes of many molecules and polyatomic ions. Keep in mind, however, that the VSEPR model, like any model, is a limited representation of reality; the model provides no information about bond lengths or the presence of multiple bonds.

Molecular Geometry

The specific three dimensional arrangement of atoms in molecules is referred to as **molecular geometry**. We can describe molecular geometry in terms of the bond distances, angles, and relative arrangements in space (Figure 5.4.1). 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).

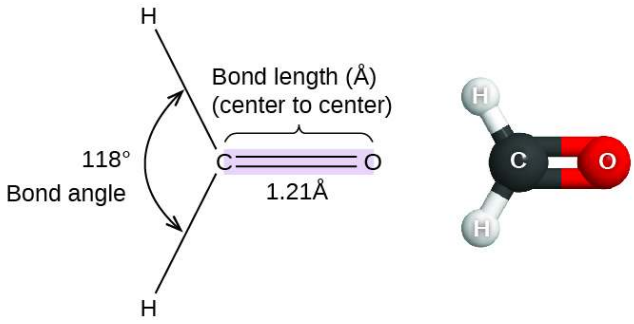
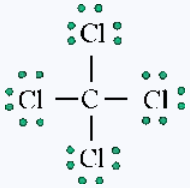


Figure* 5.4.1*: *Bond distances (lengths) and angles are shown for the formaldehyde molecule, H_2CO.*

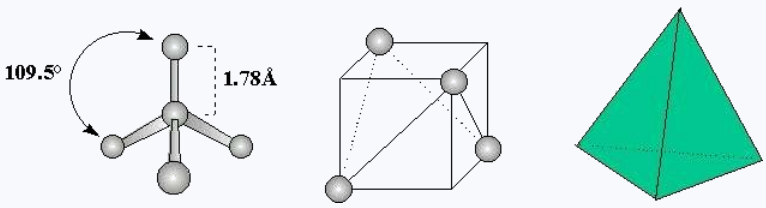
There are various instrumental techniques such as X-Ray crystallography and other experimental techniques which can be used to tell us where the atoms are located in a molecule. Using advanced techniques, very complicated structures for proteins, enzymes, DNA, and RNA have been determined. Molecular geometry is critical to the chemistry of vision, smell, taste, drug reactions, and enzyme controlled reactions, to name a few.

Example 5.4.1: Carbon Tetrachloride

The Lewis structure of carbon tetrachloride provides information about connectivities, provides information about valence orbitals, and provides information about bond character.



However, the Lewis structure provides no information about the shape of the molecule, which is defined by t*he bond angles and the bond lengths*. For carbon tetrachloride, each C-Cl bond length is 1.78Å and each Cl-C-Cl bond angle is 109.5°. Hence, carbon tetrachloride is ***tetrahedral*** in structure:



The VSEPR Model

The VSEPR model can predict the structure of nearly any molecule or polyatomic ion in which the central atom is a nonmetal, as well as the structures of many molecules and polyatomic ions with a central metal atom. The premise of the VSEPR theory is that electron pairs located in bonds and lone pairs repel each other and will therefore adopt the geometry that places electron pairs as far apart from each other as possible. This theory is very simplistic and does not account for the subtleties of orbital interactions that influence molecular shapes; however, the simple VSEPR counting procedure accurately predicts the three-dimensional structures of a large number of compounds, which cannot be predicted using the Lewis electron-pair approach.

We can use the VSEPR model to predict the geometry of most polyatomic molecules and ions by focusing only on the number of electron pairs around the *central atom*, ignoring all other valence electrons present. According to this model, valence electrons in the Lewis structure form *groups*, which may consist of a single bond, a double bond, a triple bond, a lone pair of electrons, or even a single unpaired electron, which in the VSEPR model is counted as a lone pair. Because electrons repel each other electrostatically, the most stable arrangement of electron groups (i.e., the one with the lowest energy) is the one that minimizes repulsions. Groups are positioned around the central atom in a way that produces the molecular structure with the lowest energy, as illustrated in Figure 5.4.2.

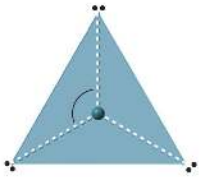
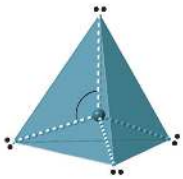
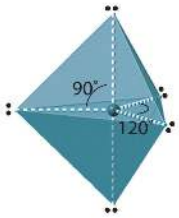
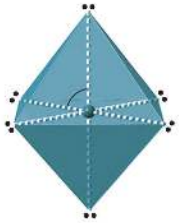
Electron Groups	2	3	4	5	6
Geometry	Linear	Trigonal planar	Tetrahedral	Trigonal bipyramidal	Octahedral
					
Predicted Bond Angles	180°	120°	109.5°	90°, 120°	90°

Figure 5.4.2: *Electron Geometries for Species with Two to Six Electron Groups. Groups are placed around the central atom in a way that produces a molecular structure with the lowest energy, that is, the one that minimizes repulsions.*

In the VSEPR model, the molecule or polyatomic ion is often given an AX_mE_n designation, where A is the central atom, X is a bonded atom, E is a nonbonding valence electron group (usually a lone pair of electrons), and m and n are integers. Each group around the central atom is designated as a bonding pair (BP) or lone (nonbonding) pair (LP). From the BP and LP interactions we can predict both the relative positions of the atoms and the bond angles. Using this information, we can describe the molecular geometry, the arrangement of the *bonded atoms* in a molecule or polyatomic ion.

Predicting Electron Pair Geometry and Molecular Structure

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

1. Draw 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 5.4.2).
4. Use the number of lone pairs to assign an AX_mE_n designation and determine the molecular geometry. Identify the LP–LP, LP–BP, or BP–BP interactions and predict deviations from ideal bond angles based on the principle that lone pairs occupy more space than multiple bonds, which occupy more space than single bonds.

We will illustrate the use of this procedure with several examples, beginning with atoms with two electron groups. In our discussion we will refer to Figure 5.4.2 and Figure 5.4.3, which summarize the common molecular geometries and idealized bond angles of molecules and ions with two to six electron groups.

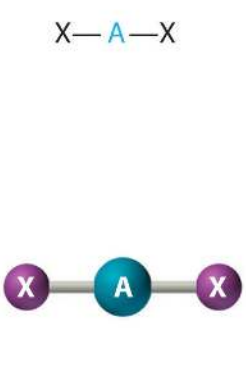
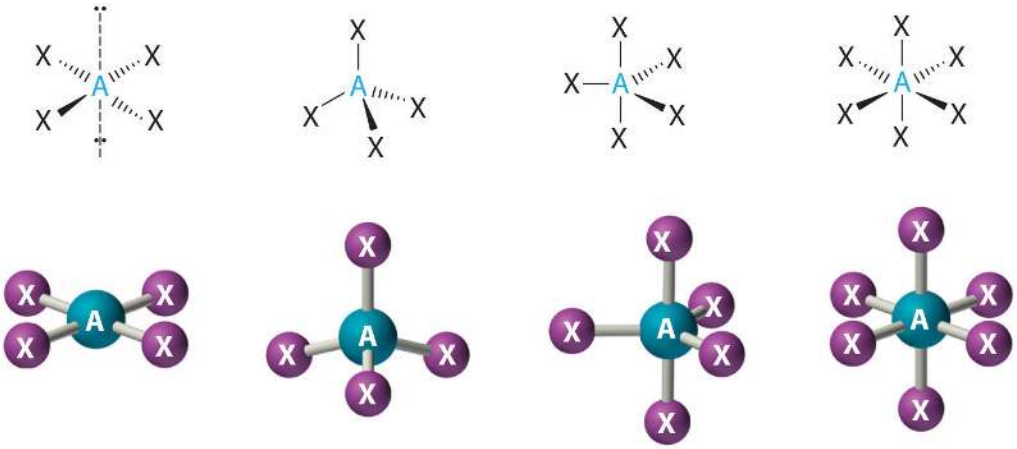
AX_mE_n Notation	AX_2	AX_2E	AX_3	AX_3E
Geometry	Linear	Bent (V-shaped)	Trigonal planar	Trigonal pyramidal
				
Idealized Bond Angles	180°	<180°	120°	<120°
AX_mE_n Notation	AX_4E_2	AX_4	AX_5	AX_6
Geometry	Square planar	Tetrahedral	Trigonal bipyramidal	Octahedral
				
Idealized Bond Angles	90°	109.5°	90°, 120°	90°

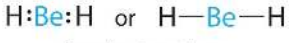
***Figure* 5.4.3:** *Common Molecular Geometries for Species with Two to Six Electron Groups. Lone pairs are shown using a dashed line.*

Two Electron Groups

Our first example is a molecule with two bonded atoms and no lone pairs of electrons, BeH_2.

AX_2: BeH_2

1. The central atom, beryllium, contributes two valence electrons, and each hydrogen atom contributes one. The Lewis electron structure is



Lewis structure

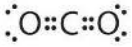
2. There are two electron groups around the central atom. We see from Figure 5.4.2 that the arrangement that minimizes repulsions places the groups 180° apart.

3. Both groups around the central atom are bonding pairs (BP). Thus BeH_2 is designated as AX_2.

4. From Figure 5.4.3 we see that with two bonding pairs, the molecular geometry that minimizes repulsions in BeH_2 is *linear*.

AX_2: CO_2

1. The central atom, carbon, contributes four valence electrons, and each oxygen atom contributes six. The Lewis electron structure is



2. The carbon atom forms two double bonds. Each double bond is a group, so there are two electron groups around the central atom. Like BeH_2, the arrangement that minimizes repulsions places the groups 180° apart.

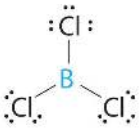
3. Once again, both groups around the central atom are bonding pairs (BP), so CO_2 is designated as AX_2.

4. VSEPR only recognizes groups around the *central* atom. Thus the lone pairs on the oxygen atoms do not influence the molecular geometry. With two bonding pairs on the central atom and no lone pairs, the molecular geometry of CO_2 is linear (Figure 5.4.3). The structure of CO_2 is shown in Figure 5.4.2.1.

Three Electron Groups

AX_3: BCl_3

1. The central atom, boron, contributes three valence electrons, and each chlorine atom contributes seven valence electrons. The Lewis electron structure is



Lewis structure

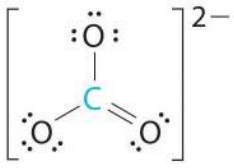
2. There are three electron groups around the central atom. To minimize repulsions, the groups are placed 120° apart (Figure 5.4.2).

3. All electron groups are bonding pairs (BP), so the structure is designated as AX_3.

4. From Figure 5.4.3 we see that with three bonding pairs around the central atom, the molecular geometry of BCl_3 is *trigonal planar*, as shown in Figure 5.4.2.

AX_3: CO_3^{2-}

1. The central atom, carbon, has four valence electrons, and each oxygen atom has six valence electrons. As you learned previously, the Lewis electron structure of one of three resonance forms is represented as

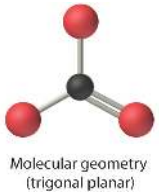


Lewis structure

2. The structure of CO_3^{2-} is a resonance hybrid. It has three identical bonds, each with a bond order of $1\frac{1}{3}$. We minimize repulsions by placing the three groups 120° apart (Figure 5.4.2).

3. All electron groups are bonding pairs (BP). With three bonding groups around the central atom, the structure is designated as AX_3.

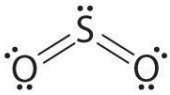
4. We see from Figure 5.4.3 that the molecular geometry of CO_3^{2-} is trigonal planar with bond angles of 120°.



In our next example we encounter the effects of lone pairs and multiple bonds on molecular geometry for the first time.

AX_2E: SO_2

1. The central atom, sulfur, has 6 valence electrons, as does each oxygen atom. With 18 valence electrons, the Lewis electron structure is shown below.



2. There are three electron groups around the central atom, two double bonds and one lone pair. We initially place the groups in a trigonal planar arrangement to minimize repulsions (Figure 5.4.2).

3. There are two bonding pairs and one lone pair, so the structure is designated as AX_2E. This designation has a total of three electron pairs, two X and one E. Because a lone pair is not shared by two nuclei, it occupies more space near the central atom than a bonding pair (Figure 5.4.4). Thus bonding pairs and lone pairs repel each other electrostatically in the order BP–BP < LP–BP < LP–LP. In SO_2, we have one BP–BP interaction and two LP–BP interactions.

4. The molecular geometry is described only by the positions of the nuclei, *not* by the positions of the lone pairs. Thus with two nuclei and one lone pair the shape is *bent*, or *V shaped*, which can be viewed as a trigonal planar arrangement with a missing vertex (Figures 9.2.2.1 and 9.2.3). The O-S-O bond angle is expected to be *less than* 120° because of the extra space taken up by the lone pair.

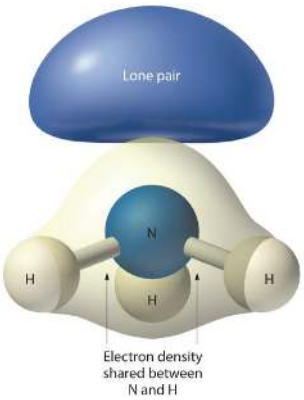
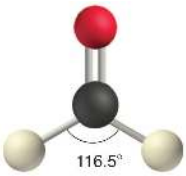


Figure 5.4.4: *The Difference in the Space Occupied by a Lone Pair of Electrons and by a Bonding Pair*

As with SO_2, this composite model of electron distribution and negative electrostatic potential in ammonia shows that a lone pair of electrons occupies a larger region of space around the nitrogen atom than does a bonding pair of electrons that is shared with a hydrogen atom.

Like lone pairs of electrons, multiple bonds occupy more space around the central atom than a single bond, which can cause other bond angles to be somewhat smaller than expected. This is because a multiple bond has a higher electron density than a single bond, so its electrons occupy more space than those of a single bond. For example, in a molecule such as CH_2O (AX_3), whose

structure is shown below, the double bond repels the single bonds more strongly than the single bonds repel each other. This causes a deviation from ideal geometry (an H–C–H bond angle of 116.5° rather than 120°).



Four Electron Groups

One of the limitations of Lewis structures is that they depict molecules and ions in only two dimensions. With four electron groups, we must learn to show molecules and ions in three dimensions.

AX_4: CH_4

1. The central atom, carbon, contributes four valence electrons, and each hydrogen atom has one valence electron, so the full Lewis electron structure is

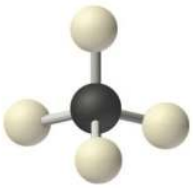


Lewis structure

2. There are four electron groups around the central atom. As shown in Figure 5.4.2, repulsions are minimized by placing the groups in the corners of a tetrahedron with bond angles of 109.5°.

3. All electron groups are bonding pairs, so the structure is designated as AX_4.

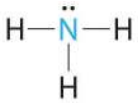
4. With four bonding pairs, the molecular geometry of methane is *tetrahedral* (Figure 5.4.3).



Molecular geometry
(tetrahedral)

AX_3E: NH_3

1. In ammonia, the central atom, nitrogen, has five valence electrons and each hydrogen donates one valence electron, producing the Lewis electron structure



Lewis structure

2. There are four electron groups around nitrogen, three bonding pairs and one lone pair. Repulsions are minimized by directing each hydrogen atom and the lone pair to the corners of a tetrahedron.

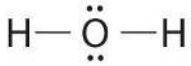
3. With three bonding pairs and one lone pair, the structure is designated as AX_3E. This designation has a total of four electron pairs, three X and one E. We expect the LP–BP interactions to cause the bonding pair angles to deviate significantly from the angles of a perfect tetrahedron.

4. There are three nuclei and one lone pair, so the molecular geometry is *trigonal pyramidal*. In essence, this is a tetrahedron with a vertex missing (Figure 5.4.3). However, the H–N–H bond angles are less than the ideal angle of 109.5° because of LP–BP

repulsions (Figure 5.4.3 and Figure 5.4.4).

AX_2E_2: H_2O

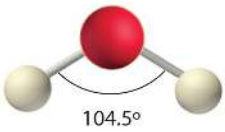
1. Oxygen has six valence electrons and each hydrogen has one valence electron, producing the Lewis electron structure



2. There are four groups around the central oxygen atom, two bonding pairs and two lone pairs. Repulsions are minimized by directing the bonding pairs and the lone pairs to the corners of a tetrahedron Figure 5.4.2.

3. With two bonding pairs and two lone pairs, the structure is designated as AX_2E_2 with a total of four electron pairs. Due to LP–LP, LP–BP, and BP–BP interactions, we expect a significant deviation from idealized tetrahedral angles.

4. With two hydrogen atoms and two lone pairs of electrons, the structure has significant lone pair interactions. There are two nuclei about the central atom, so the molecular shape is *bent*, or *V shaped*, with an H–O–H angle that is even less than the H–N–H angles in NH_3, as we would expect because of the presence of two lone pairs of electrons on the central atom rather than one. This molecular shape is essentially a tetrahedron with two missing vertices.

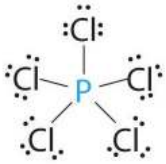


Five Electron Groups

In previous examples it did not matter where we placed the electron groups because all positions were equivalent. In some cases, however, the positions are not equivalent. We encounter this situation for the first time with five electron groups.

AX_5: PCl_5

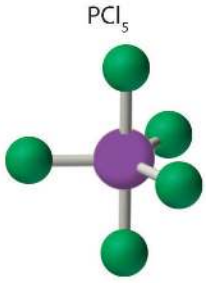
1. Phosphorus has five valence electrons and each chlorine has seven valence electrons, so the Lewis electron structure of PCl_5 is



2. There are five bonding groups around phosphorus, the central atom. The structure that minimizes repulsions is a *trigonal bipyramid*, which consists of two trigonal pyramids that share a base (Figure 5.4.2):

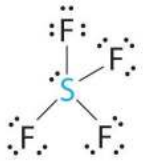
3. All electron groups are bonding pairs, so the structure is designated as AX_5. There are no lone pair interactions.

4. The molecular geometry of PCl_5 is *trigonal bipyramidal*, as shown in Figure 5.4.3. The molecule has three atoms in a plane in *equatorial* positions and two atoms above and below the plane in *axial* positions. The three equatorial positions are separated by 120° from one another, and the two axial positions are at 90° to the equatorial plane. The axial and equatorial positions are not chemically equivalent, as we will see in our next example.



AX_4E: SF_4

1. The sulfur atom has six valence electrons and each fluorine has seven valence electrons, so the Lewis electron structure is



Lewis structure

With an expanded valence, this species is an exception to the octet rule.

2. There are five groups around sulfur, four bonding pairs and one lone pair. With five electron groups, the lowest energy arrangement is a trigonal bipyramid, as shown in Figure 5.4.2.

3. We designate SF_4 as AX_4E; it has a total of five electron pairs. However, because the axial and equatorial positions are not chemically equivalent, where do we place the lone pair? If we place the lone pair in the equatorial position, we have three LP–BP repulsions at 90°. If we place it in the axial position, we have two 90° LP–BP repulsions at 90°. With fewer 90° LP–BP repulsions, we can predict that the structure with the lone pair of electrons in the equatorial position is more stable than the one with the lone pair in the axial position. We also expect a deviation from ideal geometry because a lone pair of electrons occupies more space than a bonding pair.

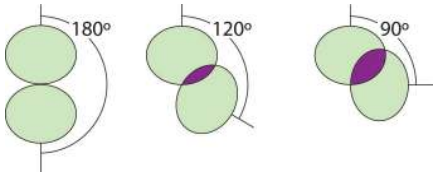
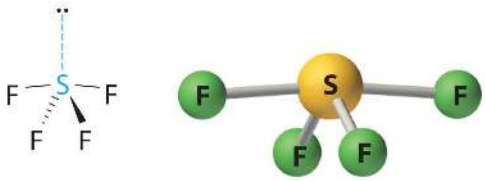


***Figure* 5.4.5:** *Illustration of the Area Shared by Two Electron Pairs versus the Angle between Them*

At 90°, the two electron pairs share a relatively large region of space, which leads to strong repulsive electron–electron interactions.

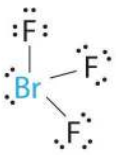
4. With four nuclei and one lone pair of electrons, the molecular structure is based on a trigonal bipyramid with a missing equatorial vertex; it is described as a *seesaw*. The F_{axial}–S–F_{axial} angle is 173° rather than 180° because of the lone pair of electrons in the equatorial plane.



Molecular geometry (seesaw)

AX_3E_2: BrF_3

1. The bromine atom has seven valence electrons, and each fluorine has seven valence electrons, so the Lewis electron structure is



Lewis structure

Once again, we have a compound that is an exception to the octet rule.

2. There are five groups around the central atom, three bonding pairs and two lone pairs. We again direct the groups toward the vertices of a trigonal bipyramid.

3. With three bonding pairs and two lone pairs, the structural designation is AX_3E_2 with a total of five electron pairs. Because the axial and equatorial positions are not equivalent, we must decide how to arrange the groups to minimize repulsions. If we place both lone pairs in the axial positions, we have six LP–BP repulsions at 90°. If both are in the equatorial positions, we have four LP–BP repulsions at 90°. If one lone pair is axial and the other equatorial, we have one LP–LP repulsion at 90° and three LP–BP repulsions at 90°:



	Lone pairs axial (a)	Lone pairs equatorial (b)	Lone pairs axial and equatorial (c)
Interactions			
90° LP–LP	0	0	1
90° LP–BP	6	4	3

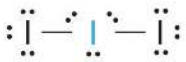
Structure (c) can be eliminated because it has a LP–LP interaction at 90°. Structure (b), with fewer LP–BP repulsions at 90° than (a), is lower in energy. However, we predict a deviation in bond angles because of the presence of the two lone pairs of electrons.

4. The three nuclei in BrF_3 determine its molecular structure, which is described as *T shaped*. This is essentially a trigonal bipyramid that is missing two equatorial vertices. The F_{axial}–Br–F_{axial} angle is 172°, less than 180° because of LP–BP repulsions (Figure 5.4.2.1).

> Because lone pairs occupy more space around the central atom than bonding pairs, electrostatic repulsions are more important for lone pairs than for bonding pairs.

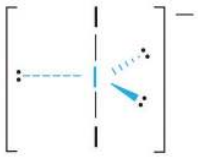
AX_2E_3: I_3^-

1. Each iodine atom contributes seven electrons and the negative charge one, so the Lewis electron structure is



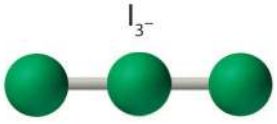
2. There are five electron groups about the central atom in I_3^-, two bonding pairs and three lone pairs. To minimize repulsions, the groups are directed to the corners of a trigonal bipyramid.

3. With two bonding pairs and three lone pairs, I_3^- has a total of five electron pairs and is designated as AX_2E_3. We must now decide how to arrange the lone pairs of electrons in a trigonal bipyramid in a way that minimizes repulsions. Placing them in the axial positions eliminates 90° LP–LP repulsions and minimizes the number of 90° LP–BP repulsions.



The three lone pairs of electrons have equivalent interactions with the three iodine atoms, so we do not expect any deviations in bonding angles.

4. With three nuclei and three lone pairs of electrons, the molecular geometry of I_3^- is linear. This can be described as a trigonal bipyramid with three equatorial vertices missing. The ion has an I–I–I angle of 180°, as expected.

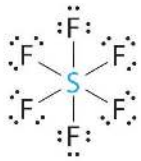


Six Electron Groups

Six electron groups form an *octahedron*, a polyhedron made of identical equilateral triangles and six identical vertices (Figure 5.4.2.)

AX_6: SF_6

1. The central atom, sulfur, contributes six valence electrons, and each fluorine atom has seven valence electrons, so the Lewis electron structure is



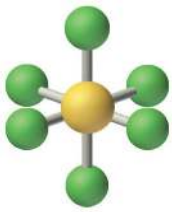
Lewis structure

With an expanded valence, this species is an exception to the octet rule.

2. There are six electron groups around the central atom, each a bonding pair. We see from Figure 5.4.2 that the geometry that minimizes repulsions is *octahedral*.

3. With only bonding pairs, SF_6 is designated as AX_6. All positions are chemically equivalent, so all electronic interactions are equivalent.

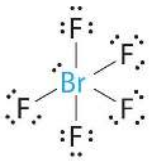
4. There are six nuclei, so the molecular geometry of SF_6 is octahedral.



Molecular geometry
(octahedral)

AX_5E: BrF_5

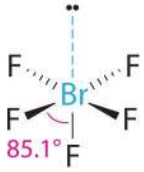
1. The central atom, bromine, has seven valence electrons, as does each fluorine, so the Lewis electron structure is



Lewis structure

With its expanded valence, this species is an exception to the octet rule.

2. There are six electron groups around the Br, five bonding pairs and one lone pair. Placing five F atoms around Br while minimizing BP–BP and LP–BP repulsions gives the following structure:



3. With five bonding pairs and one lone pair, BrF_5 is designated as AX_5E; it has a total of six electron pairs. The BrF_5 structure has four fluorine atoms in a plane in an equatorial position and one fluorine atom and the lone pair of electrons in the axial positions.

We expect all F_{axial}–Br–$F_{equatorial}$ angles to be less than 90° because of the lone pair of electrons, which occupies more space than the bonding electron pairs.

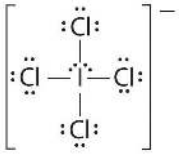
4. With five nuclei surrounding the central atom, the molecular structure is based on an octahedron with a vertex missing. This molecular structure is *square pyramidal*. The F_{axial}–B–$F_{equatorial}$ angles are 85.1°, less than 90° because of LP–BP repulsions.



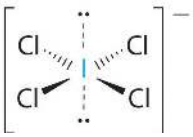
Molecular geometry
(square pyramidal)

AX_4E_2: ICl_4^-

1. The central atom, iodine, contributes seven electrons. Each chlorine contributes seven, and there is a single negative charge. The Lewis electron structure is

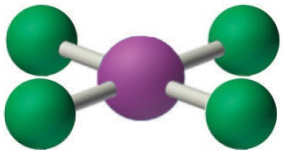


2. There are six electron groups around the central atom, four bonding pairs and two lone pairs. The structure that minimizes LP–LP, LP–BP, and BP–BP repulsions is



3. ICl_4^- is designated as AX_4E_2 and has a total of six electron pairs. Although there are lone pairs of electrons, with four bonding electron pairs in the equatorial plane and the lone pairs of electrons in the axial positions, all LP–BP repulsions are the same. Therefore, we do not expect any deviation in the Cl–I–Cl bond angles.

4. With five nuclei, the ICl4− ion forms a molecular structure that is *square planar*, an octahedron with two opposite vertices missing.



The relationship between the number of electron groups around a central atom, the number of lone pairs of electrons, and the molecular geometry is summarized in Figure 5.4.6.

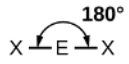
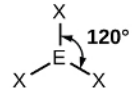
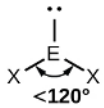
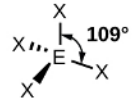
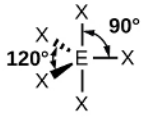
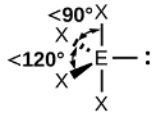
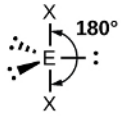
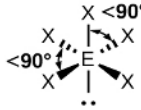
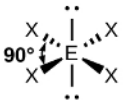
Number of electron pairs	Electron pair geometries: 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	 Linear				
3	 Trigonal planar	 Bent or angular			
4	 Tetrahedral	 Trigonal pyramid	 Bent or angular		
5	 Trigonal bipyramid	 Sawhorse or seesaw	 T-shape	 Linear	
6	 Octahedral	 Square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

***Figure* 5.4.6:** *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.*

Example 5.4.1

Using the VSEPR model, predict the molecular geometry of each molecule or ion.

1. PF_5 (phosphorus pentafluoride, a catalyst used in certain organic reactions)
2. H_3O^+ (hydronium ion)

Given: two chemical species

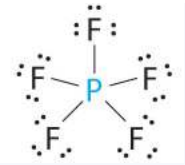
Asked for: molecular geometry

Strategy:

A. Draw the Lewis electron structure of the molecule or polyatomic ion.
B. Determine the electron group arrangement around the central atom that minimizes repulsions.
C. Assign an AX_mE_n designation; then identify the LP–LP, LP–BP, or BP–BP interactions and predict deviations in bond angles.
D. Describe the molecular geometry.

Solution:

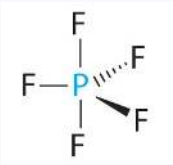
1. **A** The central atom, P, has five valence electrons and each fluorine has seven valence electrons, so the Lewis structure of PF_5 is



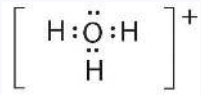
B There are five bonding groups about phosphorus. The structure that minimizes repulsions is a trigonal bipyramid (Figure 9.2.6).

C All electron groups are bonding pairs, so PF_5 is designated as AX_5. Notice that this gives a total of five electron pairs. With no lone pair repulsions, we do not expect any bond angles to deviate from the ideal.

D The PF_5 molecule has five nuclei and no lone pairs of electrons, so its molecular geometry is trigonal bipyramidal.



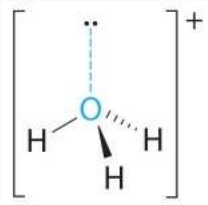
2. **A** The central atom, O, has six valence electrons, and each H atom contributes one valence electron. Subtracting one electron for the positive charge gives a total of eight valence electrons, so the Lewis electron structure is



B There are four electron groups around oxygen, three bonding pairs and one lone pair. Like NH_3, repulsions are minimized by directing each hydrogen atom and the lone pair to the corners of a tetrahedron.

C With three bonding pairs and one lone pair, the structure is designated as AX_3E and has a total of four electron pairs (three X and one E). We expect the LP–BP interactions to cause the bonding pair angles to deviate significantly from the angles of a perfect tetrahedron.

D There are three nuclei and one lone pair, so the molecular geometry is *trigonal pyramidal*, in essence a tetrahedron missing a vertex. However, the H–O–H bond angles are less than the ideal angle of 109.5° because of LP–BP repulsions:



Exercise 5.4.1

Using the VSEPR model, predict the molecular geometry of each molecule or ion.

a. XeO_3
b. PF_6^-
c. NO_2^+

Answer a

trigonal pyramidal

Answer b

octahedral

Answer c

linear

Example 5.4.2

Predict the molecular geometry of each molecule.

1. XeF_2
2. $SnCl_2$

Given: two chemical compounds

Asked for: molecular geometry

Strategy:

Use the strategy given in Example 9.2.1.

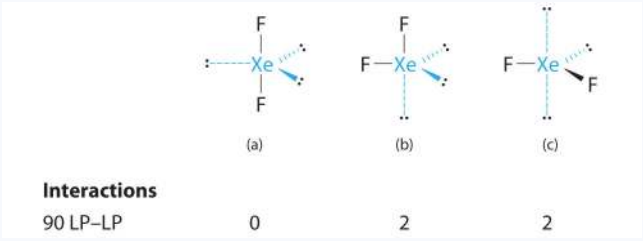
Solution:

1. **A** Xenon contributes eight electrons and each fluorine seven valence electrons, so the Lewis electron structure is



B There are five electron groups around the central atom, two bonding pairs and three lone pairs. Repulsions are minimized by placing the groups in the corners of a trigonal bipyramid.

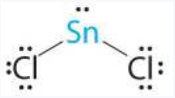
C From B, XeF_2 is designated as AX_2E_3 and has a total of five electron pairs (two X and three E). With three lone pairs about the central atom, we can arrange the two F atoms in three possible ways: both F atoms can be axial, one can be axial and one equatorial, or both can be equatorial:



The structure with the lowest energy is the one that minimizes LP–LP repulsions. Both (b) and (c) have two 90° LP–LP interactions, whereas structure (a) has none. Thus both F atoms are in the axial positions, like the two iodine atoms around the central iodine in I_3^-. All LP–BP interactions are equivalent, so we do not expect a deviation from an ideal 180° in the F–Xe–F bond angle.

D With two nuclei about the central atom, the molecular geometry of XeF_2 is linear. It is a trigonal bipyramid with three missing equatorial vertices.

2. **A** The tin atom donates 4 valence electrons and each chlorine atom donates 7 valence electrons. With 18 valence electrons, the Lewis electron structure is



B There are three electron groups around the central atom, two bonding groups and one lone pair of electrons. To minimize repulsions the three groups are initially placed at 120° angles from each other.

C From B we designate $SnCl_2$ as AX_2E. It has a total of three electron pairs, two X and one E. Because the lone pair of electrons occupies more space than the bonding pairs, we expect a decrease in the Cl–Sn–Cl bond angle due to increased LP–BP repulsions.

D With two nuclei around the central atom and one lone pair of electrons, the molecular geometry of $SnCl_2$ is bent, like SO_2, but with a Cl–Sn–Cl bond angle of 95°. The molecular geometry can be described as a trigonal planar arrangement with one vertex missing.

Exercise 5.4.2

Predict the molecular geometry of each molecule.

a. SO_3
b. XeF_4

Answer a

trigonal planar

Answer b

square planar

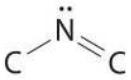
Molecules with No Single Central Atom

The VSEPR model can be used to predict the structure of somewhat more complex molecules with no single central atom by treating them as linked AX_mE_n fragments. We will demonstrate with methyl isocyanate (CH_3–N=C=O), a volatile and highly toxic molecule that is used to produce the pesticide Sevin. In 1984, large quantities of Sevin were accidentally released in Bhopal, India, when water leaked into storage tanks. The resulting highly exothermic reaction caused a rapid increase in pressure that ruptured the tanks, releasing large amounts of methyl isocyanate that killed approximately 3800 people and wholly or partially disabled about 50,000 others. In addition, there was significant damage to livestock and crops.

We can treat methyl isocyanate as linked AX_mE_n fragments beginning with the carbon atom at the left, which is connected to three H atoms and one N atom by single bonds. The four bonds around carbon mean that it must be surrounded by four bonding electron pairs in a configuration similar to AX_4. We can therefore predict the CH_3–N portion of the molecule to be roughly tetrahedral, similar to methane:

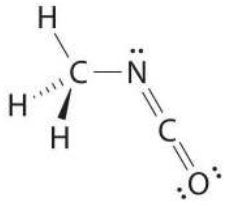


The nitrogen atom is connected to one carbon by a single bond and to the other carbon by a double bond, producing a total of three bonds, C–N=C. For nitrogen to have an octet of electrons, it must also have a lone pair:



Because multiple bonds are not shown in the VSEPR model, the nitrogen is effectively surrounded by three electron pairs. Thus according to the VSEPR model, the C–N=C fragment should be bent with an angle less than 120°.

The carbon in the –N=C=O fragment is doubly bonded to both nitrogen and oxygen, which in the VSEPR model gives carbon a total of two electron pairs. The N=C=O angle should therefore be 180°, or linear. The three fragments combine to give the following structure:



We predict that all four nonhydrogen atoms lie in a single plane, with a C–N–C angle of approximately 120°. The experimentally determined structure of methyl isocyanate confirms our prediction (Figure 5.4.8).

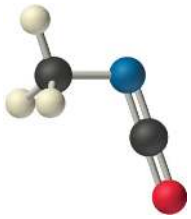


Figure* 5.4.8*: *The Experimentally Determined Structure of Methyl Isocyanate*

Certain patterns are seen in the structures of moderately complex molecules. For example, carbon atoms with four bonds (such as the carbon on the left in methyl isocyanate) are generally tetrahedral. Similarly, the carbon atom on the right has two double bonds that are similar to those in CO_2, so its geometry, like that of CO_2, is linear. Recognizing similarities to simpler molecules will help you predict the molecular geometries of more complex molecules.

Example 5.4.3

Use the VSEPR model to predict the molecular geometry of propyne ($H_3C–C≡CH$), a gas with some anesthetic properties.

Given: chemical compound

Asked for: molecular geometry

Strategy:

Count the number of electron groups around each carbon, recognizing that in the VSEPR model, a multiple bond counts as a single group. Use Figure 5.4.3 to determine the molecular geometry around each carbon atom and then deduce the structure of the molecule as a whole.

Solution:

Because the carbon atom on the left is bonded to four other atoms, we know that it is approximately tetrahedral. The next two carbon atoms share a triple bond, and each has an additional single bond. Because a multiple bond is counted as a single bond in the VSEPR model, each carbon atom behaves as if it had two electron groups. This means that both of these carbons are linear, with C–C≡C and C≡C–H angles of 180°.

Exercise 5.4.3

Predict the geometry of allene ($H_2C=C=CH_2$), a compound with narcotic properties that is used to make more complex organic molecules.

Answer

The terminal carbon atoms are trigonal planar, the central carbon is linear, and the C–C–C angle is 180°.

3D Geometries of AB_n molecules

Understanding molecular geometry in three-dimensional space is an essential skill for chemists because geometry is so critical to molecular properties and function. With the VSEPR process, you should be able to name the correct geometry for a molecule, but you should also be able to visualize what that geometry looks like in real space. Figure 5.4.9 shows some three-dimensional depictions of geometries where a central atom A is bonded to two or more X atoms. Try to keep these images in mind when considering the geometries of real molecules!

6	5	4	3	2
AX_6  octahedral	AX_5  trigonal bipyramidal	AX_4  tetrahedral	AX_3  trigonal planar	AX_2 Linear linear

6	5	4	3	2
1 lone pair of electrons				
AX_5E  square pyramidal	AX_4E  distorted tetrahedron	AX_3E  pyramidal	AX_2E  nonlinear	AXE linear
2 lone pairs of electrons				
AX_4E_2  square planar	AX_3E_2  T-shaped	AX_2E_2  bent	AXE_2 linear	

Figure* 5.4.9*: *Three-dimensional animations of common VSEPR molecular geometries*

Summary

Lewis electron structures give no information about **molecular geometry**, the arrangement of bonded atoms in a molecule or polyatomic ion, which is crucial to understanding the chemistry of a molecule. The **valence-shell electron-pair repulsion (VSEPR) model** allows us to predict which of the possible structures is actually observed in most cases. It is based on the assumption that pairs of electrons occupy space, and the lowest-energy structure is the one that minimizes electron pair–electron pair repulsions. In the VSEPR model, the molecule or polyatomic ion is given an AX_mE_n designation, where A is the central atom, X is a bonded atom, E is a nonbonding valence electron group (usually a lone pair of electrons), and m and n are integers. Each group around the central atom is designated as a bonding pair (BP) or lone (nonbonding) pair (LP). From the BP and LP interactions we can predict both the relative positions of the atoms and the angles between the bonds, called the **bond angles**. From this we can describe the **molecular geometry**. The VSEPR model can be used to predict the shapes of many molecules and polyatomic ions, but it gives no information about bond lengths and the presence of multiple bonds. A combination of VSEPR and a bonding model, such as Lewis electron structures, is necessary to understand the presence of multiple bonds.

Contributors

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Robyn Rindge (Class of '98) who now works for PDI Dreamworks (look for his name in the credits of Shrek2.). Robyn drew these rotating molecules using Infini-D (MetaCreations).

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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).

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5.4.1: 5.4.1-Limitations of VSPER

Athough the VSEPR model is useful in predicting molecular geometry, it fails to predict the shapes of isoelectronic species and transition metal compounds. This model does not take relative sizes of substituents and stereochemically inactive lone pairs into account. As a result, VSEPR cannot be applied to heavy d-block species that experience the stereochemical *inert pair effect*.

Introduction

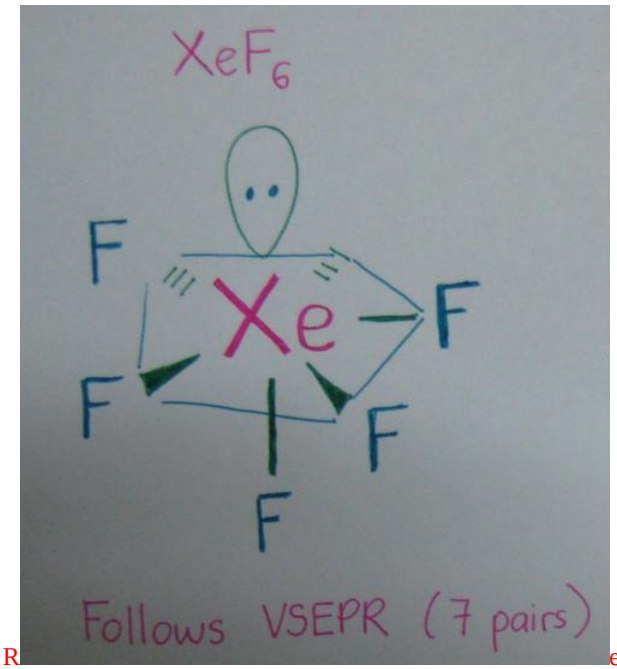
The VSEPR model is a powerful tool used by chemists to predict the shapes of molecules; yet like many other theories, it has exceptions and limitations. This article discusses in detail the various limitations of VSEPR and gives explanations for these exceptions.

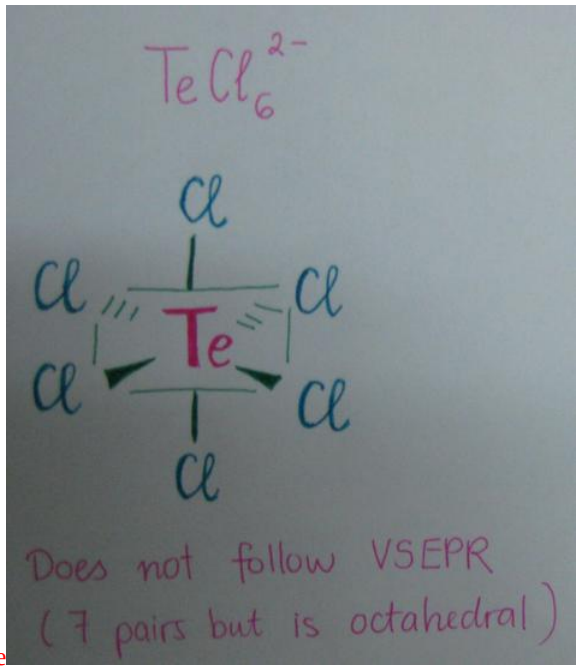
VSEPR fails for isoelectronic species

Isoelectronic species are elements, ions and molecules that share the same number of electrons. According to the VSEPR model, chemists determine the shape of the molecules based on numbers of valence electrons (i.e. bond pairs and lone pairs). However, two isoelectronic species, can differ in geometry despite the fact that they have the same numbers of valence electrons. For example, both $IF_7$and $[TeF_7]^-$ have 56 valence electrons; VSEPR theory predicts both to be pentagonal bipyramidal. However, electron diffraction and X-ray diffraction data indicate that the equatorial F atoms of $[TeF_7]^-$ are not coplanar. Moreover, the bond lengths of equatorial I-F and Te-F bonds are different. The VSEPR model fails to accommodate the correct shape for $[TeF7]^-$ and other species because it does not account for such irregularities.

VSEPR fails for transition metal compounds

The VSEPR model also fails to predict the structure of certain compounds because it does not take relative sizes of the substituents and stereochemically inactive lone pairs into account. Elements in the d-block have relatively high atomic masses and they tend to have stereochemically inactive electron pairs. In other words, valence shell s-electrons in these elements tend to adopt a non-bonding role. This is known as the inert pair effect. As a result, VSEPR does not give correct geometries for these transitional metal complex compounds.. For example, $[SeCl_6]^{2-}$, $[TeCl_6]^{2-}$,and $[BrF_6]^-$ are predicted to adopt pentagonal bipyramidal geometries according to VSEPR since the central atom can have seven electron pairs. However, due to the stereochemical inert pair effect, these molecules are found to be regular octahedral because one of the electron pairs is stereochemically inactive.





References

1. Cotton, F. Albert, and Geoffrey Wilkinson. *Advanced Inorganic Chemistry; a Comprehensive Text*. [New York]: Interscience, 1962. Print.
2. Housecroft, Catherine E., and A. G. Sharpe. *Inorganic Chemistry*. Harlow, England: Pearson Prentice Hall, 2008. Print.

Problems

1. What is the shape of $[XeF_8]^{2-}$?(Hint: Xenon contains one pair of stereochemically inactive lone pair)
2. Give some examples of isoelectronic species.
3. Why are d-block elements exceptions to VSEPR?

Answers

1. Antiprismatic
2. IF_7 and $[TeF_7]^-$
3. Because of stereochemical inert pair effect

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5.5: Geometry and Molecular Polarity

Skills to Develop

- Explain the concepts of polar covalent bonds and molecular polarity
- Assess the polarity of a molecule based on its bonding and structure

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.

This bond moment can be represented as a vector, a quantity having both direction and magnitude (Figure 5.5.1). 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.

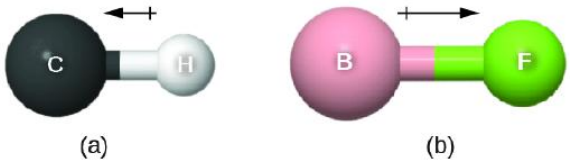


Figure 5.5.1: *(a) There is a small difference in electronegativity between C and H, represented as a short vector. (b) The electronegativity difference between B and F is much larger, so the vector representing the dipole moment is much longer.*

Molecular Polarity and Dipole Moment

Not only bonds can have dipole moments, however. 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.

In more complex molecules with polar covalent bonds, the three-dimensional geometry and the compound's symmetry determine whether there is a net dipole moment. The dipole moment of a molecule is the *vector sum* of the dipole moments of the individual bonds in the molecule. If the individual bond dipole moments cancel one another, there is no net dipole moment. Such is the case for CO_2, a linear molecule (Figure 5.5.2*a*). Each C–O bond in CO_2 is polar, yet experiments show that the CO_2 molecule has no dipole moment. Because the two C–O bond dipoles in CO_2 are equal in magnitude and oriented at 180° to each other, they cancel. As a result, the CO_2 molecule has no *net* dipole moment even though it has a substantial separation of charge. In contrast, the H_2O molecule is not linear (Figure 5.5.2*b*); it is bent in three-dimensional space, so the dipole moments do not cancel each other. Thus a molecule such as H_2O has a net dipole moment. We expect the concentration of negative charge to be on the oxygen, the more electronegative atom, and positive charge on the two hydrogens. This charge polarization allows H_2O to hydrogen-bond to other polarized or charged species, including other water molecules.

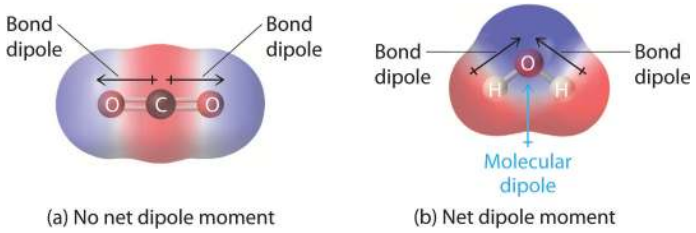
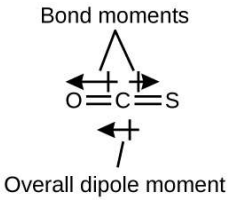


Figure 5.5.2: *How Individual Bond Dipole Moments Are Added Together to Give an Overall Molecular Dipole Moment for Two Triatomic Molecules with Different Structures. (a) In CO_2, the C–O bond dipoles are equal in magnitude but oriented in opposite*

directions (at 180°). Their vector sum is zero, so CO_2 therefore has no net dipole. (b) In H_2O, the O–H bond dipoles are also equal in magnitude, but they are oriented at 104.5° to each other. Hence the vector sum is not zero, and H_2O has a net dipole moment.

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 another example of a polar molecule. Although the polar C–Cl and C–H bonds are arranged in a tetrahedral geometry, the C–Cl bonds have a larger bond moment than the C–H bond, and the bond moments do not completely cancel each other. All of the dipoles have a upward component in the orientation shown, since carbon is more electronegative than hydrogen and less electronegative than chlorine:



Other examples of molecules with polar bonds are shown in Figure 5.5.3. In molecular geometries that are highly symmetrical (most notably tetrahedral and square planar, trigonal bipyramidal, and octahedral), individual bond dipole moments completely cancel, and there is no net dipole moment. Although a molecule like $CHCl_3$ is best described as tetrahedral, the atoms bonded to carbon are not identical. Consequently, the bond dipole moments cannot cancel one another, and the molecule has a dipole moment. Due to the arrangement of the bonds in molecules that have V-shaped, trigonal pyramidal, seesaw, T-shaped, and square pyramidal geometries, the bond dipole moments cannot cancel one another. Consequently, molecules with these geometries always have a nonzero dipole moment.

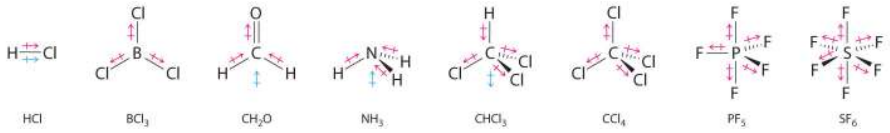


***Figure* 5.5.3**: *Molecules with Polar Bonds. Individual bond dipole moments are indicated in red. Due to their different three-dimensional structures, some molecules with polar bonds have a net dipole moment (HCl, CH_2O, NH_3, and $CHCl_3$), indicated in blue, whereas others do not because the bond dipole moments cancel (BCl_3, CCl_4, PF_5, and SF_6).*

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.

Example 5.5.4

Which molecule(s) has a net dipole moment?

a. H_2S
b. NHF_2
c. BF_3

Given: three chemical compounds

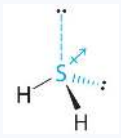
Asked for: net dipole moment

Strategy:

For each three-dimensional molecular geometry, predict whether the bond dipoles cancel. If they do not, then the molecule has a net dipole moment.

Solution:

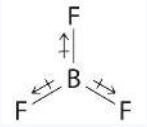
1. The total number of electrons around the central atom, S, is eight, which gives four electron pairs. Two of these electron pairs are bonding pairs and two are lone pairs, so the molecular geometry of H_2S is bent (Figure 9.2.6). The bond dipoles cannot cancel one another, so the molecule has a net dipole moment.



2. Difluoroamine has a trigonal pyramidal molecular geometry. Because there is one hydrogen and two fluorines, and because of the lone pair of electrons on nitrogen, the molecule is not symmetrical, and the bond dipoles of NHF_2 cannot cancel one another. This means that NHF_2 has a net dipole moment. We expect polarization from the two fluorine atoms, the most electronegative atoms in the periodic table, to have a greater affect on the net dipole moment than polarization from the lone pair of electrons on nitrogen.



3. The molecular geometry of BF_3 is trigonal planar. Because all the B–F bonds are equal and the molecule is highly symmetrical, the dipoles cancel one another in three-dimensional space. Thus BF_3 has a net dipole moment of zero:



Exercise 5.5.4

Which molecule(s) has a net dipole moment?

- CH_3Cl
- SO_3
- XeO_3

Answer

CH_3Cl; and XeO_3

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 5.5.4). We can use an electrically charged object to attract polar molecules, but nonpolar molecules are not attracted.

Molecular polarity is an important factor in how molecules of one type interact with other molecules. For example, polar solvents are better at dissolving polar substances, and nonpolar solvents are better at dissolving nonpolar substances. Polarity also influences the way that molecules arrange themselves in the solid and liquid states.

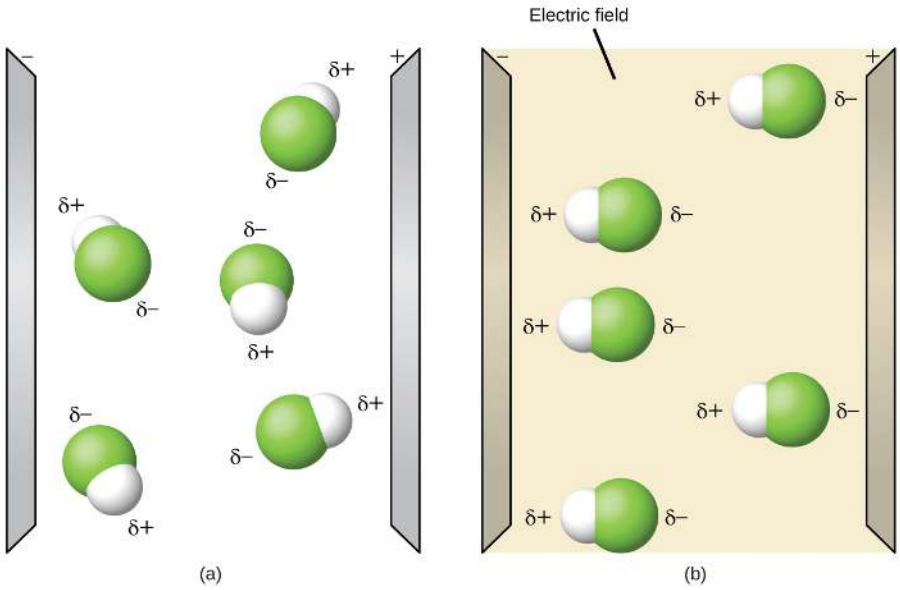


***Figure* 5.5.4**: *(a) Molecules are always randomly distributed in the liquid state in the absence of an electric field. (b) When an electric field is applied, polar molecules like HF will align to the dipoles with the field direction.*

Example 5.5.7: 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 5.5.14

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 5.5.7

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.

Summary

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. For some highly symmetrical structures, the individual bond dipole moments cancel one another, giving a dipole moment of zero. Polar molecules (those with an appreciable dipole moment) interact with electric fields, whereas nonpolar molecules do not.

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).

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CHAPTER OVERVIEW

6: Understanding Molecules with QM

6.1: Prelude to Covalent Bonding
6.2: The Born-Oppenheimer Approximation
6.3: The H_2^+ Prototypical Species
6.4: The Overlap Integral
6.5: Bonding and Antibonding Orbitals
6.6: Molecular Orbitals Can Be Ordered According to Their Energies
6.7: Molecular-Orbital Theory Does not Predict a Stable Diatomic Helium Molecule
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6.9: Summary of Molecular Orbital Theory
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6.1: Prelude to 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. Both N_2 and O_2 have fairly similar Lewis structures that contain lone pairs of electrons.



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 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.



Figure 6.1.1: 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)

6.1.1: Chemical Bonding

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.

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.

The energy of the system depends on how much the atomic orbitals of the individual atoms overlap in the geometry of the emolecule. Figure 6.1.1 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. (The overall energy is lower than the energy of the individual atoms and thus 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 molecule 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 6.1.1.

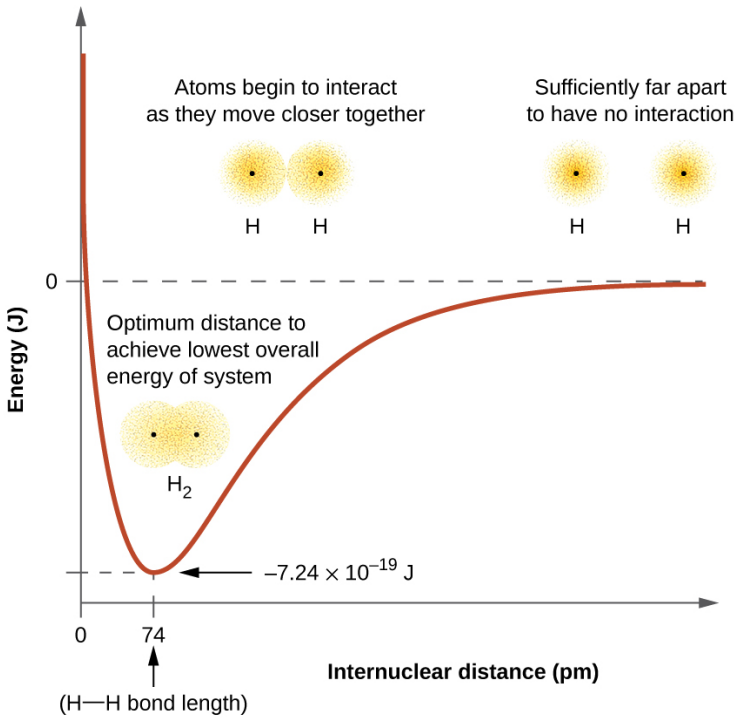


Figure 6.1.1: The interaction of two hydrogen atoms changes as a function of distance. The energy of the system changes as the atoms interact. The lowest (most stable) energy occurs at a distance of 74 pm, which is the bond length observed for the H_2 molecule.

The bond energy is the difference between the energy minimum (which occurs at the bond distance) and the energy of the two separated atoms. This is the quantity of energy released when the bond is formed. Conversely, the same amount of energy is required to break the bond. For the H_2 molecule shown in Figure 6.1.1, at the bond distance of 74 pm the system is $7.24 \times 10^{-19}\ J$ lower in energy than the two separated hydrogen atoms. This may seem like a small number. However, we know from thermochemistry that bond energies are often discussed on a per-mole basis. For example, it requires $7.24 \times 10^{-19}\ J$ to break one H–H bond, but it takes $4.36 \times 10^{5}\ J$ to break 1 mole of H–H bonds. A comparison of some bond lengths and energies is shown in Table 6.1.1. We can find many of these bonds in a variety of molecules, and this table provides average values. For example, breaking the first C–H bond in CH4 requires 439.3 kJ/mol, while breaking the first C–H bond in $\mathrm{H{-}CH_2C_6H_5}$ (a common paint thinner) requires 375.5 kJ/mol.

Table 6.1.1: Representative Bond Energies and Lengths

Bond	Length (pm)	Energy (kJ/mol)	Bond	Length (pm)	Energy (kJ/mol)
H–H	74	436	C–O	140.1	358
H–C	106.8	413	C = O	119.7	745
H–N	101.5	391	C ≡ O	113.7	1072
H–O	97.5	467	H–Cl	127.5	431
C–C	150.6	347	H–Br	141.4	366
C = C	133.5	614	H–I	160.9	298
C ≡ C	120.8	839	O–O	148	146
C–N	142.1	305	O = O	120.8	498
C = N	130.0	615	F–F	141.2	159

Bond	Length (pm)	Energy (kJ/mol)
C ≡ N	116.1	891

Bond	Length (pm)	Energy (kJ/mol)
Cl–Cl	198.8	243

Attributions

- Modified by Valeria D. Kleiman

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6.2: The Born-Oppenheimer Approximation

Using quantum mechanics to predict the chemical bonding patterns, optimal geometries, and physical and chemical properties of molecules is a large and active field of research known as *molecular quantum mechanics* or more commonly as *quantum chemistry*.

Quantum chemistry calculations allow the geometries of molecules to be computed as well as a wide range of properties. Quantum chemistry can also be used in a novel way, in which the electrons are treated using quantum mechanics but the nuclei are treated as classical particles. We use quantum mechanics to calculate the internuclear forces but then use these forces in Newton's Second Law to study the motion of the nuclei during chemical reactions. This gives us a microscopic window into the specific motions, the complex dance, executed by the nuclei during a simple or complex chemical process.

The methods of quantum chemistry have become very sophisticated, and there are various software packages that can be downloaded for carrying out the calculations of quantum chemistry.

The Born-Oppenheimer Approximation

The Born-Oppenheimer approximation is one of the basic concepts underlying the description of the quantum states of molecules. This approximation makes it possible to separate the motion of the nuclei and the motion of the electrons. This is not a new idea for us. We already made use of this approximation in the particle-in-a-box model when we explained the electronic absorption spectra of cyanine dyes without considering the motion of the nuclei. Then we discussed the translational, rotational and vibrational motion of the nuclei without including the motion of the electrons. In this chapter we will examine more closely the significance and consequences of this important approximation. Note, in this discussion nuclear refers to the atomic nuclei as parts of molecules not to the internal structure of the nucleus.

The Born-Oppenheimer approximation neglects the motion of the atomic nuclei when describing the electrons in a molecule. The physical basis for the Born-Oppenheimer approximation is the fact that the mass of an atomic nucleus in a molecule is much larger than the mass of an electron (more than 1000 times). Because of this difference, the nuclei move much more slowly than the electrons. In addition, due to their opposite charges, there is a mutual attractive force of Ze^2/r^2 acting on an atomic nucleus and an electron. This force causes both particles to be accelerated. Since the magnitude of the acceleration is inversely proportional to the mass, a = F/m, the acceleration of the electrons is large and the acceleration of the atomic nuclei is small; the difference is a factor of more than 2000. Consequently, the electrons are moving and responding to forces very quickly, and the nuclei are not. You can imagine running a 100-meters dash against someone whose acceleration is a 2000 times greater than yours. That person could literally run circles around you.

Example 6.2.1: Coupled Oscillators with Dissimilar Masses

If two particles interact in some way, and one is much heavier than the other, the light particle will move essentially as a "slave" of the heavy particle. That is, it will simply follow the heavy particle wherever it goes, *and*, it will move rapidly in response to the heavy particle motion. As an illustration of this phenomenon, consider the simple mechanical system pictured below:

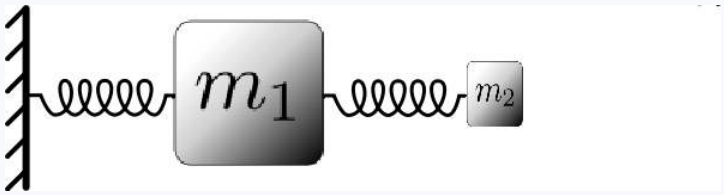


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Considering this as a classical system, we expect that the motion will be dominated by the large heavy particle (m_1), which is attached to a fixed wall by a spring. The small, light particle (m_2, which is attached to the heavy particle by a spring will simply follow the heavy particle and execute rapid oscillations around it.

So a good approximation is to describe the electronic states of a molecule by thinking that the nuclei are not moving, i.e. that they are stationary. The nuclei, however, can be stationary at different positions so the electronic wavefunction can depend on the positions of the nuclei even though their motion is neglected.

Now we look at the mathematics to see what is done in solving the Schrödinger equation after making the Born-Oppenheimer approximation. For a diatomic molecule as an example, the Hamiltonian operator is grouped into three terms

$$\hat{H}(r,R) = \hat{T}_{nuc}(R) + \frac{e^2}{4\pi\epsilon_0}\frac{Z_A Z_B}{R} + \hat{H}_{elec}(r,R) \tag{6.2.1}$$

where

$$\hat{T}_{nuc}(R) = -\frac{\hbar^2}{2m_A}\nabla_A^2 - \frac{\hbar^2}{2m_B}\nabla_B^2 \tag{6.2.2}$$

and

$$\hat{H}_{elec}(\vec{r},\vec{R}) = \frac{-\hbar^2}{2m}\sum_i \nabla_i^2 + \frac{e^2}{4\pi\epsilon_0}\left(-\sum_i \frac{Z_A}{r_{Ai}} - \sum_i \frac{Z_B}{r_{Bi}} + \frac{1}{2}\sum_i \sum_{j\neq i} \frac{1}{r_{ij}}\right) \tag{6.2.3}$$

In Equation 6.2.1, the first term represents the kinetic energy of the nuclei, the second term represents the Coulomb repulsion of the two nuclei, and the third term represents the contribution to the energy from the electrons, which consists of their kinetic energy, mutual repulsion for each other, and attraction for the nuclei. $\vec{r}$ and $\vec{R}$ are vectors specifying the positions of all the electrons and all the nuclei, respectively.

The Born-Oppenheimer approximation says that the nuclear kinetic energy terms in the complete Hamiltonian, Equation 6.2.1, can be neglected in solving for the electronic wavefunctions and energies. Consequently, the electronic wavefunction $\varphi_e(r,R)$ is found as a solution to the electronic Schrödinger equation

$$\hat{H}_{elec}(r,R)\varphi_e(r,R) = E_e(R)\varphi_e(r,R) \tag{6.2.4}$$

Even though the nuclear kinetic energy terms are neglected, the Born-Oppenheimer approximation still takes into account the variation in the positions of the nuclei in determining the electronic energy and the resulting electronic wavefunction depends upon the nuclear positions, R. As a result of the Born-Oppenheimer approximation, the molecular wavefunction can be written as a product

$$\psi_{ne}(r,R) = X_{ne}(R)\varphi_e(r,R) \tag{6.2.5}$$

This product wavefunction is called the Born-Oppenheimer wavefunction. The function $X_{ne}(R)$ is the vibrational wavefunction (describes the relative oscillations of the nuclei), which is a function of the nuclear coordinates R and depends upon both the vibrational and electronic quantum numbers or states, n and e, respectively. The electronic function, $\varphi_e(r,R)$, is a function of both the nuclear and electronic coordinates, but only depends upon the electronic quantum number or electronic state, e.

Potential Energy Curves and Surfaces

In practice the electronic Schrödinger equation is solved using approximations at particular values of R to obtain the wavefunctions $\varphi_e(r,R)$ and potential energies $V_e(R)$. The potential energies can be graphed as illustrated in Figure 6.2.1.

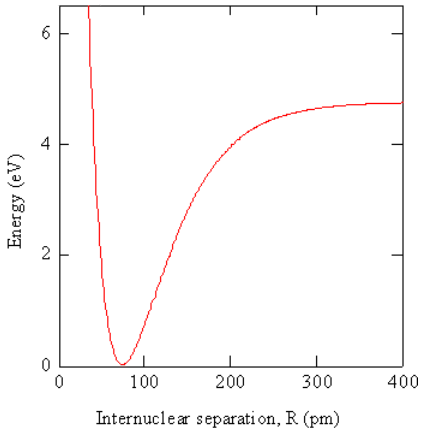


Figure 6.2.1: The potential energy function for a diatomic molecule.

The graph in Figure 6.2.1 is the energy of a diatomic molecule as a function of internuclear separation, which serves as the potential energy function for the nuclei. When R is very large there are two atoms that are weakly interacting. As R becomes smaller, the interaction becomes stronger, the energy becomes a large negative value, and we say a bond is formed between the atoms. At very small values of R, the internuclear repulsion is very large so the energy is large and positive. This energy function controls the motion of the nuclei. The equilibrium position of the nuclei is where this function is a minimum, i.e. at $R = R_0$. If we obtain the wavefunction at $R = R_0$ and use this function for all values of R, we have employed the *Crude Born-Oppenheimer* approximation.

Exercise 6.2.3

Relate Equation ??? to the one previously used in our description of molecular vibrations in terms of the harmonic oscillator model.

While the potential energy function, $V_e(R)$, for a diatomic molecule is a 1-D curve (Figure 6.2.1), molecules with more than two atoms will have multi-dimensional **potential energy surfaces** with 3N-6 (or 3N-5 for linear molecule) dimensions for the number of internal degrees of freedom.

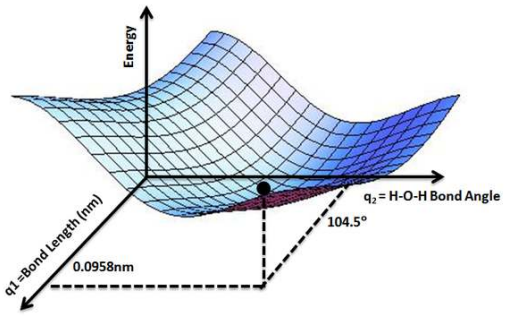


Figure 6.2.2: The potential energy surface for a water molecule: Shows the energy minimum corresponding to optimized molecular structure for water- O-H bond length of 0.0958 nm and H-O-H bond angle of 104.5°. Image used with permission from Wikipeda (AimNature)

The potential energy surface concept can be used to theoretically explore properties of structures composed of atoms, for example, finding the minimum energy shape of a molecule or computing the rates of a chemical reaction. Qualitatively the reaction coordinate diagrams (one-dimensional slices through the potential energy surfaces) have numerous applications. Chemists use reaction coordinate diagrams as both an analytical and pedagogical aid for rationalizing and illustrating kinetic and thermodynamic events. The purpose of energy profiles and surfaces is to provide a qualitative representation of how potential energy varies with molecular motion for a given reaction or process.

Exercise 6.2.4

Explain the difference between the Born-Oppenheimer approximation and the Crude Born-Oppenheimer approximation.

Summary

In this section we started with the Schrödinger equation for a diatomic molecule and separated it into two equations, an electronic Schrödinger equation and a nuclear Schrödinger equation. In order to make the separation, we had to make an approximation. We had to neglect the effect of the nuclear kinetic energy on the electrons. The fact that this assumption works can be traced to the fact that the nuclear masses are much larger than the electron mass. We then used the solution of the electronic Schrödinger equation to provide the potential energy function for the nuclear motion. The solution to the nuclear Schrödinger equation provides the vibrational wavefunctions and energies.

Contributors and Attributions

- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")
- Modified by Valeria D. Kleiman (University of Florida)

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6.3: The H_2^+ Prototypical Species

Molecular orbital theory is a conceptual extension of the orbital model, which was so successfully applied to atomic structure. As was once playfully remarked, "a molecule is nothing more than an atom with more nuclei." This may be overly simplistic, but we do attempt, as far as possible, to exploit analogies with atomic structure. Our understanding of atomic orbitals began with the exact solutions of a prototype problem – the hydrogen atom. We will begin our study of homonuclear diatomic molecules beginning with another exactly solvable prototype, the hydrogen molecule-ion H_2^+.

The Hydrogen Molecular Ion

The simplest conceivable molecule would be made of two protons and one electron, namely H_2^+. This species actually has a transient existence in electrical discharges through hydrogen gas and has been detected by mass spectrometry and it also has been detected in outer space. The Schrödinger equation for H_2^+ can be solved exactly within the Born-Oppenheimer approximation (i.e., fixed nuclei). This ion consists of two protons held together by the electrostatic force of a single electron. Clearly the two protons, two positive charges, repeal each other. The protons must be held together by an attractive Coulomb force that opposes the repulsive Coulomb force. A negative charge density between the two protons would produce the required counter-acting Coulomb force needed to pull the protons together. So intuitively, to create a chemical bond between two protons or two positively charged nuclei, a high density of negative charge between them is needed. We expect the molecular orbitals that we find to reflect this intuitive notion.

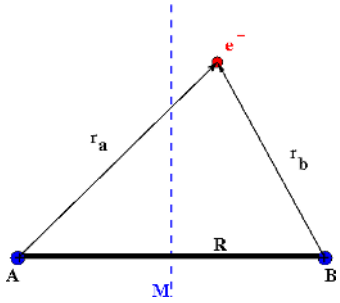


Figure 6.3.1: Hydrogen molecular ion H_2^+ with fixed nuclei A and B, internuclear distance R.

The electronic Hamiltonian for H_2^+ is

$$\begin{aligned}\hat{H}_{elec}(r,R) &= -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_A} - \frac{e^2}{4\pi\epsilon_0 r_B} + \frac{e^2}{4\pi\epsilon_0 R} \\ &= \begin{matrix}\text{Kinetic} \\ \text{contribution from}\end{matrix} e- + \begin{matrix}\text{attraction} \\ \text{nucleus A} e-\end{matrix} + \begin{matrix}\text{attraction} \\ \text{nucleus B} e-\end{matrix} + \text{A-B repulsion}\end{aligned} \tag{6.3.1}$$

where

- r_A and r_B are the distances electron from the A and B hydrogen nuclei, respectively and
- R is the distance between the two protons.

Although the Schrödinger equation for H_2^+ can be solved exactly (albeit within the Born-Oppenheimer approximation where the nuclei are fixed) because there is only one electron, we will develop approximate solutions in a manner applicable to other diatomic molecules that have more than one electron.

Linear Combination of Atomic Orbitals

For the case where the protons in H_2^+ are infinitely far apart, we have a hydrogen atom and an isolated proton when the electron is near one proton or the other. The electronic wavefunction would just be $1s_A(r)$ or $1s_B(r)$ depending upon which proton, labeled A or B, the electron is near. Here $1s_A$ denotes a 1s hydrogen atomic orbital with proton A serving as the origin of the spherical polar coordinate system in which the position **r** of the electron is specified. Similarly $1s_B$ has proton B as the origin. A useful approximation for the molecular orbital when the protons are close together therefore is a linear combination of the two atomic orbitals. The general method of using

$$\psi(r) = C_A 1s_A(r) + C_B 1s_B(r) \tag{6.3.2}$$

i.e. of finding molecular orbitals as linear combinations of atomic orbitals is called the *Linear Combination of Atomic Orbitals - Molecular Orbital (LCAO-MO) Method*. In this case we have two basis functions in our basis set, the hydrogenic atomic orbitals $1s_A$ and $1s_B$.

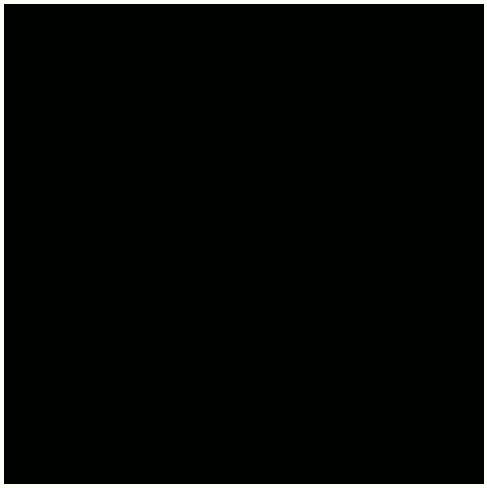
Note

A short hand notation has been used: $1s_A(r) = \varphi_{1,0}(r)$ centerd on atom A, $1s_B = \varphi_{1,0}(r)$ centered on atom B.
The coefficients C_A and C_B provide information about how much each Atomic Orbital (AO) from atom A and B contribute to the overall Molecular Orbital (MO), that contribution is given by $|C_A|^2$. and $|C_B|^2$, respectively

The Linear Combination of Atomic Orbitals (LCAO) Approximation and Interference

The LCAO approximation is an example of the molecular orbital wavefunction approximated as an expansion of a basis set of atomic orbitals on each atom of the molecule with variable coefficients that can be optimized (e.g., via the secular equations). The number of wavefunctions (solutions) extracted from optimizing the solution is equal the number of elements in the expansion. So for the expansion in Equation 6.3.2 with two atomic orbitals contributing result in two molecule orbitals.

This method yields a approximate picture of the molecular orbitals in a molecules. The figure below shows two atoms approaching along the axis of one of their $2p$ states. In the top row, the two lobes facing one another have the same sign; in the bottom row they have opposite sign. These are two different linear combinations of the same two atomic states, on different atoms and with difference phases (i.e., signs of C_A vs. C_B in the expansion). In the first example, the electron density increases between the nuclei and in the second example, a very steep-sided node between the two nuclei causes all the probability density to face away from the atom opposite.



For H_2^+, the simplest molecule, the starting function is given by Equation 6.3.2. We must determine the values for the coefficients, C_A and C_B. We could use a mathematical method (i.e. variational method)to find the optimum value for these coefficients, but for the case of H_2^+ evaluating these coefficients is easy. Since the two protons are identical, the probability that the electron is near A must equal the probability that the electron is near B. These probabilities are given by $|C_A|^2$ and $|C_B|^2$, respectively. Consider two possibilities that satisfy the condition $|C_A|^2 = |C_B|^2$; namely, $C_A = C_B = C_+$ and $C_A = -C_B = C_-$. These two cases produce two molecular orbitals:

$$\psi_+ = C_+(1s_A + 1s_B) \tag{6.3.3}$$

$$\psi_- = C_-(1s_A - 1s_B) \tag{6.3.4}$$

The probability density for finding the electron at any point in space is given by $|\psi^2|$ and the electronic charge density is just $|e\psi^2|$. The important difference between ψ_+ and ψ_- is that the charge density for ψ_+ is enhanced (Figure $6.3.2$ (bottom) between the two protons, whereas it is diminished for ψ_- as shown in Figures $6.3.2$ (top). ψ_- has a node in the middle while ψ_+ corresponds to our intuitive sense of what a chemical bond must be like. The electronic charge density is enhanced in the region between the two protons.

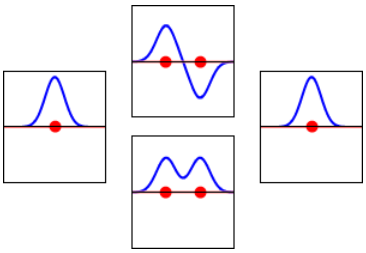


Figure 6.3.2: Electron wavefunctions for the 1s orbital of a lone hydrogen atom (left and right) and the corresponding bonding (bottom) and antibonding (top) molecular orbitals of the H_2^+ ion. The real part of the wavefunction is the blue curve, and the imaginary part is the red curve. The red dots mark the locations of the nuclei. The electron wavefunction oscillates according to the Schrödinger wave equation, and orbitals are its standing waves. The standing wave frequency is proportional to the orbital's kinetic energy. (This plot is a one-dimensional slice through the three-dimensional .)

So ψ_+ is called a *bonding molecular orbital*. If the electron were described by ψ_-, the low charge density between the two protons would not balance the Coulomb repulsion of the protons, so ψ_- is called an *antibonding molecular orbital*.

Contributors

- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")
- Rudolf Winter (Aberystwyth University)

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6.4: The Overlap Integral

For H_2^+, the simplest molecule, we must determine the values for the coefficients, C_A and C_B for the LCAO approximation for the molecular orbital as a linear combination of the two atomic orbitals

$$\psi(r) = C_A 1s_A(r) + C_B 1s_B(r) \tag{6.4.1}$$

For the case of H_2^+ evaluating these coefficients is easy. Since the two protons are identical, the probability that the electron is near A must equal the probability that the electron is near B. These probabilities are given by $|C_A|^2$ and $|C_B|^2$, respectively. Consider two possibilities that satisfy the condition

$$|C_A|^2 = |C_B|^2 \tag{6.4.2}$$

so $C_A = C_B = C_+$ and $C_A = -C_B = C_-$. These two cases produce two molecular orbitals:

$$\underbrace{\psi_+ = C_+(1s_A + 1s_B)}_{\text{bonding molecular orbital}} \tag{6.4.3}$$

and

$$\underbrace{\psi_- = C_-(1s_A - 1s_B)}_{\text{antibonding molecular orbital}} \tag{6.4.4}$$

The probability density for finding the electron at any point in space is given by $|\psi^2|$ and the electronic charge density is just $|e\psi^2|$. The important difference between ψ_+ and ψ_- is that the charge density for $|\psi_+\rangle$ is enhanced between the two protons, whereas it is diminished for $|\psi_-\rangle$ as shown in Figures 6.4.1. ψ_- has a node in the middle while $|\psi_+\rangle$ corresponds to our intuitive sense of what a chemical bond must be like. The electronic charge density is enhanced in the region between the two protons. So $|\psi_+\rangle$ is called a *bonding molecular orbital*. If the electron were described by $|\psi_-\rangle$, the low charge density between the two protons would not balance the Coulomb repulsion of the protons, so $|\psi_-\rangle$ is called an *antibonding molecular orbital*.

Now we want to evaluate C_+ and C_- and then calculate the energy. The bonding and antibonding character of ψ_+ and ψ_- also should be reflected in the energy. If $|\psi_+\rangle$ indeed describes a bonding orbital, then the energy of this state should be less than that of a proton and hydrogen atom that are separated. The calculation of the energy will tell us whether this simple theory predicts H_2^+ to be stable or not and also how much energy is required to dissociate this molecule.

The constants C_+ and C_- are evaluated from the standard normalization condition:

$$\begin{aligned} \int |\psi_\pm|^2 d\tau &= 1 \\ &= |C_\pm|^2 \cdot \left(2 \pm 2 \cdot \int 1s_A \cdot 1s_b d\tau\right) \end{aligned} \tag{6.4.5}$$

Since the atomic orbitals are normalized, the contribution from the normalized wavefunction of each AO has a value of 1. The last term is called the *overlap integral* and is symbolized by S.

The overlap integral is obtained from taking the value of $1s_B$ at a point multiply by the value of $1s_A$ at that point and sum (integrate) such a product over all of space (Figure 6.4.1). If the functions do not overlap, i.e. if one is zero when the other one is not and vice versa, these integrals then will be zero. It also is possible in general for such integrals to be zero even if the functions overlap because of the cancelation of positive and negative contributions.

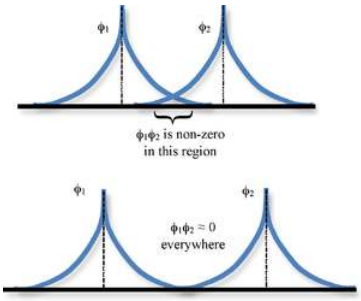


Figure 6.4.1: The wavefunctions of atomic orbitals decrease exponentially with distance. Orbital overlap is non-zero when two atoms are close together, as illustrated for 1s orbitals in the upper figure. The lower figure shows orbitals that are too far away to interact. In this case S is close to zero.

If the overlap integral is zero, for whatever reason, the functions are said to be *orthogonal*. Notice that the overlap integral ranges from 0 to 1 as the separation between the protons varies from $R = \infty$ to $R = 0$. Clearly when the protons are infinite distance apart, there is no overlap, and when $R = 0$ both functions are centered on one nucleus and $\int 1s_A \cdot 1s_B d\tau$ is normalized to 1, because $1s_A = 1s_B$.

With these considerations and using the fact that $1s$ wavefunctions are real so

$$\int 1s_A \cdot 1s_B d\tau = S \tag{6.4.6}$$

Equation 6.4.5 becomes

$$|C_{\pm}|^2(2 \pm 2S) = 1 \tag{6.4.7}$$

The solution to Equation 6.4.7 is given by

$$C_{\pm} = \frac{1}{\sqrt{2(1 \pm S)}} \tag{6.4.8}$$

Hence, the normalized molecular orbitals in Equations 6.4.3 and 6.4.4 are

$$\psi_+ = \frac{1}{\sqrt{2(1+S)}}(1s_A + 1s_B) \tag{6.4.9}$$

and

$$\psi_- = \frac{1}{\sqrt{2(1-S)}}(1s_A - 1s_B) \tag{6.4.10}$$

The energies associated with these wavefunctions requires a bit more effort to calculate though as demonstrated in the following section.

For the overlap integral of two 1s orbitals from the hydrogen dimer discussed above is difficult to evaluate analytically and is explained here. The final answer is:

$$S(R) = \int 1s_A|1s_B d\tau \tag{6.4.11}$$

$$= e^{-R/a_o}\left(1 + \frac{R}{a_o} + \frac{R^2}{3a_o^2}\right) \tag{6.4.12}$$

The overlap integral for two 1s atomic orbitals of hydrogen is graphically displayed below

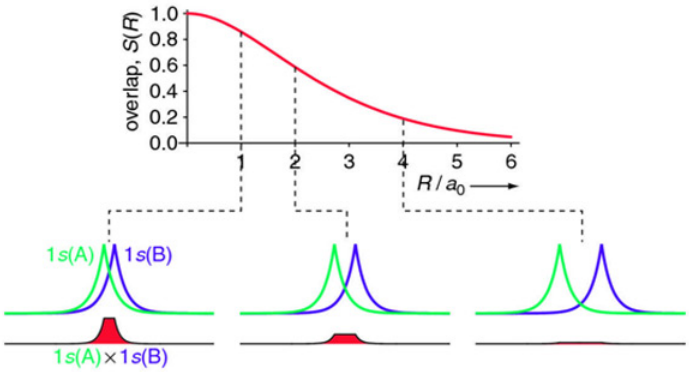


Figure 6.4.2: The overlap integral at different proton separations.

Example 6.4.1

Calculate the difference in the electronic charge density (C/pm^3) at a point halfway between the two nuclei for H_2^+ for an electron in the bonding molecular orbital compared to one in the antibonding molecular orbital.

Solution

The electronic charge density is calculated with the formula $|e\psi^2|$ where $e = 1.602 \times 10^{-19} C$

a: Bonding Molecular Orbital

First, squaring the bonding molecular orbital (Equation 6.4.9) gives us:

$$\begin{aligned}\psi_+^2 &= \frac{1}{2(1+S)}(1s_A + 1s_B)^2 \\ &= \frac{1}{2(1+S)}\frac{1}{\pi a_0^3}\left(e^{-r_A/a_0} + e^{-r_B/a_0}\right)^2 \\ &= \frac{1}{2(1+S)}\frac{1}{\pi a_0^3} \\ &= (0.561)^2 \times \left(\frac{1}{\pi \times (52.9 \text{ pm})^3}\right) = 6.7672 \times 10^{-7} \text{ pm}^{-3}\end{aligned}$$

(Note: The value of C^2 is obtained from equation 6.4.9 and the value of S is from Equation 6.4.12)

To find the density at halfway between A and B for the bonding orbital evalulate at 1/2 R,

$$r_A = \frac{1}{2}R \text{ and } r_B = \frac{1}{2}R$$

$$\psi_+^2 = 3.7 \times 10^{-7} \text{ pm}^{-3} \tag{6.4.13}$$

Now multiply this answer by e to generate the electronic charge density,

$$P = \left(3.7 \times 10^{-7} \text{ pm}^{-3}\right) \times \left(1.602 \times 10^{-19}\right) \text{ C} = 5.93 \times 10^{-26} C/pm^3 \tag{6.4.14}$$

b: Antibonding Molecular Orbital

To find the halfway between A and B for the anti-bonding orbital at $r_A = \frac{1}{2}R$ and $r_B = \frac{1}{2}R$. However, simple inspection of Equation 6.4.10 or Figure 6.4.1 shows this will be zero.

$$\text{e}\psi_-^2 = 0 \tag{6.4.15}$$

Obviously, when multiplied by e, the answer is still zero. This makes logical sense as there would be no charge density between the two atoms as there lies a node with no probability of finding an electron.

Contributors andf Attributions

- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")
- Modified by Valeria D. Kleiman

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6.5: Bonding and Antibonding Orbitals

The two molecular orbitals created via the linear combinations of atomic orbitals (LCAOs) approximation were created from the sum and the difference of two atomic orbitals. Within this approximation, the j[th] molecular orbital can be expressed as a linear combination of many atomic orbitals $\{\phi_i\}$:

$$\psi_J = \sum_i^N c_{J,i}\phi_i \tag{6.5.1}$$

A molecule will have as **many molecular orbitals as there are atomic orbitals used in the basis set** (N in Equation 6.5.1). Adding two atomic orbitals corresponds to *constructive* interference between two waves, thus reinforcing their intensity; the internuclear electron probability density is *increased*. The molecular orbital corresponding to the sum of the two H 1*s* orbitals is called a σ_{1s} combination (parts (a) and (b) of Figure 6.5.1).

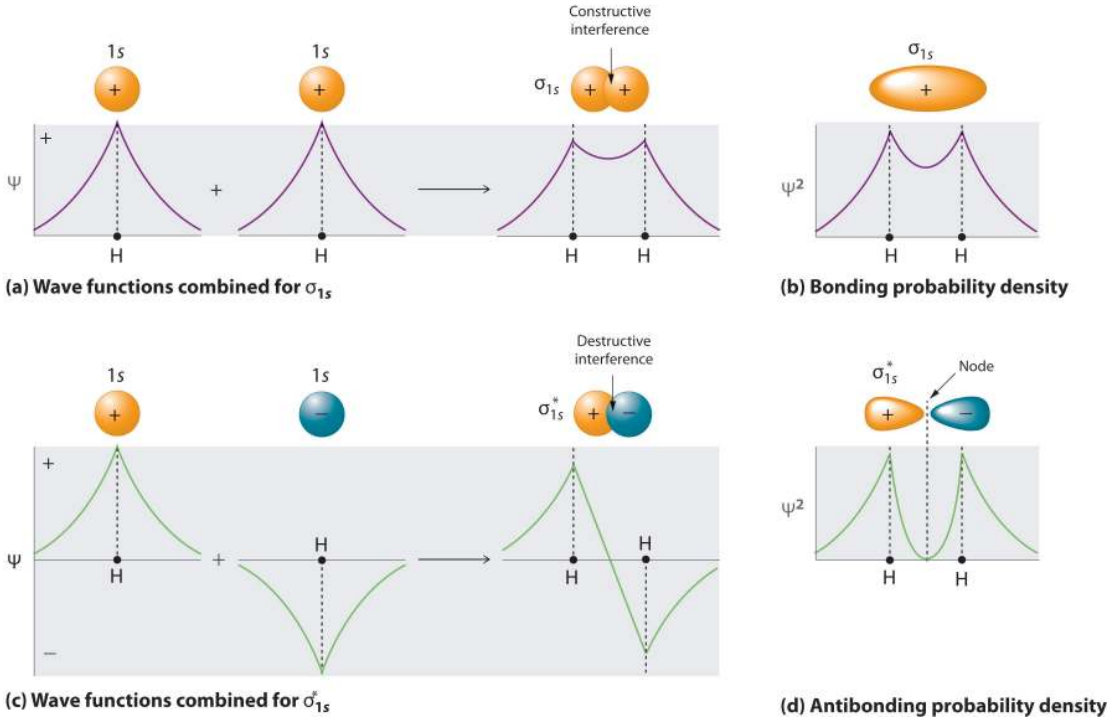


Figure 6.5.1: Molecular Orbitals for the H_2 Molecule. (a) This diagram shows the formation of a bonding σ_{1s} molecular orbital for H_2 as the sum of the wave functions (Ψ) of two H 1s atomic orbitals. (b) This plot of the square of the wave function (Ψ^2) for the bonding σ1s molecular orbital illustrates the increased electron probability density between the two hydrogen nuclei. (Recall that the probability density is proportional to the square of the wave function.) (c) This diagram shows the formation of an antibonding σ^*_{1s} molecular orbital for H_2 as the difference of the atomic orbital wavefunctions (Ψ) of two H 1s atomic orbitals. (d) This plot of the square of the wave function (Ψ2) for the σ^*_{1s} antibonding molecular orbital illustrates the node corresponding to zero electron probability density between the two hydrogen nuclei. Image used with permission (CC BY-SA-NC; anonymous by request).

In the sigma (σ) orbital, the electron density along the internuclear axis and between the nuclei has *cylindrical symmetry*; that is, all cross-sections perpendicular to the internuclear axis are circles. The subscript 1*s* denotes the atomic orbitals from which the molecular orbital was derived.

$$\sigma_{1s} = \frac{1}{\sqrt{2(1+S)}}(1s_A + 1s_B) \tag{6.5.2}$$

Conversely, subtracting one atomic orbital from another corresponds to *destructive* interference between two waves, which reduces their intensity and causes a *decrease* in the internuclear electron probability density (part (c) and part (d) in Figure 6.5.1). The resulting pattern contains a *node* where the electron density is zero. The molecular orbital corresponding to the difference is called σ^*_{1s} and has a region of zero electron probability, a nodal plane, perpendicular to the internuclear axis:

$$\sigma_{1s}^{*} = \frac{1}{\sqrt{2(1-S)}}(1s_A - 1s_B) \tag{6.5.3}$$

The electron density in the σ_{1s} molecular orbital is greatest between the two positively charged nuclei, and the resulting electron–nucleus electrostatic attractions reduce repulsions between the nuclei. Thus the σ_{1s} orbital represents a ***bonding molecular orbital***. A molecular orbital that forms when atomic orbitals or orbital lobes with the same sign interact to give increased electron probability between the nuclei due to constructive reinforcement of the wave functions. In contrast, electrons in the $\sigma_{1s}^{\star}$ orbital are generally found in the space outside the internuclear region. Because this allows the positively charged nuclei to repel one another, the $\sigma_{1s}^{\star}$ orbital is *an* ***antibonding molecular orbital*** (a molecular orbital that forms when atomic orbitals or orbital lobes of opposite sign interact to give decreased electron probability between the nuclei due to destructive reinforcement of the wave functions).

Note

Antibonding orbitals contain a node perpendicular to the internuclear axis; bonding orbitals do notal is always lower in energy (more stable) than the component atomic orbitals, whereas an antibonding molecular orbital is always higher in energy (less stable).

Because electrons in the σ_{1s} orbital interact simultaneously with both nuclei, they have a lower energy than electrons that interact with only one nucleus. This means that the σ_{1s} molecular orbital has a ***lower* energy** than either of the hydrogen 1*s* atomic orbitals. Conversely, electrons in the $\sigma^{\star}_{1s}$ orbital interact with only one hydrogen nucleus at a time. In addition, they are farther away from the nucleus than they were in the parent hydrogen 1*s* atomic orbitals. Consequently, the $\sigma^{\star}_{1s}$ molecular orbital has a ***higher* energy** than either of the hydrogen 1*s* atomic orbitals. The σ_{1s} (bonding) molecular orbital is *stabilized* relative to the 1*s* atomic orbitals, and the $\sigma^{\star}_{1s}$ (antibonding) molecular orbital is *destabilized*. The relative energy levels of these orbitals are shown in the energy-level diagram (a schematic drawing that compares the energies of the molecular orbitals (bonding, antibonding, and nonbonding) with the energies of the parent atomic orbitals) in Figure 6.5.2

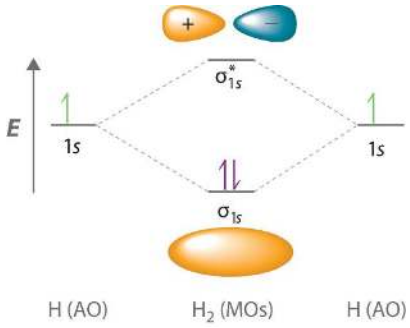


Figure 6.5.2: Molecular Orbital Energy-Level Diagram for H2. The two available electrons (one from each H atom) in this diagram fill the bonding σ1s molecular orbital. Because the energy of the σ1s molecular orbital is lower than that of the two H 1s atomic orbitals, the H2 molecule is more stable (at a lower energy) than the two isolated H atoms.

Note

A bonding molecular orbital is always lower in energy (more stable) than the component atomic orbitals, whereas an antibonding molecular orbital is always higher in energy (less stable).

Contributors and Attributions

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6.6: Molecular Orbitals Can Be Ordered According to Their Energies

The LCAO-MO method that we used for H_2^+ can be applied qualitatively to homonuclear diatomic molecules to provide additional insight into chemical bonding. A more quantitative approach also is helpful, especially for more complicated situations, like heteronuclear diatomic molecules and polyatomic molecules. When two atoms are close enough for their valence orbitals to overlap significantly, the filled inner electron shells are largely unperturbed; hence they are often ignored in constructing molecular orbitals. This means that we can focus our attention on the molecular orbitals derived from valence atomic orbitals.

Molecular Orbitals Formed from *ns* Orbitals

The molecular orbitals diagrams formatted for the dihydrogen species are similar to the diagrams to any **homonuclear diatomic molecule** with two identical alkali metal atoms (Li_2 and Cs_2, for example) is shown in part (a) in Figure 6.6.1, where M represents the metal atom. Only two energy levels are important for describing the valence electron molecular orbitals of these species: a σ_{ns} bonding molecular orbital and a σ^*_{ns} antibonding molecular orbital. Because each alkali metal (M) has an ns^1 valence electron configuration, the M_2 molecule has two valence electrons that fill the σ_{ns} bonding orbital. As a result, a bond order of 1 is predicted for all homonuclear diatomic species formed from the alkali metals (Li_2, Na_2, K_2, Rb_2, and Cs_2). The general features of these M_2 diagrams are identical to the diagram for the H_2 molecule. Experimentally, all are found to be stable in the gas phase, and some are even stable in solution.

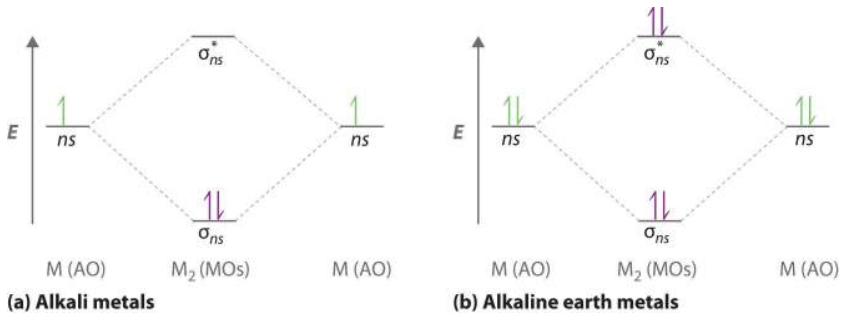


Figure 6.6.1: Molecular Orbital Energy-Level Diagrams for Alkali Metal and Alkaline Earth Metal Diatomic (M_2) Molecules. (a) For alkali metal diatomic molecules, the two valence electrons are enough to fill the σns (bonding) level, giving a bond order of 1. (b) For alkaline earth metal diatomic molecules, the four valence electrons fill both the σ_{ns} (bonding) and the σ^*_{ns} (nonbonding) levels, leading to a predicted bond order of 0. (CC BY-SA-NC; anonymous by request).

Similarly, the molecular orbital diagrams for homonuclear diatomic compounds of the alkaline earth metals (such as Be_2), in which each metal atom has an ns^2 valence electron configuration, resemble the diagram for the He_2 molecule. As shown in Figure 6.6.1*b*, this is indeed the case. All the homonuclear alkaline earth diatomic molecules have four valence electrons, which fill both the σ_{ns} bonding orbital and the σ_{ns}* antibonding orbital and give a bond order of 0. Thus Be_2, Mg_2, Ca_2, Sr_2, and Ba_2 are all expected to be unstable, in agreement with experimental data.In the solid state, however, all the alkali metals and the alkaline earth metals exist as extended lattices held together by metallic bonding. At low temperatures, Be_2 is stable.

Example 6.6.1: Sodium Dimer Ion

Use a qualitative molecular orbital energy-level diagram to predict the valence electron configuration, bond order, and likely existence of the Na_2^- ion.

Given: chemical species

Asked for: molecular orbital energy-level diagram, valence electron configuration, bond order, and stability

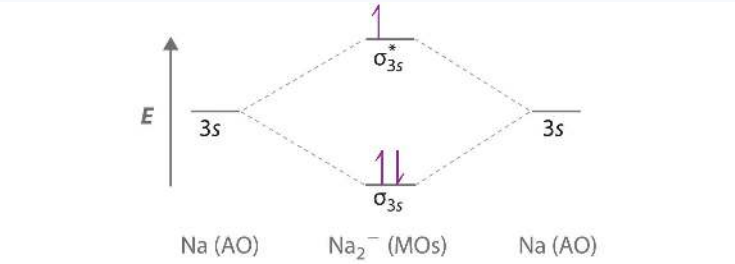
Strategy

A. Combine the two sodium valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for this system.
B. Determine the total number of valence electrons in the Na_2^- ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.
C. Calculate the bond order and predict whether the species is stable.

Solution

A Because sodium has a [Ne]$3s^1$ electron configuration, the molecular orbital energy-level diagram is qualitatively identical to the diagram for the interaction of two 1*s* atomic orbitals.

B The Na_2^- ion has a total of three valence electrons (one from each Na atom and one for the negative charge), resulting in a filled σ_{3s} molecular orbital, a half-filled σ_{3s*} and a $(\sigma_{3s})^2(\sigma^\star_{3s})^1$ electron configuration.



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C The bond order is (2-1)÷2=1/2 With a fractional bond order, we predict that the Na_2^- ion exists but is highly reactive.

Exercise 6.6.1: Calcium Dimer Cation

Use a qualitative molecular orbital energy-level diagram to predict the valence electron configuration, bond order, and likely existence of the Ca_2^+ ion.

Answer

Ca_2^+ has a $(\sigma_{4s})^2(\sigma^\star_{4s})^1$ electron configurations and a bond order of 1/2 and should exist.

Molecular Orbitals Formed from n*p* Orbitals

Atomic orbitals other than *ns* orbitals can also interact to form molecular orbitals. Because individual *p*, *d*, and *f* orbitals are not spherically symmetrical, however, we need to define a coordinate system so we know which lobes are interacting in three-dimensional space. Recall that for each *np* subshell, for example, there are np_x, np_y, and np_z orbitals. All have the same energy and are therefore degenerate, but they have different spatial orientations.

$$\sigma_{np_z} = np_z\,(A) - np_z\,(B) \tag{6.6.1}$$

Just as with *ns* orbitals, we can form molecular orbitals from *np* orbitals by taking their mathematical sum and difference. When two positive lobes with the appropriate spatial orientation overlap, as illustrated for two np_z atomic orbitals in part (a) in Figure 6.6.2, it is the mathematical *difference* of their wave functions that results in *constructive* interference, which in turn increases the electron probability density between the two atoms. The difference therefore corresponds to a molecular orbital called a σ_{np_z} *bonding molecular orbital* because, just as with the σ orbitals discussed previously, it is symmetrical about the internuclear axis (in this case, the *z*-axis):

$$\sigma_{np_z} = np_z\,(A) - np_z\,(B) \tag{6.6.2}$$

The other possible combination of the two np_z orbitals is the mathematical sum:

$$\sigma_{np_z} = np_z\,(A) + np_z\,(B) \tag{6.6.3}$$

In this combination, shown in part (b) in Figure 6.6.2, the positive lobe of one np_z atomic orbital overlaps the negative lobe of the other, leading to *destructive* interference of the two waves and creating a node between the two atoms. Hence this is an antibonding molecular orbital. Because it, too, is symmetrical about the internuclear axis, this molecular orbital is called a $\sigma_{np_z} = np_z\,(A) - np_z\,(B)$ *antibonding molecular orbital*. Whenever orbitals combine, *the bonding combination is always lower in energy* (more stable) than the atomic orbitals from which it was derived, and *the antibonding combination is higher in energy* (less stable).

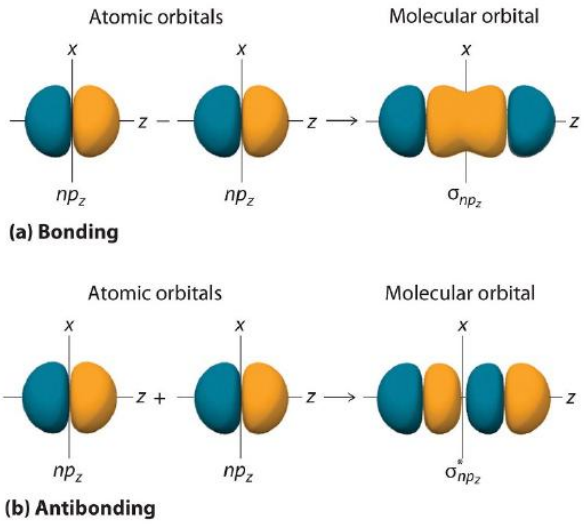


Figure 6.6.2: Formation of Molecular Orbitals from np_z Atomic Orbitals on Adjacent Atoms.(a) By convention, in a linear molecule or ion, the *z*-axis always corresponds to the internuclear axis, with +*z* to the right. As a result, the signs of the lobes of the np_z atomic orbitals on the two atoms alternate − + − +, from left to right. In this case, the σ (bonding) molecular orbital corresponds to the mathematical *difference*, in which the overlap of lobes with the same sign results in increased probability density between the nuclei. (b) In contrast, the σ* (antibonding) molecular orbital corresponds to the mathematical *sum*, in which the overlap of lobes with opposite signs results in a nodal plane of zero probability density perpendicular to the internuclear axis. (CC BY-SA-NC; anonymous by request).

The remaining *p* orbitals on each of the two atoms, np_x and np_y, do not point directly toward each other. Instead, they are perpendicular to the internuclear axis. If we arbitrarily label the axes as shown in Figure 6.6.3, we see that we have two pairs of *np* orbitals: the two np_x orbitals lying in the plane of the page, and two np_y orbitals perpendicular to the plane. Although these two pairs are equivalent in energy, the np_x orbital on one atom can interact with only the np_x orbital on the other, and the np_y orbital on one atom can interact with only the np_y on the other. These interactions are side-to-side rather than the head-to-head interactions characteristic of σ orbitals. Each pair of overlapping atomic orbitals again forms two molecular orbitals: one corresponds to the arithmetic sum of the two atomic orbitals and one to the difference. The sum of these side-to-side interactions increases the electron probability in the region above and below a line connecting the nuclei, so it is a bonding molecular orbital that is called a pi (π) orbital (a bonding molecular orbital formed from the side-to-side interactions of two or more parallel np atomic orbitals). The difference results in the overlap of orbital lobes with opposite signs, which produces a nodal plane perpendicular to the internuclear axis; hence it is an antibonding molecular orbital, called a pi star (π*) orbital An antibonding molecular orbital formed from the difference of the side-to-side interactions of two or more parallel *np* atomic orbitals, creating a nodal plane perpendicular to the internuclear axis..

$$\pi_{np_x} = np_x\,(A) + np_x\,(B) \tag{6.6.4}$$

$$\pi^{\star}_{np_x} = np_x\,(A) - np_x\,(B) \tag{6.6.5}$$

The two np_y orbitals can also combine using side-to-side interactions to produce a bonding π_{np_y} molecular orbital and an antibonding $\pi^{\star}_{np_y}$ molecular orbital. Because the np_x and np_y atomic orbitals interact in the same way (side-to-side) and have the same energy, the π_{np_x} and π_{np_y} molecular orbitals are a degenerate pair, as are the $\pi^{\star}_{np_x}$ and $\pi^{\star}_{np_y}$ molecular orbitals.

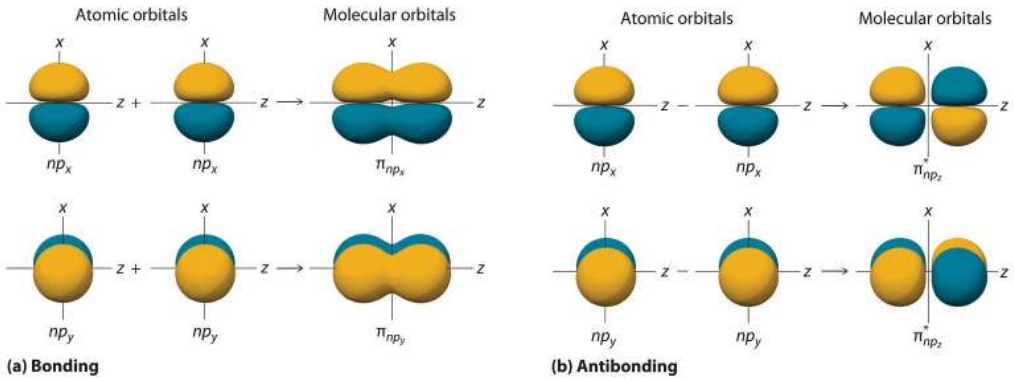


Figure 6.6.3: Formation of π Molecular Orbitals from npx and npy Atomic Orbitals on Adjacent Atoms.(a) Because the signs of the lobes of both the npx and the npy atomic orbitals on adjacent atoms are the same, in both cases the mathematical sum corresponds to a π (bonding) molecular orbital. (b) In contrast, in both cases, the mathematical difference corresponds to a π* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis. (CC BY-SA-NC; anonymous by request).

Energies for Homonuclear Diatomic Molecules

We now describe examples of systems involving period 2 homonuclear diatomic molecules, such as N_2, O_2, and F_2. When we draw a molecular orbital diagram for a molecule, there are four key points to remember:

1. The number of molecular orbitals produced is the same as the number of atomic orbitals used to create them.
2. As the overlap between two atomic orbitals increases, the difference in energy between the resulting bonding and antibonding molecular orbitals increases.
3. When two atomic orbitals combine to form a pair of molecular orbitals, the bonding molecular orbital is stabilized about as much as the antibonding molecular orbital is destabilized.
4. The interaction between atomic orbitals is greatest when they have the same energy.

Figure 6.6.4 is an energy-level diagram that can be applied to two *identical* interacting atoms that have three *np* atomic orbitals each. There are six degenerate *p* atomic orbitals (three from each atom) that combine to form six molecular orbitals, three bonding and three antibonding. The bonding molecular orbitals are lower in energy than the atomic orbitals because of the increased stability associated with the formation of a bond. Conversely, the antibonding molecular orbitals are higher in energy, as shown. The energy difference between the σ and σ* molecular orbitals is significantly greater than the difference between the two π and π* sets. The reason for this is that the atomic orbital overlap and thus the strength of the interaction are greater for a σ bond than a π bond, which means that the σ molecular orbital is more stable (lower in energy) than the π molecular orbitals.

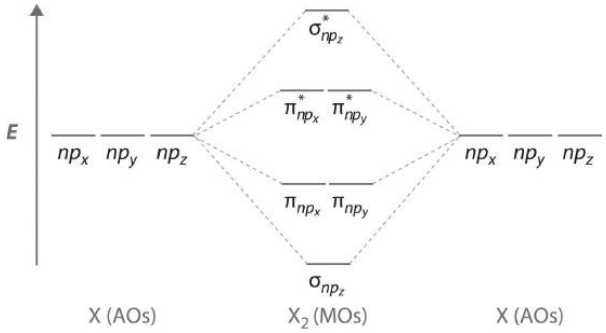


Figure 6.6.4: The Relative Energies of the σ and π Molecular Orbitals Derived from np_x, np_y, and np_z Orbitals on Identical Adjacent Atoms. Because the two np_z orbitals point directly at each other, their orbital overlap is greater, so the difference in energy between the σ and σ* molecular orbitals is greater than the energy difference between the π and π* orbitals. (CC BY-SA-NC; anonymous by request).

> *The number of molecular orbitals is always equal to the total number of atomic orbitals we started with.*

We illustrate how to use these points by constructing a molecular orbital energy-level diagram for F_2. We use the diagram in Figure 6.6.5*a*; the n = 1 orbitals (σ_{1s} and σ_{1s}*) are located well below those of the n = 2 level and are not shown. As illustrated in the

diagram, the σ_{2s} and σ_{2s}* molecular orbitals are much lower in energy than the molecular orbitals derived from the 2*p* atomic orbitals because of the large difference in energy between the 2*s* and 2*p* atomic orbitals of fluorine. The lowest-energy molecular orbital derived from the three 2*p* orbitals on each F is σ_{2p_z} and the next most stable are the two degenerate orbitals, π_{2p_x} and π_{2p_y}. For each bonding orbital in the diagram, there is an antibonding orbital, and the antibonding orbital is destabilized by about as much as the corresponding bonding orbital is stabilized. As a result, the $\sigma^{\star}_{2p_z}$ orbital is higher in energy than either of the degenerate $\pi^{\star}_{2p_x}$ and $\pi^{\star}_{2p_y}$ orbitals. We can now fill the orbitals, beginning with the one that is lowest in energy.

Each fluorine has 7 valence electrons, so there are a total of 14 valence electrons in the F_2 molecule. Starting at the lowest energy level, the electrons are placed in the orbitals according to the Pauli principle and Hund's rules. Two electrons each fill the σ_{2s} and σ_{2s}* orbitals, 2 fill the σ_{2p_z} orbital, 4 fill the two degenerate π orbitals, and 4 fill the two degenerate π^* orbitals, for a total of 14 electrons.

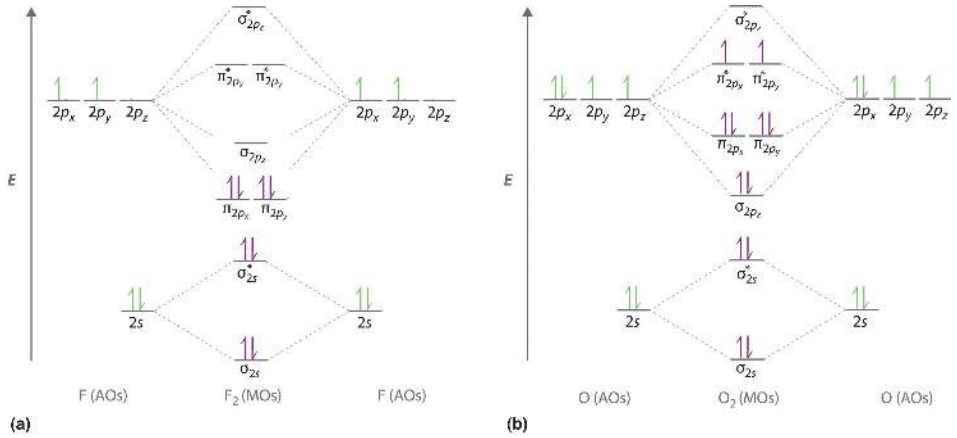


Figure 6.6.5: Molecular Orbital Energy-Level Diagrams for Homonuclear Diatomic Molecules.(a) For C_2, with 8 valence electrons (4 from each F atom). This diagram shows 6 electrons in bonding orbitals and 2 in antibonding orbitals, resulting in a bond order of 2. (b) For O_2, with 12 valence electrons (6 from each O atom), there are only 2 electrons to place in the $\left(\pi^{\star}_{np_x}, \pi^{\star}_{np_y}\right)$ pair of orbitals. Hund's rule dictates that one electron occupies each orbital, and their spins are parallel, giving the O_2 molecule two unpaired electrons. This diagram shows 8 electrons in bonding orbitals and 4 in antibonding orbitals, resulting in a predicted bond order of 2. (CC BY-SA-NC; anonymous by request).

For period 2 diatomic molecules to the left of N_2 in the periodic table, a slightly different molecular orbital energy-level diagram is needed because the σ_{2p_z} molecular orbital is slightly *higher* in energy than the degenerate $\pi^{\star}_{np_x}$ and $\pi^{\star}_{np_y}$ orbitals. The difference in energy between the 2*s* and 2*p* atomic orbitals increases from Li_2 to F_2 due to increasing nuclear charge and poor screening of the 2*s* electrons by electrons in the 2*p* subshell. The bonding interaction between the 2*s* orbital on one atom and the $2p_z$ orbital on the other is most important when the two orbitals have similar energies. This interaction decreases the energy of the σ_{2s} orbital and increases the energy of the σ_{2p_z} orbital. Thus for Li_2, Be_2, B_2, C_2, and N_2, the σ_{2p_z} orbital is higher in energy than the σ_{3p_z} orbitals, as shown in Figure 6.6.6. Experimentally, the energy gap between the *ns* and *np* atomic orbitals *increases* as the nuclear charge increases (Figure 6.6.6). Thus for example, the σ_{2p_z} molecular orbital is at a lower energy than the $\pi_{2p_{x,y}}$ pair.

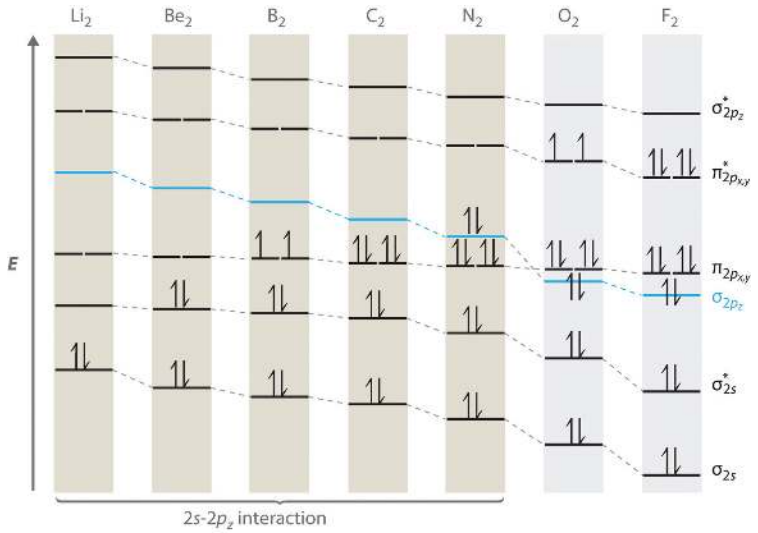


Figure 6.6.6: Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements. Unlike earlier diagrams, only the molecular orbital energy levels for the molecules are shown here. For simplicity, the atomic orbital energy levels for the component *atoms* have been omitted. For Li_2 through N_2, the σ_{2p_z} orbital is higher in energy than the $\pi_{2p_{x,y}}$ orbitals. In contrast, the σ_{2p_z} orbital is *lower* in energy than the $\pi_{2p_{x,y}}$ orbitals for O_2 and F_2 due to the increase in the energy difference between the 2*s* and 2*p* atomic orbitals as the nuclear charge increases across the row. (CC BY-SA-NC; anonymous by request).

Example 6.6.2: Diatomic Sulfur

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in S_2, a bright blue gas at high temperatures.

Given: chemical species

Asked for: molecular orbital energy-level diagram, bond order, and number of unpaired electrons

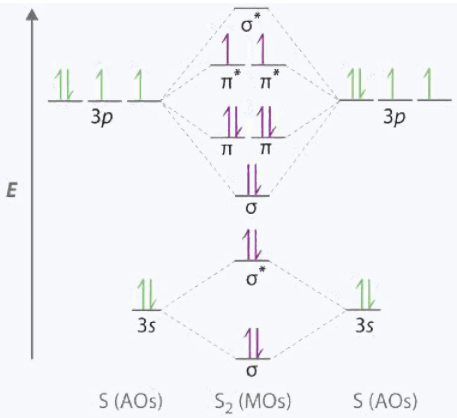
Strategy:

A. Write the valence electron configuration of sulfur and determine the type of molecular orbitals formed in S_2. Predict the relative energies of the molecular orbitals based on how close in energy the valence atomic orbitals are to one another.
B. Draw the molecular orbital energy-level diagram for this system and determine the total number of valence electrons in S_2.
C. Fill the molecular orbitals in order of increasing energy, being sure to obey the Pauli principle and Hund's rule.
D. Calculate the bond order and describe the bonding.

Solution:

A Sulfur has a $[Ne]3s^23p^4$ valence electron configuration. To create a molecular orbital energy-level diagram similar to those in Figures 6.6.6 and 6.6.7, we need to know how close in energy the 3*s* and 3*p* atomic orbitals are because their energy separation will determine whether the $\pi_{3p_{x,y}}$ or the σ_{3p_z}> molecular orbital is higher in energy. Because the *ns*–*np* energy gap *increases* as the nuclear charge increases, the σ_{3p_z} molecular orbital will be lower in energy than the $\pi_{3p_{x,y}}$ pair.

B The molecular orbital energy-level diagram is as follows:



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Each sulfur atom contributes 6 valence electrons, for a total of 12 valence electrons.

C Ten valence electrons are used to fill the orbitals through π_{3p_x} and π_{3p_y}, leaving 2 electrons to occupy the degenerate $\pi^{\star}_{3p_x}$ and $\pi^{\star}_{3p_y}$ pair. From Hund's rule, the remaining 2 electrons must occupy these orbitals separately with their spins aligned. With the numbers of electrons written as superscripts, the electron configuration of S_2 is $(\sigma_{3s})^2(\sigma^{\star}_{3s})^2(\sigma_{3p_z})^2(\pi_{3p_{x,y}})^4(\pi_{3p^{\star}_{x,y}})^2$ with 2 unpaired electrons. The bond order is (8 − 4) ÷ 2 = 2, so we predict an S=S double bond.

Exercise 6.6.2

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in the peroxide ion (O_2^{2-}).

Answer

$(\sigma_{2s})^2(\sigma^{\star}_{2s})^2(\sigma_{2p_z})^2\left(\pi_{2p_{x,y}}\right)^4(\pi_{2p^{\star}_{x,y}})^4$ bond order of 1; no unpaired electrons

Molecular Orbitals Formed from *ns* with n*p* Orbitals

Although many combinations of atomic orbitals form molecular orbitals, we will discuss only one other interaction: an *ns* atomic orbital on one atom with an np_z atomic orbital on another. As shown in Figure 6.6.7, the sum of the two atomic wave functions ($ns + np_z$) produces a σ bonding molecular orbital. Their difference ($ns - np_z$) produces a σ* antibonding molecular orbital, which has a nodal plane of zero probability density perpendicular to the internuclear axis.

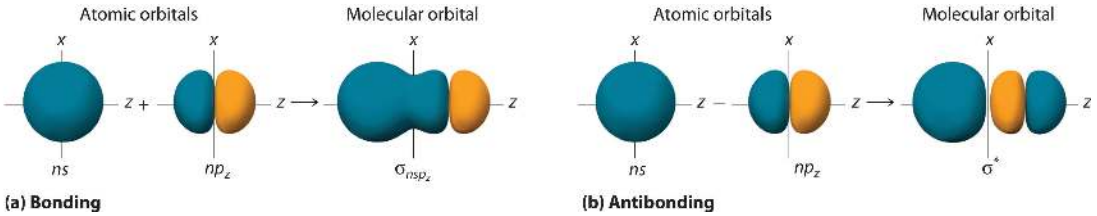


Figure 6.6.7: Formation of Molecular Orbitals from an *ns* Atomic Orbital on One Atom and an np_z Atomic Orbital on an Adjacent Atom.(a) The mathematical sum results in a σ (bonding) molecular orbital, with increased probability density between the nuclei. (b) The mathematical difference results in a σ* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis. (CC BY-SA-NC; anonymous by request).

6.6: Molecular Orbitals Can Be Ordered According to Their Energies is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

6.7: Molecular-Orbital Theory Does not Predict a Stable Diatomic Helium Molecule

Bond Order

In the Lewis electron structures, the number of electron pairs holding two atoms together was called the *bond order*. Within the molecular orbital approach, *bond order* is defined as one-half the *net* number of bonding electrons:

$$\text{bond order} = \frac{\text{number of bonding electrons} - \text{number of antibonding electrons}}{2} \tag{6.7.1}$$

To calculate the bond order of H_2, we know that the σ_{1s} (bonding) molecular orbital contains two electrons, while the $\sigma^{\star}_{1s}$ (antibonding) molecular orbital is empty. The bond order of H_2 is therefore

$$\text{bond order} = \frac{2-0}{2} = 1 \tag{6.7.2}$$

This result corresponds to the single covalent bond; double and triple bonds contain four or six electrons, respectively, and correspond to bond orders of 2 and 3.

We can use energy-level diagrams to describe the bonding in other pairs of atoms and ions where n = 1, such as the H_2^+ ion, the He_2^+ ion, and the He_2 molecule. Again, we fill the lowest-energy molecular orbitals first while being sure not to violate the Pauli principle or Hund's Rules.

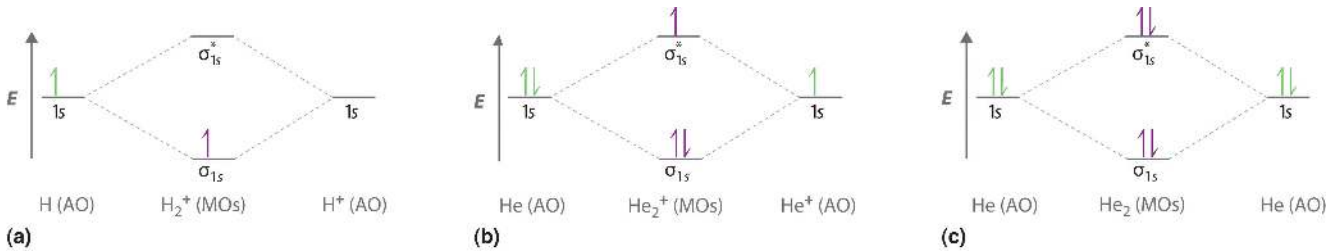


Figure 6.7.1: Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1*s* Atomic Orbitals. (a) The H_2^+ ion, (b) the He_2^+ ion, and (c) the He_2 molecule are shown here. Image used with permission (CC BY-SA-NC; anonymous by request).

Figure 6.7.1*a* shows the energy-level diagram for the H_2^+ ion, which contains two protons and only one electron. The single electron occupies the σ_{1s} bonding molecular orbital, giving a $(\sigma_{1s})^1$ electron configuration. The number of electrons in an orbital is indicated by a superscript. In this case, the bond order is (via Equation 6.7.1)

$$\text{bond order} = \frac{1-0}{2} = 1/2 \tag{6.7.3}$$

Because the bond order is greater than zero, the H_2^+ ion should be more stable than an isolated H atom and a proton. We can therefore use a molecular orbital energy-level diagram and the calculated bond order to predict the relative stability of species such as H_2^+. With a bond order of only 1/2 the bond in H_2^+ should be weaker than in the H_2 molecule, and the H–H bond should be longer. As shown in Table 6.7.1, these predictions agree with the experimental data.

Table 6.7.1: Molecular Orbital Electron Configurations, Bond Orders, Bond Lengths, and Bond Energies for some Simple Homonuclear Diatomic Molecules and Ions

Species	Electron Configuration	Bond Order	Bond Length (pm)	Bond Energy (kJ/mol)
$\mathbf{H_2^+}$	$(\sigma_{1s})^1$	1/2	106	269
$\mathbf{H_2}$	$(\sigma_{1s})^2$	1	74	436
$\mathbf{He_2^+}$	$(\sigma_{1s})^2(\sigma^{\star}_{1s})^1$	1/2	108	251
$\mathbf{He_2}$	$(\sigma_{1s})^2(\sigma^{\star}_{1s})^2$	0	5,500	4.6×10^{-5}

Figure 6.7.1*b* is the molecular orbital energy-level diagram for He_2^{2+}. This ion has a total of three valence electrons. Because the first two electrons completely fill the σ_{1s} molecular orbital, the Pauli principle states that the third electron must be in the $\sigma_{1s}^{\star}$ antibonding orbital, giving a $(\sigma_{1s})^2(\sigma_{1s}^{\star})^1$ electron configuration. This electron configuration gives a bond order (via Equation 6.7.1) of

$$\text{bond order} = \frac{2-1}{2} = 1/2 \tag{6.7.4}$$

As with H_2^+, the He_2^+ ion should be stable, but the He–He bond should be weaker and longer than in H_2. In fact, the He_2^+ ion can be prepared, and its properties are consistent with our predictions (Table 6.7.1).

Example 6.7.1: The He_2^{2+} ion

Use a molecular orbital energy-level diagrams to predict the bond order and stability of the He_2^{2+} ion.

Given: chemical species

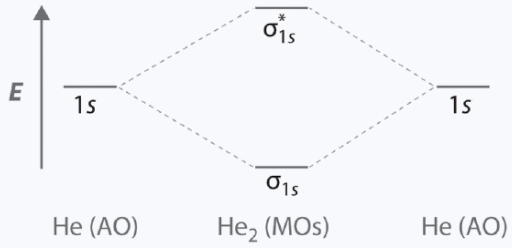
Asked for: molecular orbital energy-level diagram, bond order, and stability

Strategy:

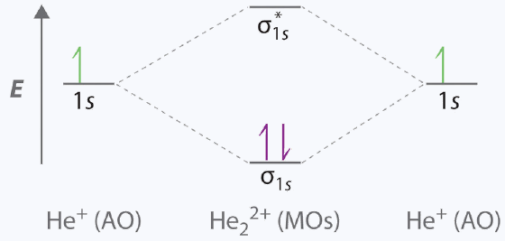
A. Combine the two He valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for the system.
B. Determine the total number of valence electrons in the He_2^{2+} ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.
C. Calculate the bond order and predict whether the species is stable.

Solution:

A Two He 1*s* atomic orbitals combine to give two molecular orbitals: a σ_{1s} bonding orbital at lower energy than the atomic orbitals and a $\sigma_{1s}^{\star}$ antibonding orbital at higher energy. The bonding in any diatomic molecule with two He atoms can be described using the following molecular orbital diagram:



B The He_2^{2+} ion has only two valence electrons (two from each He atom minus two for the +2 charge). We can also view He_2^{2+} as being formed from two He^+ ions, each of which has a single valence electron in the 1*s* atomic orbital. We can now fill the molecular orbital diagram:



The two electrons occupy the lowest-energy molecular orbital, which is the bonding (σ_{1s}) orbital, giving a $(\sigma_{1s})^2$ electron configuration. To avoid violating the Pauli principle, the electron spins must be paired.

C So the bond order is (via Equation 6.7.1)

$$\frac{2-0}{2} = 1$$

He_2^{2+} is therefore predicted to contain a single He–He bond. Thus it should be a stable species.

Exercise 6.7.1: The H_2^{2-} Ion

Use a molecular orbital energy-level diagram to predict the valence-electron configuration and bond order of the H_2^{2-} ion. Is this a stable species?

Answer

H_2^{2-} has a valence electron configuration of $(\sigma_{1s})^2(\sigma_{1s}^\star)^2$ with a bond order of 0. It is therefore predicted to be unstable.

The Helium Dimer

Finally, we examine the He_2 molecule, formed from two He atoms with $1s^2$ electron configurations. Figure $6.7.1c$ is the molecular orbital energy-level diagram for He_2. With a total of four valence electrons, both the σ_{1s} bonding and $\sigma_{1s}^\star$ antibonding orbitals must contain two electrons. This gives a $(\sigma_{1s})^2(\sigma_{1s}^\star)^1$ electron configuration, with a predicted bond order (via Equation 6.7.1) of

$$\text{bond order} = \frac{2-2}{2} = 0 \tag{6.7.5}$$

which indicates that the He_2 molecule has no net covalent bond and is not a stable species.

The ability to track bond order to bond strength is due to the fact that the energy difference between the anti-bonding $\sigma_{1s}^\star$ molecular orbital and the original $1s$ atomic orbital is *larger* than the energy difference between the bonding σ_{1s} molecular orbital and the $1s$ atomic orbitals. This was derived previously where the stabilization energy (ΔE_+) of the σ_{1s} molecular orbital is less than the destabilization energy (ΔE_-) of the anti-bonding $\sigma_{1s}^\star$ molecular orbital:

$$\Delta E_\pm = E_\pm - E_H \tag{6.7.6}$$

$$= \frac{e^2}{4\pi\epsilon_0 R} + \frac{J \pm K}{1 \pm S} \tag{6.7.7}$$

Hence, the anti-bonding $\sigma_{1s}^\star$ molecular orbital is more destabilized relative to the atomic orbitals than the bonding σ_{1s} molecular orbital is stabilized relative to the $1s$ atomic orbitals (E_H.

The fact that the anti-bonding MO energy difference is larger than the bonding σ_{1s} molecular orbital energy difference is the true reason that helium dimer is not predicted to exist with a covalent bond. Of the four valence electrons in helium dimer, two will fill the bonding σ_{1s} molecular orbital, and the other two will fill the anti-bonding $\sigma_{1s}^\star$ molecular orbital. The two electrons in the bonding σ_{1s} molecular orbital will achieve some stabilization relative to the $1s$ atomic orbitals, but the two electrons in the anti-bonding $\sigma_{1s}^\star$ molecular orbital will achieve *greater* de-stabilization relative to their position in the atomic orbitals. The net result is a less stable molecule than if the electrons remained in their respective $1s$ atomic orbitals.

> *The electrons in antibonding orbitals cancel (and exceed) the stabilization resulting from electrons in bonding orbitals. Consequently, any system that has equal numbers of bonding and antibonding electrons will have a bond order of 0, and it is predicted to be unstable and therefore not to exist in nature (at least as a covalent bonding).*

However, Van der Waals Helium Dimers do exist

Based on molecular orbital theory discussed above, the He_2 molecule should not exist since no covalent bond formed between the helium atoms (Equation 6.7.5). However, the molecular orbital description above neglects the van der Waals force that exists between the atoms as demonstrated by the existence of liquid helium (at 4 K). So a "molecule" composed of two helium atoms bound by the van der Waals force may exist by this attractive force instead - and it does.

A helium dimer molecule bound by Van der Waals forces was first proposed by John Clarke Slater in 1928 and observed in 1993 by Gentry and coworkers. Interestingly, He_2 is the largest known molecule of two atoms when in its ground state with an extremely long bond length with a separation of about 5,200 pm. The binding energy is only $4.6 \times 10^{-5}\ kJ/mol$, so the He−He bond is 5,000 times weaker than the covalent bond in the hydrogen molecule (Table 6.7.1).

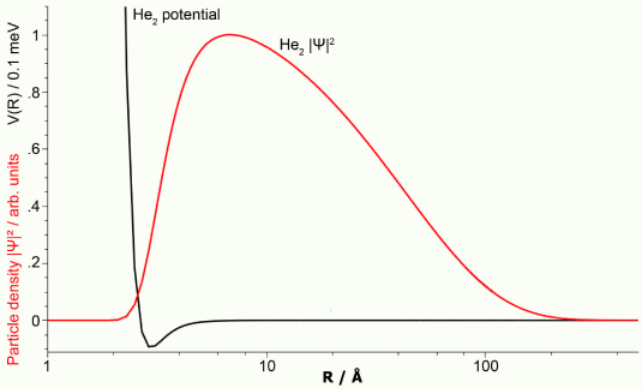


Figure 6.7.2: The weak helium-helium Van der Waals potential decrease leads to the particle probability density distribution leaking more into the classically forbidden region (i..e, tunneling). This effect allows the wavefunction to extend to sizes of fullerenes, the diameter of DNA and even small viruses (He_2 potential and wavefunction taken from Przybytek 2010), while the classical turning point is located at 13.6 Å, the overall wavefunction extends to more than 200 Å. Image used with permission (Inspire; http://inspirehep.net/record/1415151/plots)

Conclusion

The decrease in energy caused by the bonding orbital (constructive interference of the atomic orbitals) is canceled by the increase in energy caused by the antibonding orbital (destructive interference of the atomic orbitals), so it is not energetically favorable for the helium atoms to be in such proximity, so if that situation arises, they'll separate quickly since there's no force keeping them there.

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6.8: Molecular Orbital Theory Predicts that Molecular Oxygen is Paramagnetic

In general chemistry courses, students learn that covalent bonds can come as either single, double or triple bonds, which are identifies by their bond order. Both bond length and bond energy changes as the bond order increases and as the number of electrons shared between two atoms in a molecule increases, the bond order of a bond increases, the strength of the bond increases and the distance between nuclei decreases (Table 6.8.1).

Table 6.8.1: General Correlation between Bond Strength, length and order in Covalent bonds

Bond	Bond Order	Bond Enthalpy (kJ/mol)	Bond Length (Å)
C−C	1	348	1.54
C=C	2	614	1.34
C≡C	3	839	1.20
N−N	1	163	1.47
N=N	2	418	1.24
N≡N	3	941	1.10

The above trend can be observed in the first row diatomics in Figure 6.8.1. The bond order can be determined directly form the molecular orbital electron configurations.

$$\text{bond order} = \frac{\text{number of electrons in bonding MOs} - \text{number of electrons in antbonding MOs}}{2} \tag{6.8.1}$$

For diatomics, the occupations can correlate to bond length, bond energies (Figure 6.8.1) and behavior in applied magnetic fields.

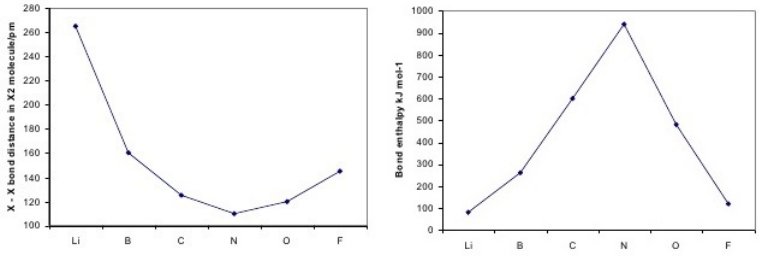


Figure 6.8.1: Plot of bond length (left) and bond energy (right) for first row diatomics.

Example 6.8.1: Molecular Oxygen

Arrange the following four molecular oxygen species in order of increasing bond length: O_2^+, O_2, O_2^-, and O_2^{2-}.

Solution

The bond length in the oxygen species can be explained by the positions of the electrons in molecular orbital theory. To obtain the molecular orbital energy-level diagram for O_2, we need to place 12 valence electrons (6 from each O atom) in the energy-level diagram shown in Figure 6.8.1. We again fill the orbitals according to Hund's rules and the Pauli principle, beginning with the orbital that is lowest in energy. Two electrons each are needed to fill the σ_{2s} and σ_{2s}* orbitals, two more to fill the σ_{2p_z} orbital, and 4 to fill the degenerate $\pi^*_{2p_x}$ and $\pi^*_{2p_y}$ orbitals. According to Hund's first rule, the last 2 electrons must be placed in separate π^* orbitals with their spins parallel, giving a multiplicity of 3 (a triplet state) with two unpaired electrons. This leads to a predicted bond order of

$$\frac{8-4}{2} = 2$$

which corresponds to a double bond, in agreement with experimental data: the O–O bond length is 120.7 pm, and the bond energy is 498.4 kJ/mol at 298 K.

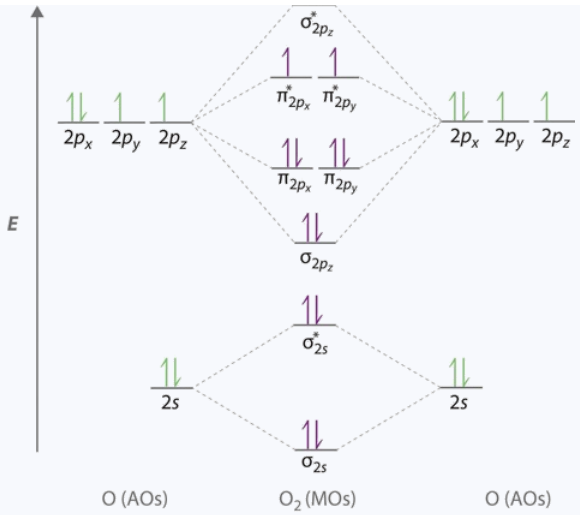


Figure 6.8.1: Molecular Orbital Energy-Level Diagrams for O_2. With 12 valence electrons (6 from each O atom), there are only 2 electrons to place in the $\left(\pi^*_{np_x}, \pi^*_{np_y}\right)$ pair of orbitals. Hund's first rule dictates that one electron occupies each orbital, and their spins are parallel, giving the O_2 molecule two unpaired electrons. This diagram shows 8 electrons in bonding orbitals and 4 in antibonding orbitals, resulting in a predicted bond order of 2. Image used with permission (CC BY-SA-NC; Anonymous by request).

The bond order is determined from the the electron configurations via Equation 6.8.1. The electron configurations for the four species are contrasted below.

- O_2:

$$\sigma^2_{1s}\sigma^{*\,2}_{1s}\sigma^2_{2s}\sigma^{*\,2}_{2s}\sigma^2_{2p}\pi^2_{2p_y}\pi^{*\,2}_{2p_y}\pi^1_{2p_x}\pi^{*\,1}_{2p_y}$$

  From Equation 6.8.1, the bond order for O_2 is 2 (i.e., a double bond).

- O_2^+:

$$\sigma^2_{1s}\sigma^{*\,2}_{1s}\sigma^2_{2s}\sigma^{*\,2}_{2s}\sigma^2_{2p}\pi^2_{2p_y}\pi^{*\,2}_{2p_y}\pi^1_{2p_x}\pi^{*\,0}_{2p_y}$$

  From Equation 6.8.1, the bond order for O_2^+ is 2.5. An alternative and equally valid configuration is

$$\sigma^2_{1s}\sigma^{*\,2}_{1s}\sigma^2_{2s}\sigma^{*\,2}_{2s}\sigma^2_{2p}\pi^2_{2p_y}\pi^{*\,2}_{2p_y}\pi^0_{2p_x}\pi^{*\,1}_{2p_y}$$

- O_2^-:

$$\sigma^2_{1s}\sigma^{*\,2}_{1s}\sigma^2_{2s}\sigma^{*\,2}_{2s}\sigma^2_{2p}\pi^2_{2p_y}\pi^{*\,2}_{2p_y}\pi^2_{2p_x}\pi^{*\,1}_{2p_y}$$

  From Equation 6.8.1, the bond order for O_2^- is 1.5. An alternative and equally valid configuration is

$$\sigma^2_{1s}\sigma^{*\,2}_{1s}\sigma^2_{2s}\sigma^{*\,2}_{2s}\sigma^2_{2p}\pi^2_{2p_y}\pi^{*\,2}_{2p_y}\pi^1_{2p_x}\pi^{*\,2}_{2p_y}$$

- O_2^{2-}:

$$\sigma^2_{1s}\sigma^{*\,2}_{1s}\sigma^2_{2s}\sigma^{*\,2}_{2s}\sigma^2_{2p}\pi^2_{2p_y}\pi^{*\,2}_{2p_y}\pi^2_{2p_x}\pi^{*\,2}_{2p_y}$$

  From Equation 6.8.1, the bond order for O_2^{2-} is 1.

The bond order decreases and the bond length increases in the order. The predicted order of increasing bondlength then is $O_2^+ < O_2 < O_2^- < O_2^{2-}$. This trend is confirmed experimentally with O_2^+ (112.2 pm), O_2 (121 pm), O_2^- (128 pm) and O_2^{2-} (149 pm).

Molecular Oxygen is Paramagnetic

We now turn to a molecular orbital description of the bonding in O_2. It so happens that the molecular orbital description of this molecule provided an explanation for a long-standing puzzle that could not be explained using other bonding models. None of the other bonding models (e.g., Valence Bond theory or Lewis bonding) can predict the presence of two unpaired electrons in O_2.

Chemists had long wondered why, unlike most other substances, liquid O_2 is attracted into a magnetic field. As shown in Figure 6.8.2, it actually remains suspended between the poles of a magnet until the liquid boils away. The only way to explain this behavior was for O_2 to have unpaired electrons, making it paramagnetic. This result was one of the earliest triumphs of molecular orbital theory over the other bonding approaches.



Figure 6.8.2: Liquid O_2 Suspended between the Poles of a Magnet.Because the O_2 molecule has two unpaired electrons, it is paramagnetic. Consequently, it is attracted into a magnetic field, which allows it to remain suspended between the poles of a powerful magnet until it evaporates.

Advanced: Spin Barriers

The magnetic properties of O_2 are not just a laboratory curiosity; they are absolutely crucial to the existence of life. Because Earth's atmosphere contains 20% oxygen, all organic compounds, including those that compose our body tissues, should react rapidly with air to form H_2O, CO_2, and N_2 in an exothermic reaction. Fortunately for us, however, this reaction is very, very slow. The reason for the unexpected stability of organic compounds in an oxygen atmosphere is that virtually all organic compounds, as well as H_2O, CO_2, and N_2, have only paired electrons, whereas oxygen has two unpaired electrons. Thus the reaction of O_2 with organic compounds to give H_2O, CO_2, and N_2 would require that at least one of the electrons on O_2 change its spin during the reaction. This would require a large input of energy, an obstacle that chemists call a *spin barrier*.

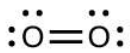
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6.9: Summary of Molecular Orbital Theory

Learning Objectives

- 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:



A Lewis structure is shown. It is made up of two oxygen atoms, each with two lone pairs of electrons, bonded together with a double bond.

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 6.9.1), 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.

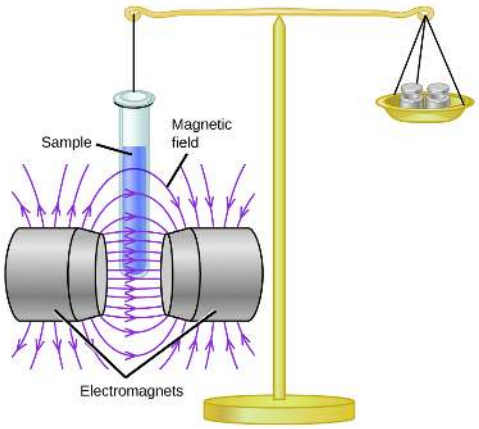


Figure 6.9.1: A Gouy balance compares the mass of a sample in the presence of a magnetic field with the mass with the electromagnet turned off to determine the number of unpaired electrons in a sample.

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.



Video 6.9.1: 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 (levitating frog [www.youtube.com])

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 6.9.1 summarizes the main points of the two complementary bonding theories. Both theories provide different, useful ways of describing molecular structure.

Table \(\PageIndex{1}\): 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	

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 6.9.2). 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.

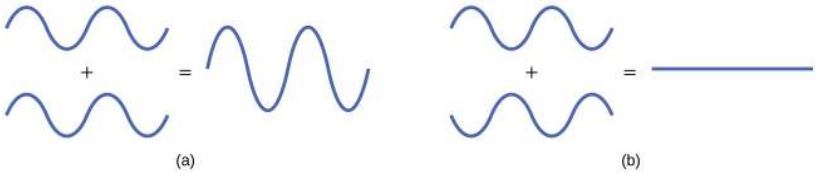


Figure 6.9.2: (a) When in-phase waves combine, constructive interference produces a wave with greater amplitude. (b) When out-of-phase waves combine, destructive interference produces a wave with less (or no) amplitude.

A pair of diagrams are shown and labeled, “a” and “b.” Diagram a shows two identical waves with two crests and two troughs. They are drawn one above the other with a plus sign in between and an equal sign to the right. To the right of the equal sign is a much taller wave with a same number of troughs and crests. Diagram b shows two waves with two crests and two troughs, but they are mirror images of one another rotated over a horizontal axis. They are drawn one above the other with a plus sign in between and an equal sign to the right. To the right of the equal sign is a flat line.

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 6.9.3. 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 σ_s^* 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 σ_s^* 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.

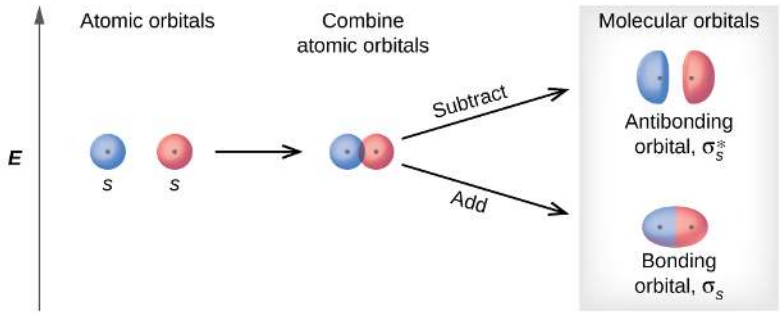
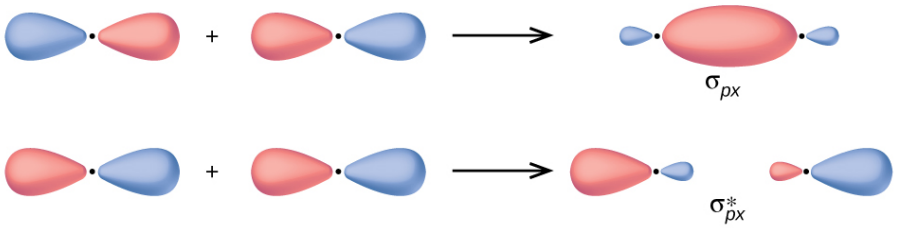


Figure 6.9.3: Sigma (σ) and sigma-star (σ*) molecular orbitals are formed by the combination of two s atomic orbitals. The plus (+) signs indicate the locations of nuclei.

A diagram is shown that depicts a vertical upward-facing arrow that lies to the left of all the other portions of the diagram and is labeled, “E.” To the immediate right of the midpoint of the arrow are two circles each labeled with a positive sign, the letter S, and the phrase, “Atomic orbitals.” These are followed by a right-facing horizontal arrow that points to the same two circles labeled with plus signs, but they are now touching and are labeled, “Combine atomic orbitals.” Two right-facing arrows lead to the last portion of the diagram, one facing upward and one facing downward. The upper arrow is labeled, “Subtract,” and points to two oblong ovals labeled with plus signs, and the phrase, “Antibonding orbitals sigma subscript s superscript asterisk.” The lower arrow is labeled, “Add,” and points to an elongated oval with two plus signs that is labeled, “Bonding orbital sigma subscript s.” The heading over the last section of the diagram are the words, “Molecular orbitals.”

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 6.9.4). 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 σ_{px}^* (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.



Two horizontal rows of diagrams are shown. The upper diagram shows two equally-sized peanut-shaped orbitals with a plus sign in between them connected to a merged orbital diagram by a right facing arrow. The merged diagram has a much larger oval at the center and much smaller ovular orbitals on the edge. It is labeled, “sigma subscript p x.” The lower diagram shows two equally-sized peanut-shaped orbitals with a plus sign in between them connected to a split orbital diagram by a right facing arrow. The split diagram has a much larger oval at the outer ends and much smaller ovular orbitals on the inner edges. It is labeled, “sigma subscript p x superscript asterisk”.

Figure 6.9.4: Combining wave functions of two p atomic orbitals along the internuclear axis creates two molecular orbitals, σp 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 6.9.5. 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.

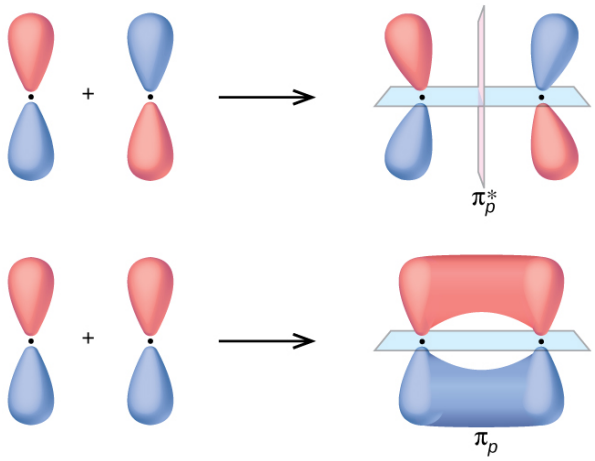


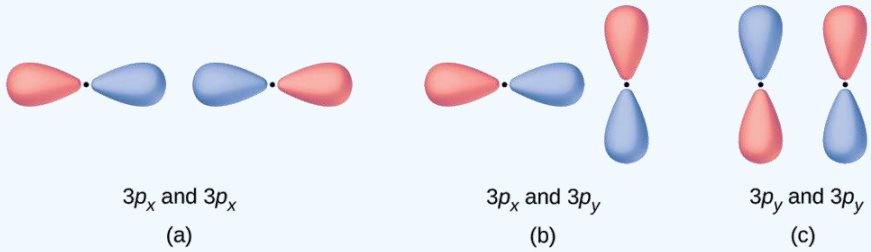
Figure 6.9.5: Side-by-side overlap of each two p orbitals results in the formation of two π molecular orbitals. Combining the out-of-phase orbitals results in an antibonding molecular orbital with two nodes. One contains the internuclear axis, and one is perpendicular to the axis. Combining the in-phase orbitals results in a bonding orbital. There is a node (blue plane) containing the internuclear axis with the two lobes of the orbital located above and below this node.

Two horizontal rows of diagrams are shown. The upper and lower diagrams both begin with two vertical peanut-shaped orbitals with a plus sign in between followed by a right-facing arrow. The upper diagram shows the same vertical peanut orbitals bending slightly away from one another and separated by a dotted line. It is labeled, “pi subscript p superscript asterisk.” The lower diagram shows the horizontal overlap of the two orbitals and is labeled, “pi subscript p.”

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 π_{py}^* 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 6.9.1: 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.



Three diagrams are shown and labeled “a,” “b,” and “c.” Diagram a shows two horizontal peanut-shaped orbitals laying side-by-side. They are labeled, “3 p subscript x and 3 p subscript x.” Diagram b shows one vertical and one horizontal peanut-shaped orbital which are at right angles to one another. They are labeled, “3 p subscript x and 3 p subscript y.” Diagram c shows two vertical peanut-shaped orbitals laying side-by-side and labeled, “3 p subscript y and 3 p subscript y.”

Solution

a. This is an in-phase combination, resulting in a σ_{3p} orbital
b. This 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. This is an out-of-phase combination, resulting in a π^*_{3p} orbital.

Exercise 6.9.1

Label the molecular orbital shown as σ or π, bonding or antibonding and indicate where the node occurs.



Two orbitals are shown lying end-to-end. Each has one enlarged and one small side. The small sides are facing one another

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.



Two orbitals are shown lying end-to-end. Each has one enlarged and one small side. The small sides are facing one another and are separated by a vertical dotted line.

Application: 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 (Figure 6.9.6). 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.

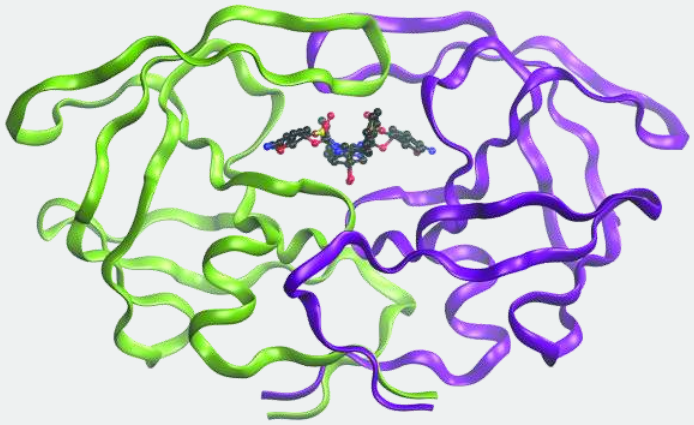


Figure 6.9.6: The molecule shown, HIV-1 protease, is an important target for pharmaceutical research. By designing molecules that bind to this protein, scientists are able to drastically inhibit the progress of the disease.

A diagram of a molecule is shown. The image shows a tangle of ribbon-like, intertwined, pink and green curling lines with a complex ball and stick model in the center.

6.9.1: Molecular Orbital Energy Diagrams

The relative energy levels of atomic and molecular orbitals are typically shown in a molecular orbital diagram (Figure 6.9.7). 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*).

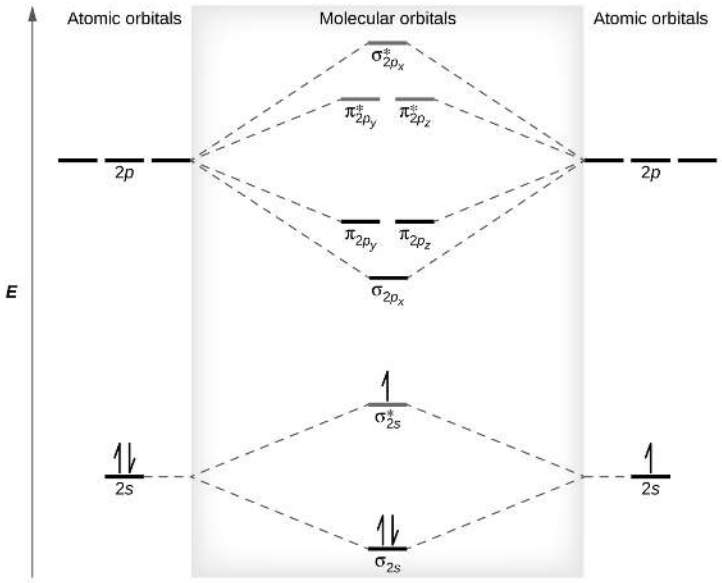


Figure 6.9.7: This is the molecular orbital diagram for the homonuclear diatomic Be_2^+, showing the molecular orbitals of the valence shell only. The molecular orbitals are filled in the same manner as atomic orbitals, using the Aufbau principle and Hund's rule.

A diagram is shown that has an upward-facing vertical arrow running along the left side labeled, "E." At the bottom center of the diagram is a horizontal line labeled, "sigma subscript 2 s," that has two vertical half arrows drawn on it, one facing up and one facing down. This line is connected to the right and left by upward-facing, dotted lines to two more horizontal lines, each labeled, "2 s." The line on the left has two vertical half arrows drawn on it, one facing up and one facing down while the line of the right has one half arrow facing up drawn on it. These two lines are connected by upward-facing dotted lines to another line in the center of the diagram, but further up from the first. It is labeled, "sigma subscript 2 s superscript asterisk." This horizontal line has one upward-facing vertical half-arrow drawn on it. Moving farther up the center of the diagram is a long horizontal line labeled, "sigma subscript 2 p subscript x," which lies below two horizontal lines. These two horizontal lines lie side-by-side, and labeled, "pi subscript 2 p subscript y," and, "pi subscript 2 p subscript z." Both the bottom and top lines are connected to the right and left by upward-facing, dotted lines to three more horizontal lines, each labeled, "2 p." These sets of lines are connected by upward-facing dotted lines to another single line and then pair of double lines in the center of the diagram, but farther up from the lower lines. They are labeled, "sigma subscript 2 p subscript x superscript asterisk," and, ""pi subscript 2 p subscript y superscript asterisk," and, "pi subscript 2 p subscript z superscript asterisk," respectively. The left and right sides of the diagram have headers that read, "Atomic orbitals," while the center is header reads "Molecular orbitals".

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 6.9.7). 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.

6.9.2: 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. 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.

6.9.3: 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 σ_{1s} bonding orbital; the electron configuration is $(\sigma_{1s})^2$. We represent this configuration by a molecular orbital energy diagram (Figure 6.9.8) in which a single upward arrow indicates one electron in an orbital, and two (upward and downward) arrows indicate two electrons of opposite spin.

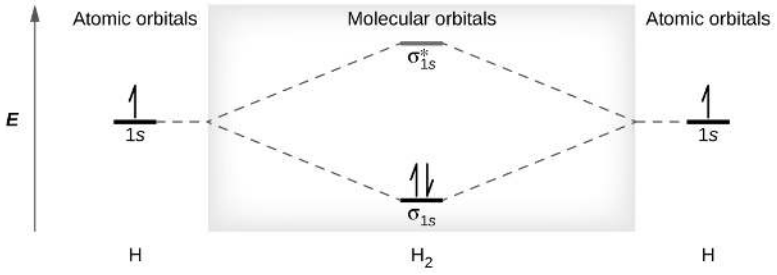


Figure 6.9.8: The molecular orbital energy diagram predicts that H_2 will be a stable molecule with lower energy than the separated atoms.

A diagram is shown that has an upward-facing vertical arrow running along the left side labeled “E.” At the bottom center of the diagram is a horizontal line labeled, “sigma subscript 1 s,” that has two vertical half arrows drawn on it, one facing up and one facing down. This line is connected to the right and left by upward-facing, dotted lines to two more horizontal lines, each labeled, “1 s,” and each with one vertical half-arrow facing up drawn on it. These two lines are connected by upward-facing dotted lines to another line in the center of the diagram, but farther up from the first, and labeled, “sigma subscript 1 s superscript asterisk.” The left and right sides of the diagram have headers that read, ”Atomic orbitals,” while the center header reads, “Molecular orbitals.” The bottom left and right are labeled “H” while the center is labeled “H subscript 2.”

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 $(\sigma_{1s})^2(\sigma^*_{1s})^2$ as in Figure 6.9.9. The net energy change would be zero, so there is no driving force for helium atoms to form the diatomic molecule. In fact, helium exists as discrete atoms rather than as diatomic molecules. The bond order in a hypothetical dihelium molecule would be zero.

$$\text{bond order in } He_2 = \frac{(2-2)}{2} = 0$$

A bond order of zero indicates that no bond is formed between two atoms.

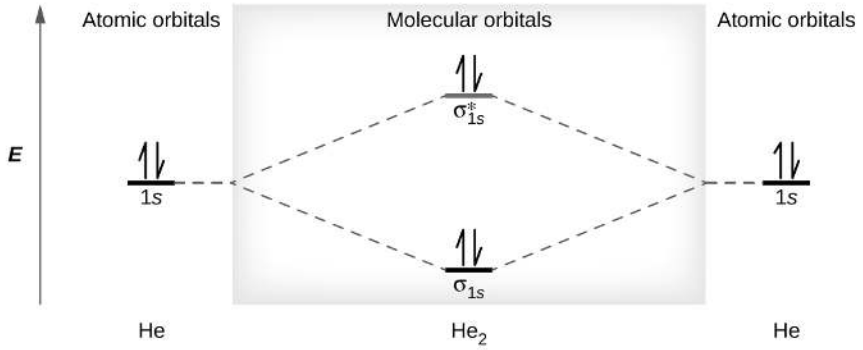


Figure 6.9.9: The molecular orbital energy diagram predicts that He_2 will not be a stable molecule, since it has equal numbers of bonding and antibonding electrons.

A diagram is shown that has an upward-facing vertical arrow running along the left side labeled, “E.” At the bottom center of the diagram is a horizontal line labeled, “sigma subscript 1 s,” that has two vertical half arrows drawn on it, one facing up and one facing down. This line is connected to the right and left by upward-facing, dotted lines to two more horizontal lines, each labeled, “1 s,” and each with one vertical half-arrow facing up and one facing down drawn on it. These two lines are connected by upward-facing dotted lines to another line in the center of the diagram, but farther up from the first, and labeled, “sigma subscript 1 s superscript asterisk.” This line has one upward-facing and one downward-facing vertical arrow drawn on it. The left and right sides of the diagram have headers that read, “Atomic orbitals,” while the center header reads, “Molecular orbitals.” The bottom left and right are labeled, “H e,” while the center is labeled, “H e subscript 2.”

6.9.4: 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 6.9.1).

Table 6.9.1: 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	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2px})^2(\pi_{2py},\ \pi_{2pz})^4(\pi^*_{2py}, \pi^*_{2pz})^2$	2
F_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2px})^2(\pi_{2py},\ \pi_{2pz})^4(\pi^*_{2py},\ \pi^*_{2pz})^4$	1
Ne_2 (unstable)	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2px})^2(\pi_{2py},\ \pi_{2pz})^4(\pi^*_{2py}, \pi^*_{2pz})^4(\sigma^*_{2px})^2$	0

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.

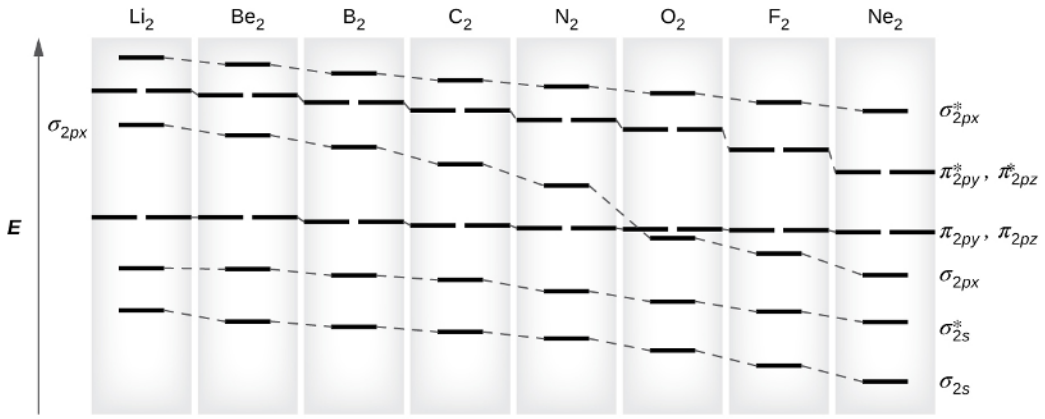


Figure 6.9.10: This shows the MO diagrams for each homonuclear diatomic molecule in the second period. The orbital energies decrease across the period as the effective nuclear charge increases and atomic radius decreases. Between N_2 and O_2, the order of the orbitals changes.

A graph is shown in which the y-axis is labeled, “E,” and appears as a vertical, upward-facing arrow. Across the top, the graph reads, “L i subscript 2,” “B e subscript 2,” “B subscript 2,” “C subscript 2,” “N subscript 2,” “O subscript 2,” “F subscript 2,” and “Ne subscript 2.” Directly below each of these element terms is a single pink line, and all lines are connected to one another by a dashed line, to create an overall line that decreases in height as it moves from left to right across the graph. This line is labeled, “sigma subscript 2 p x superscript asterisk”. Directly below each of these lines is a set of two pink lines, and all lines are connected to one another by a dashed line, to create an overall line that decreases in height as it moves from left to right across the graph. It is consistently lower than the first line. This line is labeled, “pi subscript 2 p y superscript asterisk,” and, “pi subscript 2 p z superscript asterisk.” Directly below each of these double lines is a single pink line, and all lines are connected to one another by a dashed line, to create an overall line that decreases in height as it moves from left to right across the graph. It has a distinctive drop at the label, “O subscript 2.” This line is labeled, “sigma subscript 2 p x.” Directly below each of these lines is a set of two pink lines, and all lines are connected to one another by a dashed line to create an overall line that decreases very slightly in height as it moves from left to right across the graph. It is consistently lower than the third line until it reaches the point labeled, “O subscript 2.” This line is labeled, “pi subscript 2 p y,” and, “pi subscript 2 p z.” Directly below each of these lines is a single blue line, and all lines are connected to one another by a dashed line to create an overall line that decreases in height as it moves from left to right across the graph. This line is labeled, “sigma subscript 2 s superscript asterisk.” Finally, directly below each of these lines is a single blue line, and all lines are connected to one another by a dashed line to create an overall line that decreases in height as it moves from left to right across the graph. This line is labeled. “sigma subscript 2 s.”

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 6.9.10. 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.

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 6.9.11). Similarly, the antibonding orbitals also undergo s-p mixing, with the σ_{s*} becoming more stable and the σ_{p*} becoming less stable.

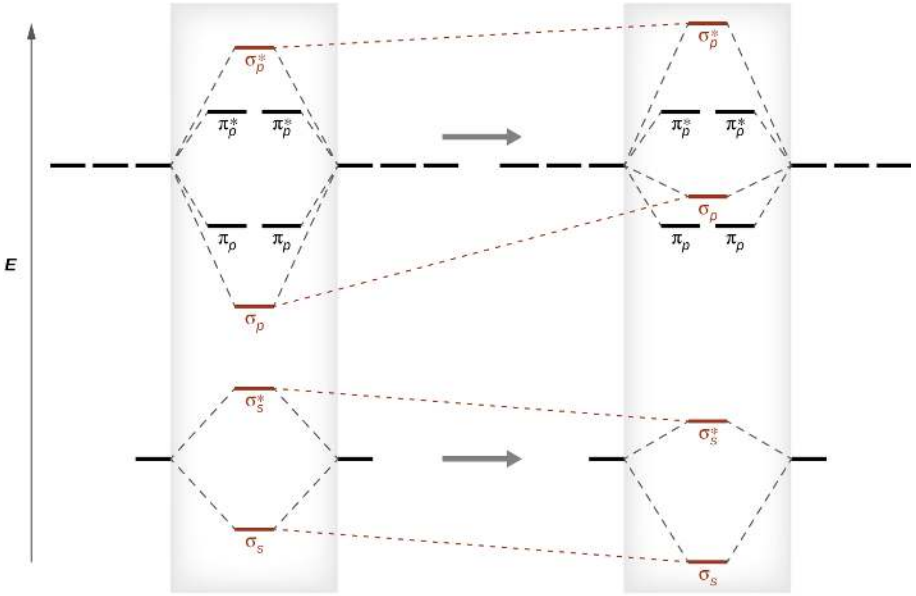


Figure 6.9.11: Without mixing, the MO pattern occurs as expected, with the σ_p orbital lower in energy than the σ_p orbitals. When s-p mixing occurs, the orbitals shift as shown, with the σ_p orbital higher in energy than the π_p orbitals.

A diagram is shown. At the bottom left of the diagram is a horizontal line that is connected to the right and left by upward-facing, dotted lines to two more horizontal lines. Those two lines are connected by upward-facing dotted lines to another line in the center of the diagram but farther up from the first. Each of the bottom two central lines has a vertical downward-facing arrow. Above this structure is a horizontal line that is connected to the right and left by upward-facing, dotted lines to two sets of three horizontal lines and those two lines are connected by upward-facing dotted lines to another line in the center of the diagram, but further up from the first. In between the horizontal lines of this structure are two pairs of horizontal lines that are above the first line but below the second and connected by dotted lines to the side horizontal lines. The bottom and top central lines each have an upward-facing vertical arrow. These two structures are redrawn on the right side of the diagram, but this time, the central lines of the bottom structure are moved downward in relation to the side lines. The upper portion of the structure has its central lines shifted upward in relation to the side lines. This structure also shows the bottom line appearing above the set of two lines.

s-p mixing occurs when the *s* and *p* orbitals 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 exhibit negligible s-p mixing (not sufficient to change the energy ordering), and their MO diagrams follow the normal pattern, as shown in Figure 6.9.7. 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 6.9.11, 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 6.9.1, Be_2 and Ne_2 molecules would have a bond order of 0, and these molecules do not exist.

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 an appreciable concentration in lithium vapor at temperatures near the boiling point of the element. All of the other molecules in Table 6.9.1 with a bond order greater than zero are also known.

The O_2 molecule has enough electrons to half fill the $(\pi^*_{2py}, \pi^*_{2pz})$ 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 6.9.10). 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.

Application: Band Theory in Extended Systems

When two identical atomic orbitals on different atoms combine, two molecular orbitals result (e.g., H_2 in Figure 6.9.8). 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 6.9.12) shows the bands for three important classes of materials: insulators, semiconductors, and conductors.

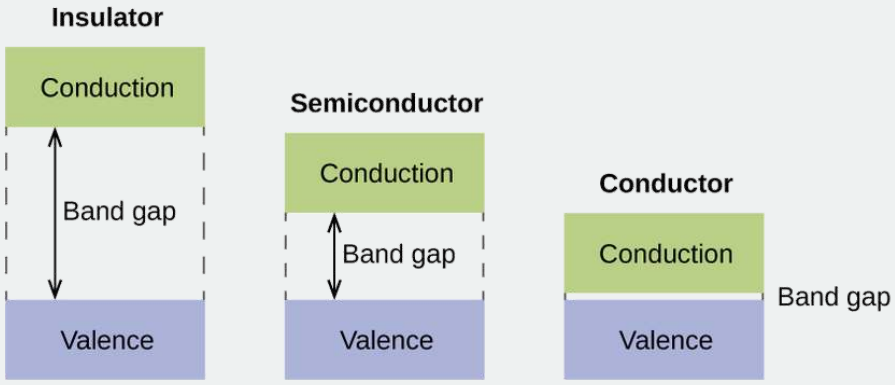


Figure 6.9.12: Molecular orbitals in solids are so closely spaced that they are described as bands. The valence band is lower in energy and the conduction band is higher in energy. The type of solid is determined by the size of the "band gap" between the valence and conduction bands. Only a very small 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.

This figure shows three diagrams. The first is labeled, "Insulator," and it consists of two boxes. The "conduction" box is above and the "valence" box is below. A large gap marked by 4 dashed lines contains a double-headed arrow. One head pointing towards the "conduction box" and the other towards the "valence" box. The arrow is labeled, "Band gap." The second diagram is similar to the first, but the band gap is about half as large. This diagram is labeled, "Semiconductor." The third diagram is similar to the other two, but the band gap is about a fifth that of the "Semiconductor" diagram. This diagram is labeled, "Conductor."

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 6.9.2: 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 6.9.7. Each oxygen atom contributes six electrons, so the diagram appears as shown in Figure 6.9.7.

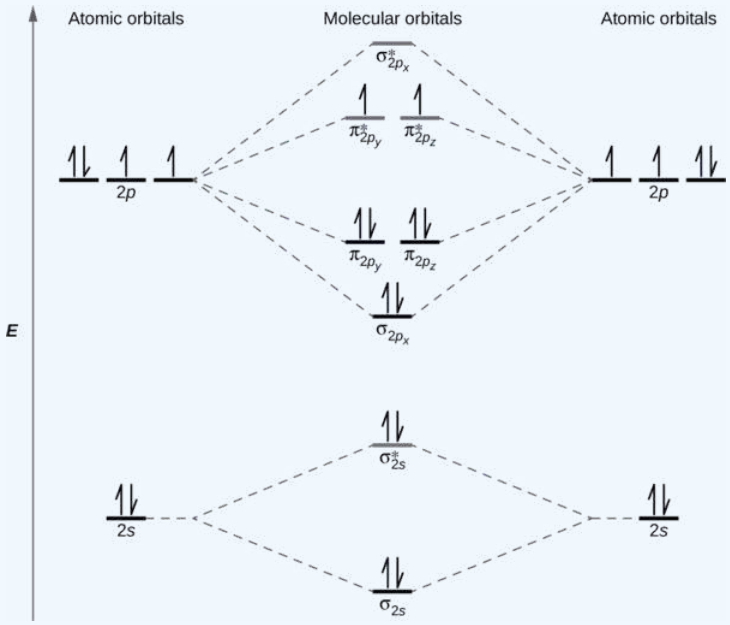


Figure 6.9.13: The molecular orbital energy diagram for O_2 predicts two unpaired electrons.

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 6.9.2

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 6.9.3: 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 6.9.3

How many unpaired electrons would be present on a Be_2^{2-} ion? Would it be paramagnetic or diamagnetic?

Answer

two, paramagnetic

6.9.5: Key Concepts and Summary

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.

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6.10: Valence Bond Theory

Skills to Develop

- To describe the bonding in simple compounds using valence bond theory.

Although the VSEPR model is a simple and useful method for qualitatively predicting the structures of a wide range of compounds, it is *not* infallible. It predicts, for example, that H_2S and PH_3 should have structures similar to those of H_2O and NH_3, respectively. In fact, structural studies have shown that the H–S–H and H–P–H angles are more than 12° smaller than the corresponding bond angles in H_2O and NH_3, even though the electron groups should have more space around the larger atoms. More disturbing, the VSEPR model predicts that the simple group 2 halides (MX_2), which have four valence electrons, should all have linear X–M–X geometries. Instead, many of these species, including SrF_2 and BaF_2, are significantly bent. A more sophisticated treatment of bonding is needed for systems such as these. In this section, we present a quantum mechanical description of bonding, in which bonding electrons are viewed as being localized between the nuclei of the bonded atoms.

As we have talked about using Lewis structures to depict the bonding in covalent compounds, we have been very vague in our language about the actual nature of the chemical bonds themselves. We know that a covalent bond involves the 'sharing' of a pair of electrons between two atoms - but how does this happen, and how does it lead to the formation of a bond holding the two atoms together?

The **valence bond theory** is introduced to describe bonding in covalent molecules. In this model, bonds are considered to form from the overlapping of two atomic orbitals on different atoms, each orbital containing a single electron. In looking at simple inorganic molecules such as H_2 or HF, our present understanding of s and p atomic orbitals will suffice. To explain the bonding in organic molecules, however, we will need to introduce the concept of **hybrid orbitals**.

Valence Bond Theory: A Localized Bonding Approach

The simplest case to consider is the hydrogen molecule, H_2. When we say that the two electrons from each of the hydrogen atoms are shared to form a covalent bond between the two atoms, what we mean in valence bond theory terms is that the two spherical 1*s* orbitals overlap, allowing the two electrons to form a pair within the two overlapping orbitals. In simple terms, we can say that both electrons now spend more time *between* the two nuclei and thus hold the atoms together. As we will see, the situation is not quite so simple as that, because the electron pair must still obey quantum mechanics - that is, the two electrons must now occupy a *shared orbital space*. This will be the essential principle of valence bond theory.

You learned previously that as two hydrogen atoms approach each other from an infinite distance, the energy of the system reaches a minimum. This region of minimum energy in the energy diagram corresponds to the formation of a covalent bond between the two atoms at an H–H distance of 74 pm (Figure 6.10.1). According to quantum mechanics, bonds form between atoms because their atomic orbitals overlap, with each region of overlap accommodating a *maximum of two electrons with opposite spin*, in accordance with the Pauli principle. In this case, a bond forms between the two hydrogen atoms when the singly occupied 1*s* atomic orbital of one hydrogen atom overlaps with the singly occupied 1*s* atomic orbital of a second hydrogen atom. Electron density between the nuclei is increased because of this orbital overlap and results in a *localized electron-pair bond* (Figure 6.10.1).

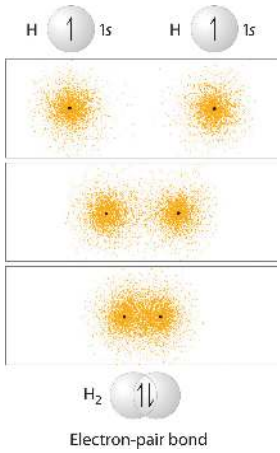


Figure 6.10.1: *Overlap of Two Singly Occupied Hydrogen 1s Atomic Orbitals Produces an H–H Bond in H_2. The formation of H_2 from two hydrogen atoms, each with a single electron in a 1s orbital, occurs as the electrons are shared to form an electron-pair bond, as indicated schematically by the gray spheres and black arrows. The orange electron density distributions show that the formation of an H_2 molecule increases the electron density in the region between the two positively charged nuclei.*

Although Lewis and VSEPR structures also contain localized electron-pair bonds, neither description uses an atomic orbital approach to predict the stability of the bond. Doing so forms the basis for valence bond theory, which is built on two assumptions:

1. The strength of a covalent bond is proportional to the amount of overlap between atomic orbitals; that is, the greater the overlap, the more stable the bond.
2. An atom can use different combinations of atomic orbitals to maximize the overlap of orbitals used by bonded atoms.

Maximum overlap occurs between orbitals with the same spatial orientation and similar energies.

Figure 6.10.2shows an electron-pair bond formed by the overlap of two *ns* atomic orbitals, two *np* atomic orbitals, and an *ns* and an *np* orbital where *n* = 2. Notice that bonding overlap occurs when the interacting atomic orbitals overlap *in phase* (represented by colors in Figure 6.10.2).

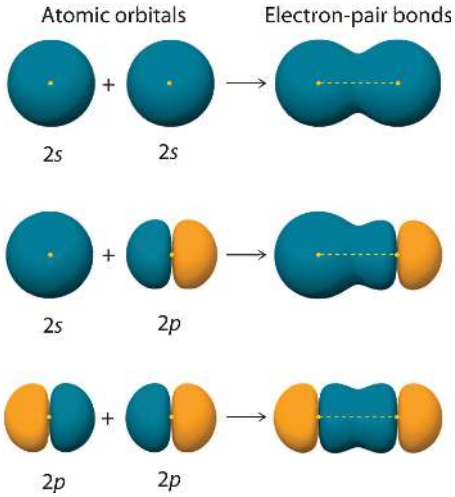


Figure 6.10.2 *: Three Different Ways to Form an Electron-Pair Bond. An electron-pair bond can be formed by the overlap of any of the following combinations of two singly occupied atomic orbitals: two ns atomic orbitals (a), an ns and an np atomic orbital (b), and two np atomic orbitals (c) where n = 2. The positive lobe is indicated in yellow, and the negative lobe is in blue.*

As another example, consider the Cl_2 molecule. The valence electron configuration of each Cl atom is $3s^23p^5$, with one *p* orbital containing only one electron. According to valence bond theory, the two half-filled *p* orbitals will overlap in an end-to-end fashion, as in Figure 6.10.2*c*, to contain a bonding electron pair. Thus, the Cl_2 molecule also contains a single bond comprised of two *p* orbitals.

Sigma and Pi Bonds

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 6.10.3 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.

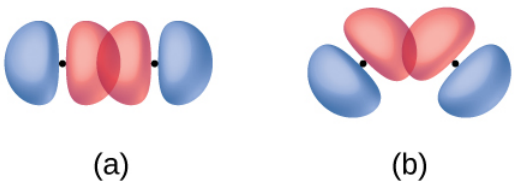


***Figure* 6.10.3**: *(a) The overlap of two p orbitals is greatest when the orbitals are directed end to end. (b) Any other arrangement results in less overlap. The dots indicate the locations of the nuclei.*

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 6.10.4. 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.

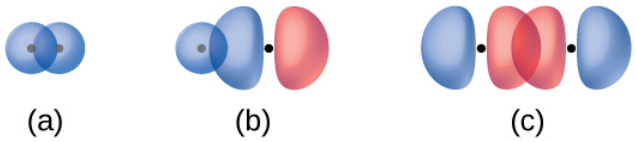


***Figure* 6.10.4**: *Sigma (σ) bonds form from the overlap of the following: (a) two s orbitals, (b) an s orbital and a p orbital, and (c) two p orbitals. The dots indicate the locations of the nuclei.*

This is not the only way that *p* orbitals can interact with each other, however. 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 6.10.5. 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.

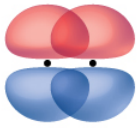
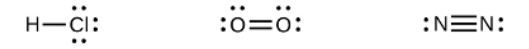


***Figure* 6.10.5**: *Pi (π) bonds form from the side-by-side overlap of two p orbitals. The dots indicate the location of the nuclei.*

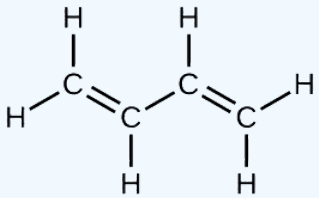
While all single bonds are σ bonds, multiple bonds consist of both σ and π bonds. As the Lewis structures suggest, O_2 contains a double bond, and N_2 contains a triple bond. The double bond consists of one σ bond and one π bond, and the triple bond consists of one σ bond and two π bonds. Between any 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.



As seen in 6.2: Molecules and Bonds, an average carbon-carbon single bond is 347 kJ/mol, while in a carbon-carbon double bond, the π bond increases the bond strength by 267 kJ/mol. Adding an additional π bond causes a further increase of 225 kJ/mol. We can see a similar pattern when we compare other σ and π bonds. Thus, each individual π bond is generally weaker than a corresponding σ bond between the same two atoms. In a σ bond, there is a greater degree of orbital overlap than in a π bond.

Example 6.10.1: 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.



Butadiene

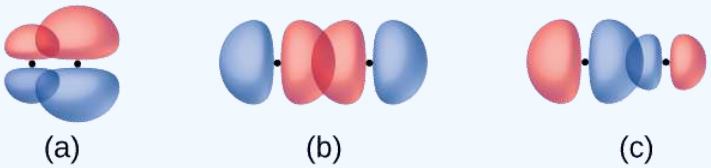
Solution

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.

? Exercise 6.10.1

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.

Polyatomic Molecules

What about molecules containing more than two atoms? Let's examine the bonds in BeH_2, for example. According to the VSEPR model, BeH_2 is a linear compound with four valence electrons and two Be–H bonds. Its bonding can also be described using an atomic orbital approach. Beryllium has a $1s^2 2s^2$ electron configuration, and each H atom has a $1s^1$ electron configuration. Because the Be atom has a filled 2*s* subshell, however, it has no singly occupied orbitals available to overlap with the singly occupied 1*s* orbitals on the H atoms. If a singly occupied 1*s* orbital on hydrogen were to overlap with a filled 2*s* orbital on beryllium, the resulting bonding orbital would contain *three* electrons, but the maximum allowed by quantum mechanics is *two*. How then is beryllium able to bond to two hydrogen atoms? One way would be to add enough energy to excite one of its 2*s* electrons into an empty 2*p* orbital and reverse its spin, in a process called **promotion**:



In this excited state, the Be atom would have two singly occupied atomic orbitals (the 2*s* and one of the 2*p* orbitals), each of which could overlap with a singly occupied 1*s* orbital of an H atom to form an electron-pair bond. Although this would produce BeH_2, the two Be–H bonds would not be equivalent: the 1*s* orbital of one hydrogen atom would overlap with a Be 2*s* orbital, and the 1*s* orbital of the other hydrogen atom would overlap with an orbital of a different energy, a Be 2*p* orbital. Experimental evidence indicates, however, that the two Be–H bonds have identical energies. To resolve this discrepancy and explain how molecules such as BeH_2 form, scientists developed the concept of hybridization, discussed in the next section.

Glossary

overlap
coexistence of orbitals from two different atoms sharing the same region of space, leading to the formation of a covalent bond

node
plane separating different lobes of orbitals, where the probability of finding an electron is zero

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

sigma bond (σ bond)

covalent bond formed by overlap of atomic orbitals along the internuclear axis

valence bond theory

description of bonding that involves atomic orbitals overlapping to form σ or π bonds, within which pairs of electrons are shared

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6.E: Advanced Theories of Covalent Bonding (Exercises)

6.E.0.1: 8.1: Valence Bond Theory

6.E.0.1: Chapter Exercises

1. Explain how σ and π bonds are similar and how they are different.
2. 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 8.2.1 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 H_2 and Cl_2 to solve for the energy of one mole of HCl bonds.

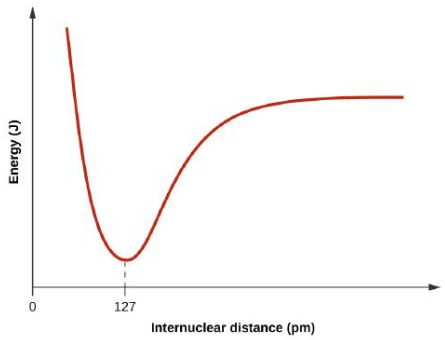
$$H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)} \quad \Delta H^{\circ}_{rxn} = -184.7\ kJ/mol \tag{6.E.1}$$

3. Explain why bonds occur at specific average bond distances instead of the atoms approaching each other infinitely close.
4. 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.
5. 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.
6. How many σ and π bonds are present in the molecule HCN?
7. 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?
8. 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

6.E.0.1: Solutions

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).

2



When H and Cl are separate (the x axis) the energy is at a particular value. As they approach, it decreases to a minimum at 127 pm (the bond distance), and then it increases sharply as you get closer.

a. (a) H–Cl431 kJ/mol 427kJmol×mol6.022×1023bonds×1000 JkJ=7.09×10−19
b. (b) We know Hess's law related to bond energies: ΔH°=ΣΔH∘BDE(broken)−ΣΔH∘BDE(formed) We are given the enthalpy of reaction

$$-184.7kJ/mol = (\Delta H \circ BDE(H-H) + \Delta H \circ BDE(Cl-Cl)) - (2\Delta H \circ BDE(H-Cl)) \tag{6.E.2}$$

$$H-His436kJ/molandCl-Clis243 \tag{6.E.3}$$

$$-184.7kJ/mol = (436+243)-2x = 679-2x \tag{6.E.4}$$

$$2x = 863.7kJ/mol \tag{6.E.5}$$

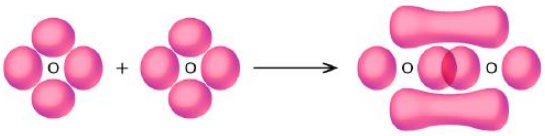
$$x = 432\ kJ/mol \tag{6.E.6}$$

This is very close to the value from part (a).

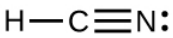
3. The specific average bond distance is the distance with the lowest energy. At distances less than the bond distance, the positive charges on the two nuclei repel each other, and the overall energy increases.

4. The single bond present in each molecule results from overlap of the relevant orbitals: F 2*p* orbitals in F_2, the H 1*s* and F 2*p* orbitals in HF, and the Cl 3*p* orbital and Br 4*p* orbital in ClBr.

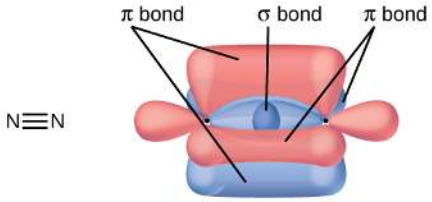
5. Bonding: One σ bond and one π bond. The *s* orbitals are filled and do not overlap. The *p* orbitals overlap along the axis to form a σ bond and side by side to form the π bond.



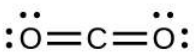
6. H– C ≡ N has two σ (H–C and C–N) and two π (making the CN triple bond).



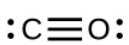
7. No, two of the *p* orbitals (one on each N) will be oriented end-to-end and will form a σ bond.



8. (a) 2 σ 2 π;



(b) 1 σ 2 π;



6.E.0.1: 8.2: Hybrid Atomic Orbitals

6.E.1: Chemistry End of Chapter Exercises

Why is the concept of hybridization required in valence bond theory?

Hybridization is introduced to explain the geometry of bonding orbitals in valance bond theory.

Give the shape that describes each hybrid orbital set:

(a) sp^2

(b) sp^3d

(c) sp

(d) sp^3d^2

Explain why a carbon atom cannot form five bonds using sp^3d hybrid orbitals.

There are no *d* orbitals in the valence shell of carbon.

What is the hybridization of the central atom in each of the following?

(a) BeH_2

(b) SF_6

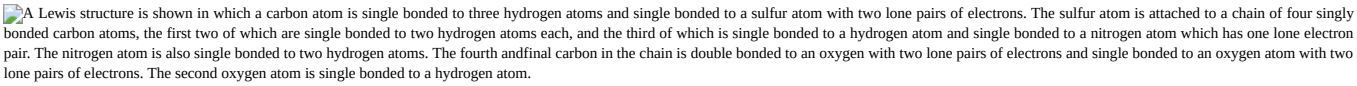
(c) PO_4^{3-}

(d) PCl_5

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.

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

Methionine, $CH_3SCH_2CH_2CH(NH_2)CO_2H$, is an amino acid found in proteins. Draw a Lewis structure of this compound. What is the hybridization type of each carbon, oxygen, the nitrogen, and the sulfur?


A Lewis structure is shown in which a carbon atom is single bonded to three hydrogen atoms and single bonded to a sulfur atom with two lone pairs of electrons. The sulfur atom is attached to a chain of four singly bonded carbon atoms, the first two of which are single bonded to two hydrogen atoms each, and the third of which is single bonded to a hydrogen atom and single bonded to a nitrogen atom which has one lone electron pair. The nitrogen atom is also single bonded to two hydrogen atoms. The fourth andfinal carbon in the chain is double bonded to an oxygen with two lone pairs of electrons and single bonded to an oxygen atom with two lone pairs of electrons. The second oxygen atom is single bonded to a hydrogen atom.

Sulfuric acid is manufactured by a series of reactions represented by the following equations:

$$S_8(s) + 8\,O_2(g) \longrightarrow 8\,SO_2(g)$$

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

$$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(l)$$

Draw a Lewis structure, predict the molecular geometry by VSEPR, and determine the hybridization of sulfur for the following:

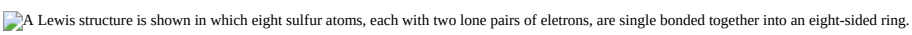
(a) circular S_8 molecule

(b) SO_2 molecule

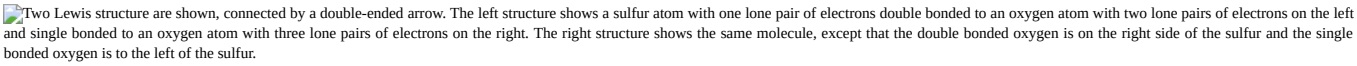
(c) SO_3 molecule

(d) H_2SO_4 molecule (the hydrogen atoms are bonded to oxygen atoms)

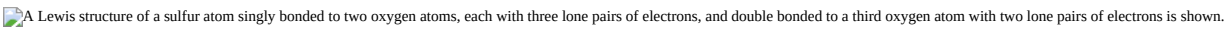
(a) Each S has a bent (109°) geometry, sp^3


A Lewis structure is shown in which eight sulfur atoms, each with two lone pairs of eletrons, are single bonded together into an eight-sided ring.

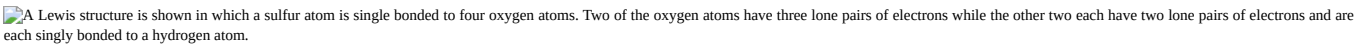
(b) Bent (120°), sp^2


Two Lewis structure are shown, connected by a double-ended arrow. The left structure shows a sulfur atom with one lone pair of electrons double bonded to an oxygen atom with two lone pairs of electrons on the left and single bonded to an oxygen atom with three lone pairs of electrons on the right. The right structure shows the same molecule, except that the double bonded oxygen is on the right side of the sulfur and the single bonded oxygen is to the left of the sulfur.

(c) Trigonal planar, sp^2


A Lewis structure of a sulfur atom singly bonded to two oxygen atoms, each with three lone pairs of electrons, and double bonded to a third oxygen atom with two lone pairs of electrons is shown.

(d) Tetrahedral, sp^3


A Lewis structure is shown in which a sulfur atom is single bonded to four oxygen atoms. Two of the oxygen atoms have three lone pairs of electrons while the other two each have two lone pairs of electrons and are each singly bonded to a hydrogen atom.

Two important industrial chemicals, ethene, C_2H_4, and propene, C_3H_6, are produced by the steam (or thermal) cracking process:

$$2\,C_3H_8(g) \longrightarrow C_2H_4(g) + C_3H_6(g) + CH_4(g) + H_2(g)$$

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.

For many years after they were discovered, it was believed that the noble gases could not form compounds. Now we know that belief to be incorrect. A mixture of xenon and fluorine gases, confined in a quartz bulb and placed on a windowsill, is found to slowly produce a white solid. Analysis of the compound indicates that it contains 77.55% Xe and 22.45% F by mass.

(a) What is the formula of the compound?

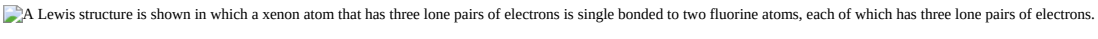
(b) Write a Lewis structure for the compound.

(c) Predict the shape of the molecules of the compound.

(d) What hybridization is consistent with the shape you predicted?

(a) XeF_2

(b)


A Lewis structure is shown in which a xenon atom that has three lone pairs of electrons is single bonded to two fluorine atoms, each of which has three lone pairs of electrons.

(c) linear (d) sp^3d

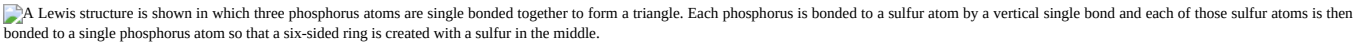
Consider nitrous acid, HNO_2 (HONO).

(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?

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 Lewis structure is shown in which three phosphorus atoms are single bonded together to form a triangle. Each phosphorus is bonded to a sulfur atom by a vertical single bond and each of those sulfur atoms is then bonded to a single phosphorus atom so that a six-sided ring is created with a sulfur in the middle.

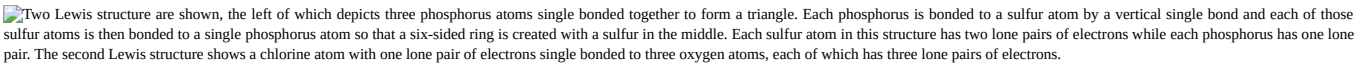
(a) Write Lewis structures for P_4S_3 and the ClO_3^- ion.

(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.

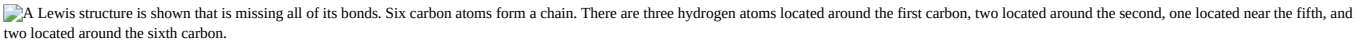
(d) Determine the oxidation states and formal charge of the atoms in P_4S_3 and the ClO_3^- ion.

(a)

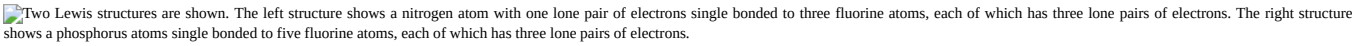

Two Lewis structure are shown, the left of which depicts three phosphorus atoms single bonded together to form a triangle. Each phosphorus is bonded to a sulfur atom by a vertical single bond and each of those sulfur atoms is then bonded to a single phosphorus atom so that a six-sided ring is created with a sulfur in the middle. Each sulfur atom in this structure has two lone pairs of electrons while each phosphorus has one lone pair. The second Lewis structure shows a chlorine atom with one lone pair of electrons single bonded to three oxygen atoms, each of which has three lone pairs of electrons.

(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 $-1\frac{1}{3}$, Cl +5, O –2. Formal charges: P 0; S 0; Cl +2: O –1

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.)


A Lewis structure is shown that is missing all of its bonds. Six carbon atoms form a chain. There are three hydrogen atoms located around the first carbon, two located around the second, one located near the fifth, and two located around the sixth carbon.

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.


Two Lewis structures are shown. The left structure shows a nitrogen atom with one lone pair of electrons single bonded to three fluorine atoms, each of which has three lone pairs of electrons. The right structure shows a phosphorus atoms single bonded to five fluorine atoms, each of which has three lone pairs of electrons.

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.

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?

6.E.1.1: 8.3: Multiple Bonds

6.E.1.1: Chemistry End of Chapter Exercises

The bond energy of a C–C single bond averages 347 kJ mol^{-1}; that of a C≡C triple bond averages 839 kJ mol^{-1}. Explain why the triple bond is not three times as strong as a single bond.

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.

For the carbonate ion, CO_3^{2-}, draw all of the resonance structures. Identify which orbitals overlap to create each bond.

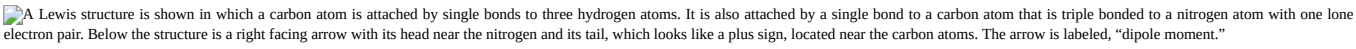
A useful solvent that will dissolve salts as well as organic compounds is the compound acetonitrile, H_3CCN. It is present in paint strippers.

(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.

(a)


A Lewis structure is shown in which a carbon atom is attached by single bonds to three hydrogen atoms. It is also attached by a single bond to a carbon atom that is triple bonded to a nitrogen atom with one lone electron pair. Below the structure is a right facing arrow with its head near the nitrogen and its tail, which looks like a plus sign, located near the carbon atoms. The arrow is labeled, “dipole moment.”

(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.

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?

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)

(a) sp^2; (b) *sp*; (c) sp^2; (d) sp^3; (e) sp^3; (f) sp^3d; (g) sp^3

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

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

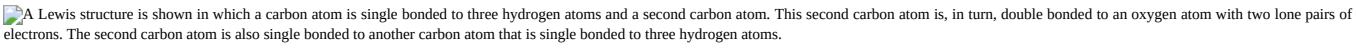
(c) nitrogen dioxide (NO_2) central N hybridization

(d) phosphate ion (PO_4^{3-}) central P hybridization

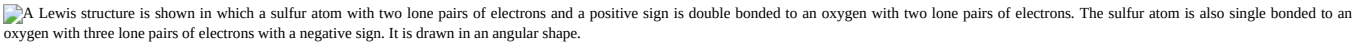
(a) sp^2, delocalized; (b) *sp*, localized; (c) sp^2, delocalized; (d) sp^3, delocalized

For each of the following structures, determine the hybridization requested and whether the electrons will be delocalized:

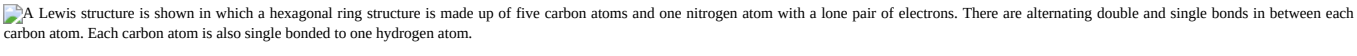
(a) Hybridization of each carbon


A Lewis structure is shown in which a carbon atom is single bonded to three hydrogen atoms and a second carbon atom. This second carbon atom is, in turn, double bonded to an oxygen atom with two lone pairs of electrons. The second carbon atom is also single bonded to another carbon atom that is single bonded to three hydrogen atoms.

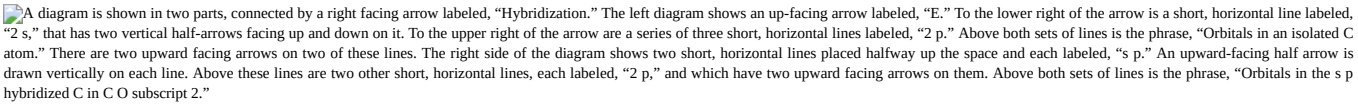
(b) Hybridization of sulfur


A Lewis structure is shown in which a sulfur atom with two lone pairs of electrons and a positive sign is double bonded to an oxygen with two lone pairs of electrons. The sulfur atom is also single bonded to an oxygen with three lone pairs of electrons with a negative sign. It is drawn in an angular shape.

(c) All atoms


A Lewis structure is shown in which a hexagonal ring structure is made up of five carbon atoms and one nitrogen atom with a lone pair of electrons. There are alternating double and single bonds in between each carbon atom. Each carbon atom is also single bonded to one hydrogen atom.

Draw the orbital diagram for carbon in CO_2 showing how many carbon atom electrons are in each orbital.



Each of the four electrons is in a separate orbital and overlaps with an electron on an oxygen atom.

6.E.1.1: 8.4: Molecular Orbital Theory

6.E.2: Chemistry End of Chapter Exercises

Sketch the distribution of electron density in the bonding and antibonding molecular orbitals formed from two *s* orbitals and from two *p* orbitals.

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

(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.

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?

Can a molecule with an odd number of electrons ever be diamagnetic? Explain why or why not.

An odd number of electrons can never be paired, regardless of the arrangement of the molecular orbitals. It will always be paramagnetic.

Can a molecule with an even number of electrons ever be paramagnetic? Explain why or why not.

Why are bonding molecular orbitals lower in energy than the parent atomic orbitals?

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.

Calculate the bond order for an ion with this configuration:

$$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2px})^2(\pi_{2py},\ \pi_{2pz})^4(\pi^*_{2py},\ \pi^*_{2pz})^3$$

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.

The pairing of the two bonding electrons lowers the energy of the system relative to the energy of the nonbonded electrons.

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+}

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^-

(a) H_2 bond order = 1, H_2^+ bond order = 0.5, H_2^- bond order = 0.5, strongest bond is H_2; (b) O_2 bond order = 2, O_2^{2+} bond order = 3; O_2^{2-} bond order = 1, strongest bond is O_2^{2+}; (c) Li_2 bond order = 1, Be_2^+ bond order = 0.5, Be_2 bond order = 0, strongest bond is Li_2;(d) F_2 bond order = 1, F_2^+ bond order = 1.5, F_2^- bond order = 0.5, strongest bond is F_2^+; (e) N_2 bond order = 3, N_2^+ bond order = 2.5, N_2^- bond order = 2.5, strongest bond is N_2

For the first ionization energy for an N_2 molecule, what molecular orbital is the electron removed from?

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

(a) H_2; (b) N_2; (c) O; (d) C_2; (e) B_2

Which of the period 2 homonuclear diatomic molecules are predicted to be paramagnetic?

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?

Yes, fluorine is a smaller atom than Li, so atoms in the 2*s* orbital are closer to the nucleus and more stable.

True or false: Boron contains $2s^2 2p^1$ valence electrons, so only one *p* orbital is needed to form molecular orbitals.

What charge would be needed on F_2 to generate an ion with a bond order of 2?

2+

Predict whether the MO diagram for S_2 would show s-p mixing or not.

Explain why N_2^{2+} is diamagnetic, while O_2^{4+}, which has the same number of valence electrons, is paramagnetic.

N_2 has s-p mixing, so the π orbitals are the last filled in N_2^{2+}. O_2 does not have s-p mixing, so the σ_p orbital fills before the π orbitals.

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^-

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CHAPTER OVERVIEW

7: Models for Polyatomic Molecules

7.1: Orbital Hybridization

7.2: Hybrid Atomic Orbitals

7.3: Multiple Bonding and Molecular Orbitals

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7.1: Orbital Hybridization

The localized **valence bond theory** uses a process called **hybridization**, in which atomic orbitals that are similar in energy but not equivalent are combined mathematically to produce sets of equivalent orbitals that are properly oriented to form bonds. These new combinations are called hybrid atomic orbitals because they are produced by combining (*hybridizing*) two or more atomic orbitals from the same atom.

Hybridization of *s* and *p* Orbitals

In BeH_2, we can generate two equivalent orbitals by combining the 2*s* orbital of beryllium and any one of the three degenerate 2*p* orbitals. By taking the sum and the difference of Be 2*s* and $2p_z$ atomic orbitals, for example, we produce two new orbitals with major and minor lobes oriented along the *z*-axes, as shown in Figure 7.1.1.

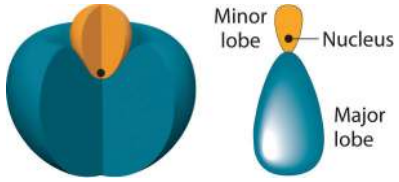


Figure* 7.1.1*: *The position of the atomic nucleus with respect to an sp hybrid orbital. The nucleus is actually located slightly inside the minor lobe, not at the node separating the major and minor lobes.*

Because the difference A − B can also be written as A + (−B), in Figure 7.1.2 and subsequent figures we have reversed the phase(s) of the orbital being subtracted, which is the same as multiplying it by −1 and adding. This gives us Equation 7.1.2, where the value $\frac{1}{\sqrt{2}}$ is needed mathematically to indicate that the 2*s* and 2*p* orbitals contribute equally to each hybrid orbital.

$$sp = \frac{1}{\sqrt{2}}(2s + 2p_z) \tag{7.1.1}$$

and

$$sp = \frac{1}{\sqrt{2}}(2s - 2p_z) \tag{7.1.2}$$

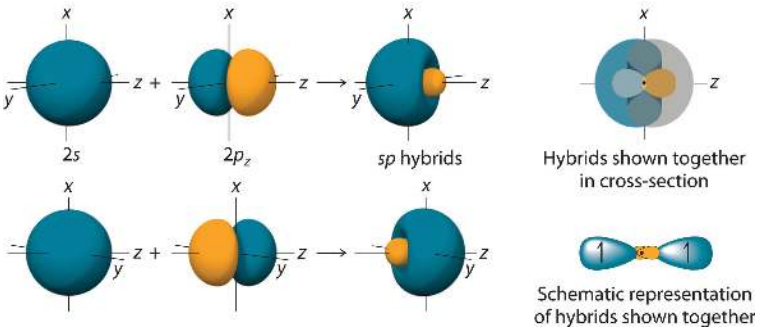
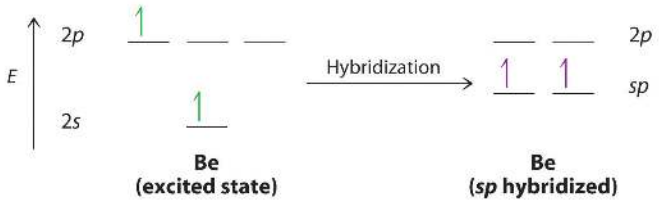


Figure* 7.1.2*: *The Formation of sp Hybrid Orbitals. Taking the sum and difference of an ns and an np atomic orbital where n = 2 gives two equivalent sp hybrid orbitals oriented at 180° to each other.*

The nucleus resides just inside the minor lobe of each orbital. In this case, the new orbitals are called *sp hybrids* because they are formed from one *s* and one *p* orbital. The two new orbitals are equivalent in energy, and their energy is between the energy values associated with pure *s* and *p* orbitals, as illustrated in this diagram:



Each singly occupied *sp* hybrid orbital can now form an electron-pair bond with the singly occupied 1*s* atomic orbital of one of the H atoms. As shown in Figure 7.1.3, each *sp* orbital on Be has the correct orientation for the major lobes to overlap with the 1*s* atomic orbital of an H atom. The formation of two energetically equivalent Be–H bonds produces a linear BeH_2 molecule. Thus valence bond theory does what neither the Lewis electron structure nor the VSEPR model is able to do; it explains why the bonds in BeH_2 are equivalent in energy and why BeH_2 has a linear geometry.

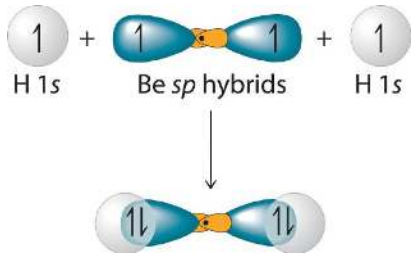


***Figure* 7.1.3**: *Explanation of the Bonding in BeH_2 Using sp Hybrid Orbitals. Each singly occupied sp hybrid orbital on beryllium can form an electron-pair bond with the singly occupied 1s orbital of a hydrogen atom. Because the two sp hybrid orbitals are oriented at a 180° angle, the BeH_2 molecule is linear.*

Because both promotion and hybridization require an input of energy, the formation of a set of singly occupied hybrid atomic orbitals is energetically uphill. The overall process of forming a compound with hybrid orbitals will be energetically favorable *only* if the amount of energy released by the formation of covalent bonds is greater than the amount of energy used to form the hybrid orbitals (Figure 7.1.4). As we will see, some compounds are highly unstable or do not exist because the amount of energy required to form hybrid orbitals is greater than the amount of energy that would be released by the formation of additional bonds.

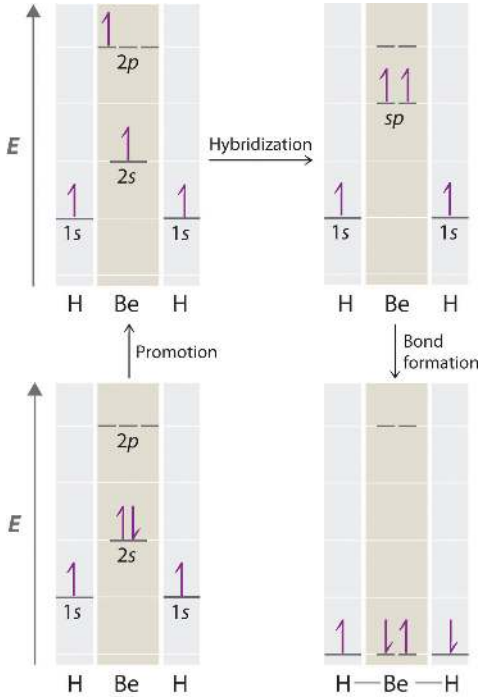
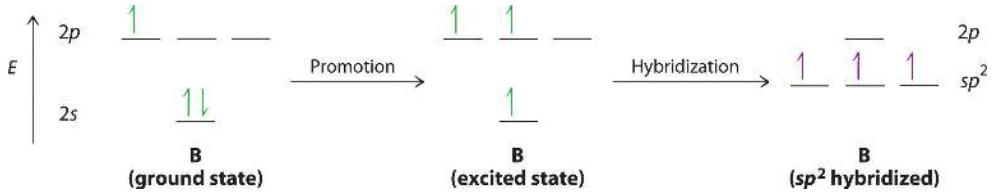


***Figure* 7.1.4**: *A Hypothetical Stepwise Process for the Formation of BeH_2 from a Gaseous Be Atom and Two Gaseous H Atoms. The promotion of an electron from the 2s orbital of beryllium to one of the 2p orbitals is energetically uphill. The overall process of forming a BeH_2 molecule from a Be atom and two H atoms will therefore be energetically favorable only if the amount of energy released by the formation of the two Be–H bonds is greater than the amount of energy required for promotion and hybridization.*

The concept of hybridization also explains why boron, with a $2s^22p^1$ valence electron configuration, forms three bonds with fluorine to produce BF_3, as predicted by the Lewis and VSEPR approaches. With only a single unpaired electron in its ground state, boron should form only a single covalent bond. By the promotion of one of its 2*s* electrons to an unoccupied 2*p* orbital, however, followed by the hybridization of the three singly occupied orbitals (the 2*s* and two 2*p* orbitals), boron acquires a set of three equivalent hybrid orbitals with one electron each, as shown here:



The hybrid orbitals are degenerate and are oriented at 120° angles to each other (Figure 7.1.5). Because the hybrid atomic orbitals are formed from one *s* and two *p* orbitals, boron is said to be *sp*^{2} *hybridized* (pronounced "s-p-two" or "s-p-squared"). The singly occupied *sp*^{2} hybrid atomic orbitals can overlap with the singly occupied orbitals on each of the three F atoms to form a trigonal planar structure with three energetically equivalent B–F bonds.

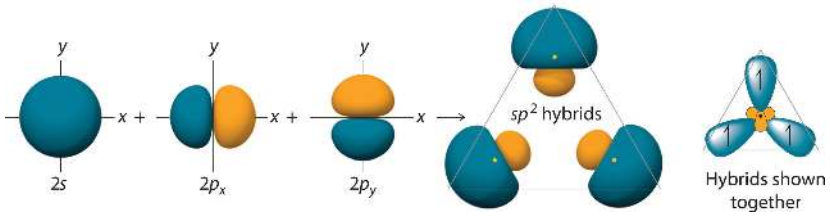
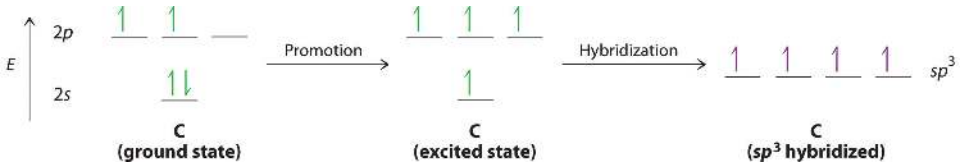


Figure 7.1.5: *Formation of sp*^{2} *Hybrid Orbitals. Combining one ns and two np atomic orbitals gives three equivalent sp*^{2} *hybrid orbitals in a trigonal planar arrangement; that is, oriented at 120° to one another.*

Looking at the 2*s*^{2}2*p*^{2} valence electron configuration of carbon, we might expect carbon to use its two unpaired 2*p* electrons to form compounds with only two covalent bonds. We know, however, that carbon typically forms compounds with four covalent bonds. We can explain this apparent discrepancy by the hybridization of the 2*s* orbital and the three 2*p* orbitals on carbon to give a set of four degenerate *sp*^{3} ("s-p-three" or "s-p-cubed") hybrid orbitals, each with a single electron:



The large lobes of the hybridized orbitals are oriented toward the vertices of a tetrahedron, with 109.5° angles between them (Figure 7.1.6). Like all the hybridized orbitals discussed earlier, the *sp*^{3} hybrid atomic orbitals are predicted to be equal in energy. Thus, methane (CH_4) is a tetrahedral molecule with four equivalent C-H bonds.

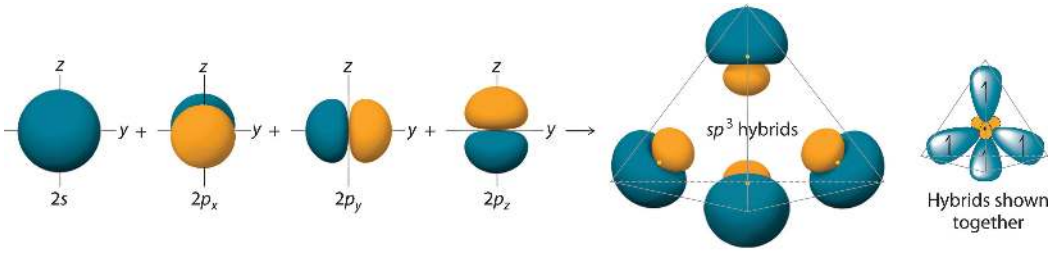


Figure 7.1.6: *Formation of sp*^{3} *Hybrid Orbitals. Combining one ns and three np atomic orbitals results in four sp*^{3} *hybrid orbitals oriented at 109.5° to one another in a tetrahedral arrangement.*

In addition to explaining why some elements form more bonds than would be expected based on their valence electron configurations, and why the bonds formed are equal in energy, valence bond theory explains why these compounds are so stable: the amount of energy released increases with the number of bonds formed. In the case of carbon, for example, much more energy is released in the formation of four bonds than two, so compounds of carbon with four bonds tend to be more stable than those with only two. Carbon does form compounds with only two covalent bonds (such as CH_2 or CF_2), but these species are highly reactive, unstable intermediates that only form in certain chemical reactions.

> *Valence bond theory explains the number of bonds formed in a compound and the relative bond strengths.*

The bonding in molecules such as NH_3 or H_2O, which have lone pairs on the central atom, can also be described in terms of hybrid atomic orbitals. In NH_3, for example, N, with a $2s^2 2p^3$ valence electron configuration, can hybridize its 2*s* and 2*p* orbitals to produce four sp^3 hybrid orbitals. Placing five valence electrons in the four hybrid orbitals, we obtain three that are singly occupied and one with a pair of electrons:



The three singly occupied sp^3 lobes can form bonds with three H atoms, while the fourth orbital accommodates the lone pair of electrons. Similarly, H_2O has an sp^3 hybridized oxygen atom that uses two singly occupied sp^3 lobes to bond to two H atoms, and two to accommodate the two lone pairs predicted by the VSEPR model. Such descriptions explain the approximately tetrahedral distribution of electron pairs on the central atom in NH_3 and H_2O. Unfortunately, however, recent experimental evidence indicates that in NH_3 and H_2O, the hybridized orbitals are *not* entirely equivalent in energy, making this bonding model an active area of research.

Example 7.1.1

Use the VSEPR model to predict the number of electron pairs and molecular geometry in each compound and then describe the hybridization and bonding of all atoms except hydrogen.

a. H_2S
b. $CHCl_3$

Given: two chemical compounds

Asked for: number of electron pairs and molecular geometry, hybridization, and bonding

Strategy:

A. Using the VSEPR approach to determine the number of electron pairs and the molecular geometry of the molecule.
B. From the valence electron configuration of the central atom, predict the number and type of hybrid orbitals that can be produced. Fill these hybrid orbitals with the total number of valence electrons around the central atom and describe the hybridization.

Solution:

1. **A** H_2S has four electron pairs around the sulfur atom with two bonded atoms, so the VSEPR model predicts a molecular geometry that is bent, or V shaped. **B** Sulfur has a $3s^2 3p^4$ valence electron configuration with six electrons, but by hybridizing its 3*s* and 3*p* orbitals, it can produce four sp^3 hybrids. If the six valence electrons are placed in these orbitals, two have electron pairs and two are singly occupied. The two sp^3 hybrid orbitals that are singly occupied are used to form S–H bonds, whereas the other two have lone pairs of electrons. Together, the four sp^3 hybrid orbitals produce an approximately tetrahedral arrangement of electron pairs, which agrees with the molecular geometry predicted by the VSEPR model.
2. **A** The $CHCl_3$ molecule has four valence electrons around the central atom. In the VSEPR model, the carbon atom has four electron pairs, and the molecular geometry is tetrahedral. **B** Carbon has a $2s^2 2p^2$ valence electron configuration. By hybridizing its 2*s* and 2*p* orbitals, it can form four sp^3 hybridized orbitals that are equal in energy. Eight electrons around the central atom (four from C, one from H, and one from each of the three Cl atoms) fill three sp^3 hybrid orbitals to form C–Cl bonds, and one forms a C–H bond. Similarly, the Cl atoms, with seven electrons each in their 3*s* and 3*p* valence subshells, can be viewed as sp^3 hybridized. Each Cl atom uses a singly occupied sp^3 hybrid orbital to form a C–Cl bond and three hybrid orbitals to accommodate lone pairs.

Exercise 7.1.1

Use the VSEPR model to predict the number of electron pairs and molecular geometry in each compound and then describe the hybridization and bonding of all atoms except hydrogen.

a. the BF_4^- ion
b. hydrazine ($H_2N–NH_2$)

Answer a

B is sp^3 hybridized; F is also sp^3 hybridized so it can accommodate one B–F bond and three lone pairs. The molecular geometry is tetrahedral.

Answer b

Each N atom is sp^3 hybridized and uses one sp^3 hybrid orbital to form the N–N bond, two to form N–H bonds, and one to accommodate a lone pair. The molecular geometry about each N is trigonal pyramidal.

In the hybridization model, the number of hybrid orbitals used by the central atom is the same as the number of electron groups around the central atom. Thus,

- 2 electron groups (linear) = sp hybridization
- 3 electron groups (trigonal planar) = sp^2 hybridization
- 4 electron groups (tetrahedral) = sp^3 hybridization

What about hypervalent molecules, with more than 4 electron groups around the central atom? In the past, the hybridization model has been extended to hypervalent molecules by invoking the participation of *d* orbitals, with designations such as sp^3d for trigonal bipyramidal and sp^3d^2 for octahedral molecules. However, modern chemical calculations have largely discredited this description by showing that *d* orbitals do not participate significantly in the bonding of hypervalent molecules. Like all models of chemical bonding, the hybridization model is only useful within its proper limits.

> *The hybridization model is most useful for describing molecules with only linear, trigonal planar, and tetrahedral centers, such as most organic and biological molecules.*

Summary

Hybridization increases the overlap of bonding orbitals and explains the molecular geometries of many species whose geometry cannot be explained using a VSEPR approach. The *localized bonding* model (called **valence bond theory**) assumes that covalent bonds are formed when atomic orbitals overlap and that the strength of a covalent bond is proportional to the amount of overlap. It also assumes that atoms use combinations of atomic orbitals (*hybrids*) to maximize the overlap with adjacent atoms. The formation of **hybrid atomic orbitals** can be viewed as occurring via **promotion** of an electron from a filled ns^2 subshell to an empty *np* valence orbital, followed by **hybridization**, the combination of the orbitals to give a new set of (usually) equivalent orbitals that are oriented properly to form bonds. The combination of an *ns* and an *np* orbital gives rise to two equivalent **sp hybrids** oriented at 180°, whereas the combination of an *ns* and two or three *np* orbitals produces three equivalent $\boldsymbol{sp^2}$ **hybrids** or four equivalent $\boldsymbol{sp^3}$ **hybrids**, respectively.

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7.2: Hybrid Atomic Orbitals

Learning Objectives

- 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 7.2.1, 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.

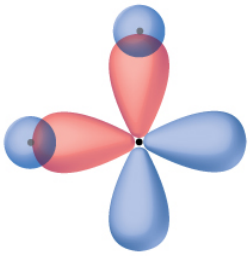


Figure 7.2.1: The hypothetical overlap of two of the 2p orbitals on an oxygen atom (red) with the 1s orbitals of two hydrogen atoms (blue) would produce a bond angle of 90°. This is not consistent with experimental evidence.[1]

Two peanut-shaped orbitals lie perpendicular to one another. They overlap with spherical orbitals to the left and top of the diagram.

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 7.2.2). 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.

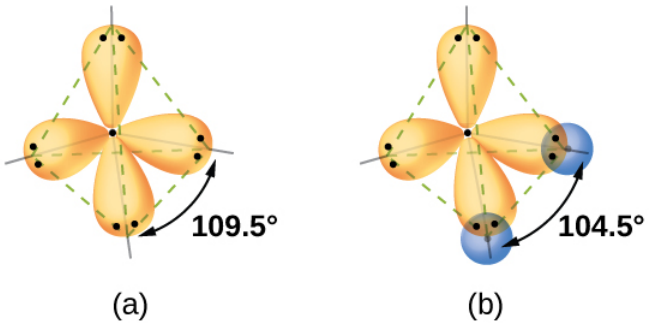


Figure 7.2.2: (a) A water molecule has four regions of electron density, so VSEPR theory predicts a tetrahedral arrangement of hybrid orbitals. (b) Two of the hybrid orbitals on oxygen contain lone pairs, and the other two overlap with the 1s orbitals of hydrogen atoms to form the O–H bonds in H_2O. This description is more consistent with the experimental structure.

Two diagrams are shown and labeled “a” and “b.” Diagram a shows two peanut-shaped orbitals lying in a tetrahedral arrangement around the letter “O.” Diagram b shows the same two orbitals, but they now overlap to the top and to the left with two spherical orbitals, each labeled “H.” A pair of electrons occupies each lobe of the peanut-shaped orbitals.

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.

7.2.1: 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 7.2.3). 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.

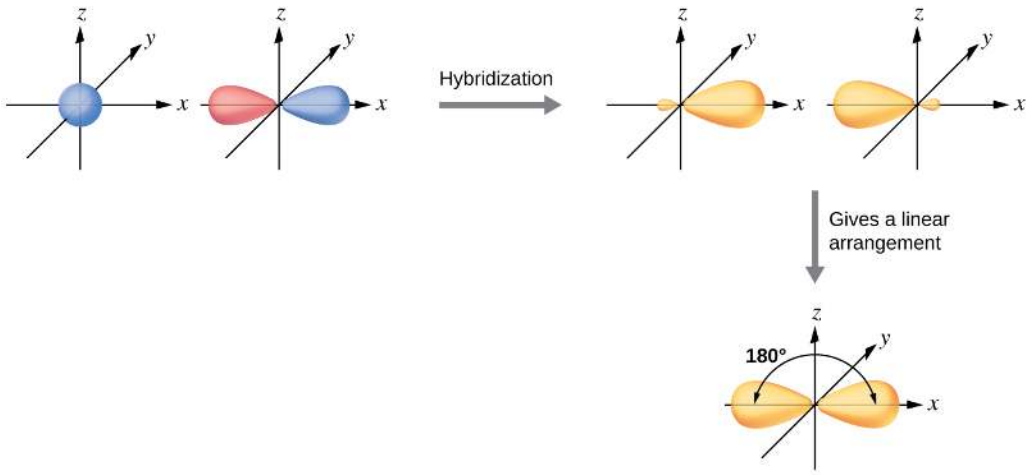


Figure 7.2.3: Hybridization of an s orbital (blue) and a p orbital (red) of the same atom produces two sp hybrid orbitals (yellow). Each hybrid orbital is oriented primarily in just one direction. Note that each sp orbital contains one lobe that is significantly larger than the other. The set of two sp orbitals are oriented at 180°, which is consistent with the geometry for two domains.

A series of three diagrams connected by a right-facing arrow that is labeled, "Hybridization," and a downward-facing arrow labeled, "Gives a linear arrangement," are shown. The first diagram shows a blue spherical orbital and a red, peanut-shaped orbital, each placed on an X, Y, Z axis system. The second diagram shows the same two orbitals, but they are now purple and have one enlarged lobe and one smaller lobe. Each lies along the x-axis in the drawing. The third diagram shows the same two orbitals, but their smaller lobes now overlap along the x-axis while their larger lobes are located at and labeled as "180 degrees" from one another.

We illustrate the electronic differences in an isolated Be atom and in the bonded Be atom in the orbital energy-level diagram in Figure 7.2.4. 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.

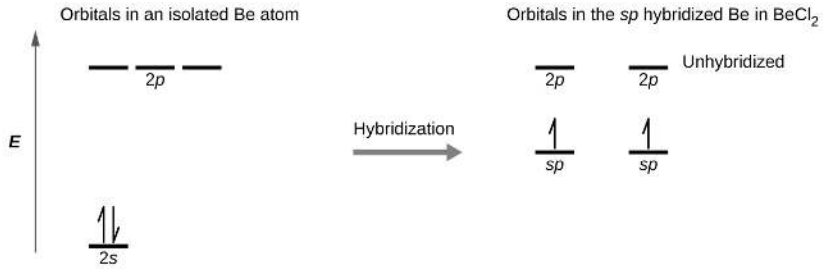


Figure 7.2.4: This orbital energy-level diagram shows the sp hybridized orbitals on Be in the linear $BeCl_2$ molecule. Each of the two sp hybrid orbitals holds one electron and is thus half filled and available for bonding via overlap with a Cl 3p orbital.

A diagram is shown in two parts, connected by a right facing arrow labeled, “Hybridization.” The left diagram shows an up-facing arrow labeled, “E.” To the lower right of the arrow is a short, horizontal line labeled, “2 s,” that has two vertical half-arrows facing up and down on it. To the upper right of the arrow are a series of three short, horizontal lines labeled, “2 p.” Above these two sets of lines is the phrase, “Orbitals in an isolated B e atom.” The right side of the diagram shows two short, horizontal lines placed halfway up the space and each labeled, “s p.” An upward-facing half arrow is drawn vertically on each line. Above these lines are two other short, horizontal lines, each labeled, “2 p.” Above these two sets of lines is the phrase, “Orbitals in the s p hybridized B e in B e C l subscript 2.”

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.

7.2.2: 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 7.2.5).

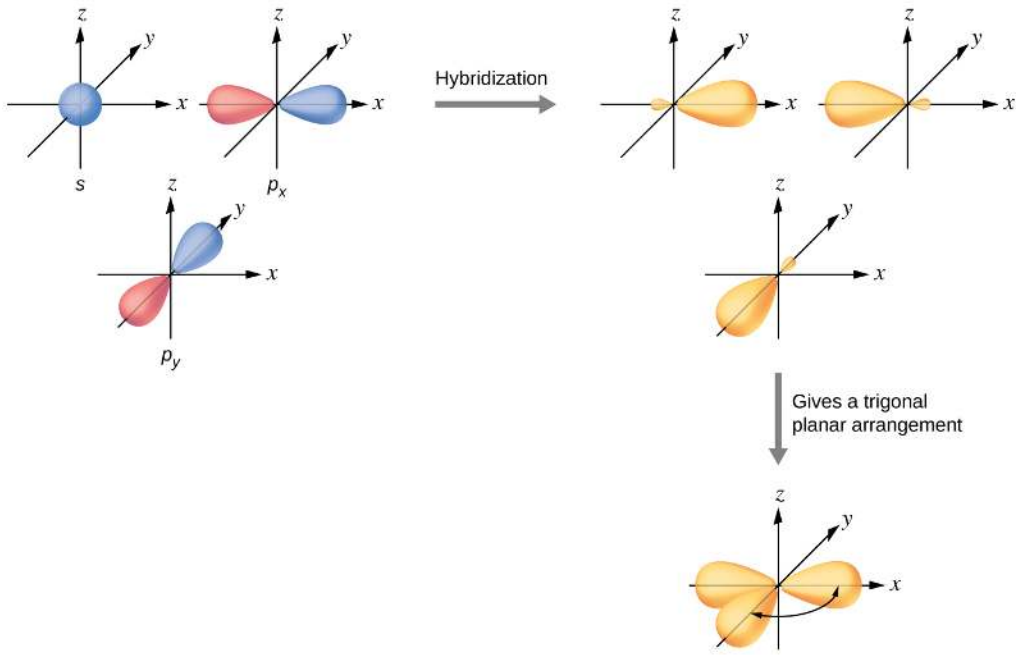


Figure 7.2.5: The hybridization of an s orbital (blue) and two p orbitals (red) produces three equivalent sp^2 hybridized orbitals (yellow) oriented at 120° with respect to each other. The remaining unhybridized p orbital is not shown here, but is located along the z axis.

A series of three diagrams connected by a right-facing arrow that is labeled, “Hybridization,” and a downward-facing arrow labeled, “Gives a trigonal planar arrangement,” are shown. The first diagram shows a blue spherical orbital and two red, peanut-shaped orbitals, each placed on an X, Y, Z axis system. The two red orbitals are located on the x and z axes, respectively. The second diagram shows the same three orbitals, but they are now purple and have one enlarged lobe and one smaller lobe. Each lies in a different axis in the drawing. The third diagram shows the same three orbitals, but their smaller lobes now overlap while their larger lobes are located at and labeled as “120 degrees” from one another.

Although quantum mechanics yields the “plump” orbital lobes as depicted in Figure 7.2.5, sometimes for clarity these orbitals are drawn thinner and without the minor lobes, as in Figure 7.2.6, 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.

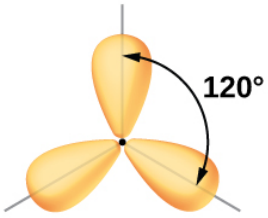


Figure 7.2.6: This alternate way of drawing the trigonal planar sp^2 hybrid orbitals is sometimes used in more crowded figures.

Three balloon-like orbitals are shown, and connect together near their narrower ends in one plane. The angle between a pair of lobes is labeled, “120 degrees.”

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 7.2.7).

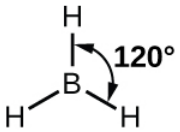


Figure 7.2.7: BH_3 is an electron-deficient molecule with a trigonal planar structure.

A boron atom is shown connected to three hydrogen atoms, which are arranged around it like a pyramid. The angle from one line connecting the boron atom to a hydrogen atom to another line connecting the boron atom to a hydrogen atom is labeled, “120 degrees.”

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 7.2.8. 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.

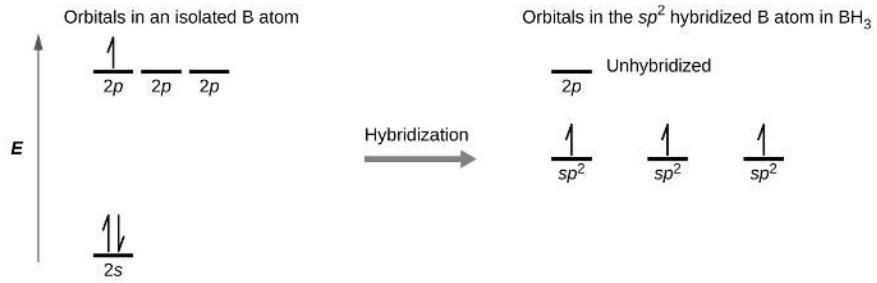


Figure 7.2.8: In an isolated B atom, there are one 2s and three 2p valence orbitals. When boron is in a molecule with three regions of electron density, three of the orbitals hybridize and create a set of three sp^2 orbitals and one unhybridized 2p orbital. The three half-filled hybrid orbitals each overlap with an orbital from a hydrogen atom to form three σ bonds in BH_3.

A diagram is shown in two parts, connected by a right facing arrow labeled, “Hybridization.” The left diagram shows an up-facing arrow labeled “E.” To the lower right of the arrow is a short, horizontal line labeled, “2 s,” that has two vertical half-arrows facing up and down on it. To the upper right of the arrow are a series of three short, horizontal lines labeled, “2 p.” Above both sets of these lines is the phrase, “Orbitals in an isolated B atom.” One of the lines has a vertical, up-facing arrow drawn on it. The right side of the diagram shows three short, horizontal lines placed halfway up the space and each labeled, “s p superscript 2.” An upward-facing half arrow is drawn vertically on each line. Above these lines is one other short, horizontal line, labeled, “2 p.” Above both sets of lines is the phrase, “Orbitals in the s p superscript 2 hybridized B atom in B H subscript 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 7.2.9), 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.

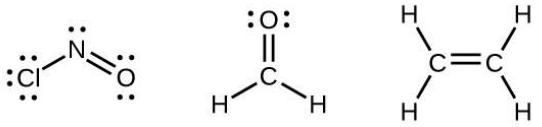


Figure 7.2.9: The central atom(s) in each of the structures shown contain three regions of electron density and are sp^2 hybridized. As we know from the discussion of VSEPR theory, a region of electron density contains all of the electrons that point in one direction. A lone pair, an unpaired electron, a single bond, or a multiple bond would each count as one region of electron density.

Three Lewis structures are shown. The left-hand structure shows a chlorine atom surrounded by three lone pairs of electrons single bonded to a nitrogen atom with one lone pair of electrons and double bonded to an oxygen atom with two lone pairs of electrons. The middle structure shows a carbon atom single bonded to two hydrogen atoms and double bonded to an oxygen atom that has two lone pairs of electrons. The right-hand structure shows two carbon atoms, double bonded to one another and each single bonded to two hydrogen atoms.

7.2.3: 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 7.2.10). Each of these hybrid orbitals points toward a different corner of a tetrahedron.

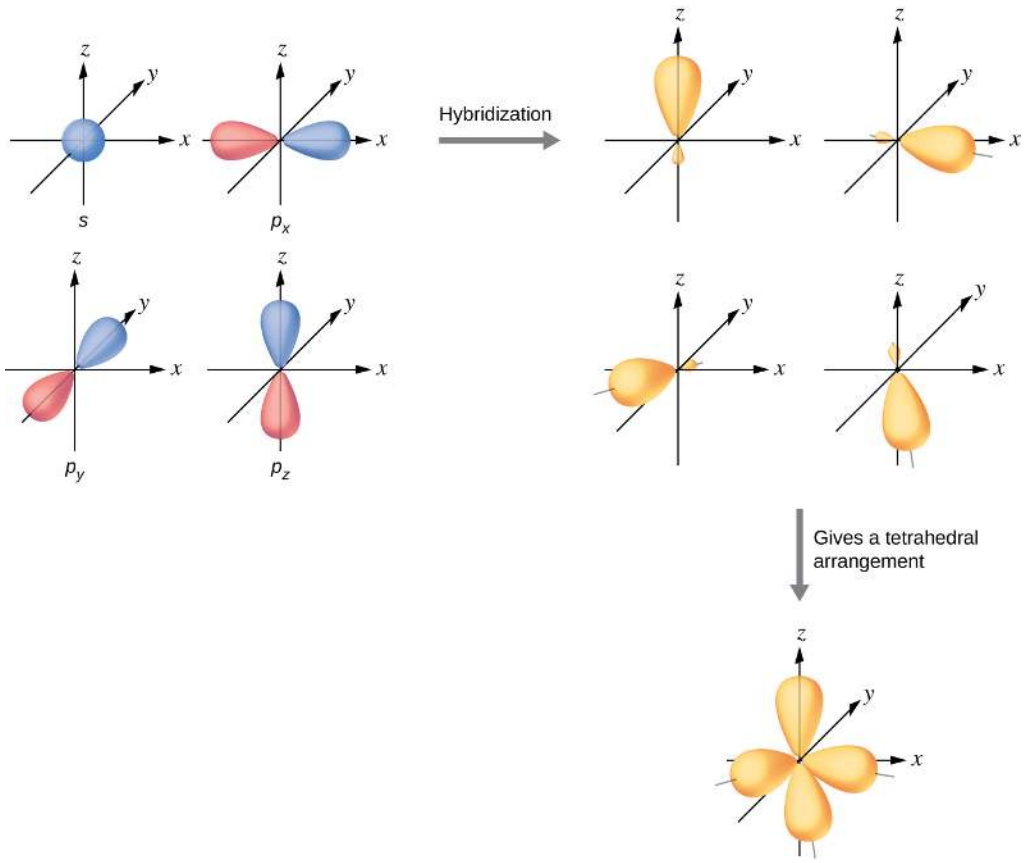


Figure 7.2.10: The hybridization of an s orbital (blue) and three p orbitals (red) produces four equivalent sp^3 hybridized orbitals (yellow) oriented at 109.5° with respect to each other.

A series of three diagrams connected by a right-facing arrow that is labeled, “Hybridization,” and a downward-facing arrow labeled, “Gives a tetrahedral arrangement,” are shown. The first diagram shows a blue spherical orbital and three red, peanut-shaped orbitals, each placed on an x, y, z axis system. The three red orbitals are located on the x , y and z axes, respectively. The second diagram shows the same four orbitals, but they are now purple and have one enlarged lobe and one smaller lobe. Each lies in a different axis in the drawing. The third diagram shows the same four orbitals, but their smaller lobes now overlap to form a tetrahedral structure.

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 7.2.11. 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.

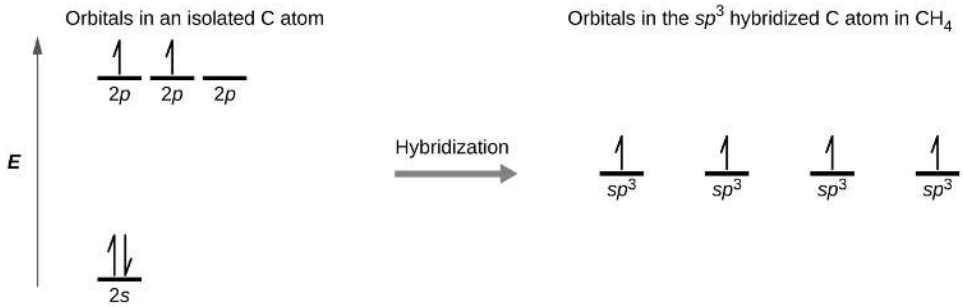


Figure 7.2.11: The four valence atomic orbitals from an isolated carbon atom all hybridize when the carbon bonds in a molecule like CH_4 with four regions of electron density. This creates four equivalent sp^3 hybridized orbitals. Overlap of each of the hybrid orbitals with a hydrogen orbital creates a C–H σ bond.

A diagram is shown in two parts, connected by a right facing arrow labeled, “Hybridization.” The left diagram shows an up-facing arrow labeled “E.” To the lower right of the arrow is a short, horizontal line labeled, “2 s,” that has two vertical half-arrows facing up and down on it. To the upper right of the arrow are a series of three short, horizontal lines labeled, “2 p.” Two of the lines have a vertical, up-facing arrow drawn on them. Above both sets of lines is the phrase, “Orbitals in an isolated C atom.” The right side of the diagram shows four short, horizontal lines placed halfway up the space and each labeled, “s p superscript 3.” An upward-facing half arrow is drawn vertically on each line. Above these lines is the phrase, “Orbitals in the s p superscript 3 hybridized C atom in C H subscript 4.”

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 7.2.10). 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 7.2.12. 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.

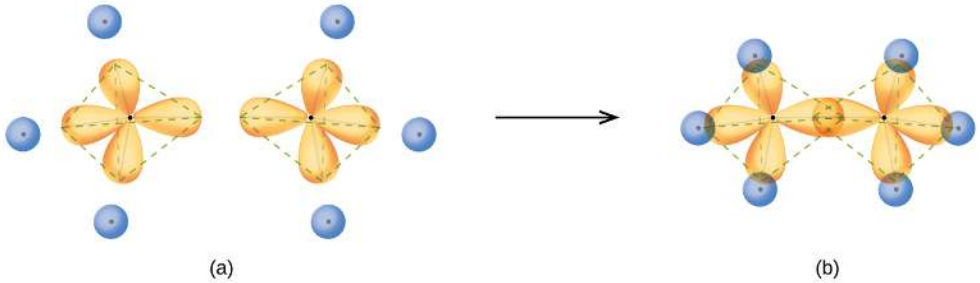


Figure 7.2.12: (a) In the ethane molecule, C_2H_6, each carbon has four sp^3 orbitals. (b) These four orbitals overlap to form seven σ bonds.

Two diagrams are shown and labeled “a” and “b.” Diagram a shows two carbon atoms, each surrounded by their four s p subscript three hybridized orbitals in a three dimensional arrangement. Each of the orbitals is shown overlapping with a spherical hydrogen atom. Diagram b shows the same general arrangement, but the hydrogen atoms are just represented by an, “H” and their spherical orbitals are not shown.

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.

7.2.4: 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^3d 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^3d^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).

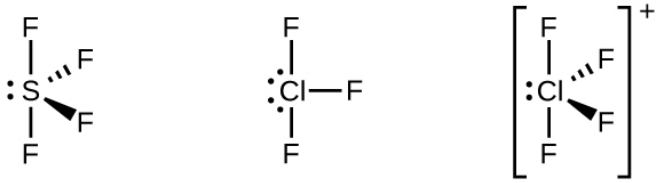


Figure 7.2.13: The three compounds pictured exhibit sp^3d hybridization in the central atom and a trigonal bipyramid form. SF_4 and ClF_4^+ *have one lone pair of electrons on the central atom, and* ClF_3 *has two lone pairs giving it the T-shape shown.*

Three Lewis structures are shown along with designations of molecular shape. The left image shows a sulfur atom singly bonded to four fluorine atoms. The sulfur atom has one lone pair of electrons while each fluorine has three. Two fluorine atoms are drawn vertically up and down from the sulfur while the other two are shown going into and out of the page. The second structure shows one chlorine atom singly bonded to three fluorine atoms. The chlorine has two lone pairs of electrons while each fluorine has three. Two fluorine atoms are drawn vertically up and down from the sulfur while the other is shown horizontally. The right structure shows a chlorine atom singly bonded to four fluorine atoms. The chlorine atom has one lone pair of electrons and a superscript plus sign, while each fluorine has three lone pairs of electrons. Two fluorine atoms are drawn vertically up and down from the sulfur while the other two are shown going into and out of the page.

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 7.2.13) 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 ClF_4^+. (The electrons on fluorine atoms are omitted for clarity.)

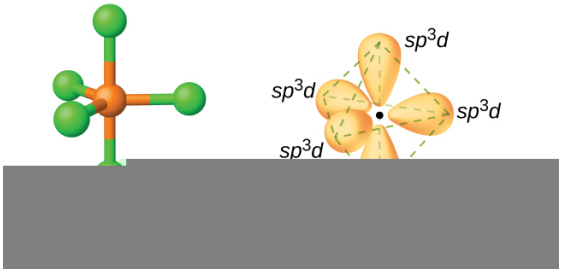


Figure 7.2.14: (a) The five regions of electron density around phosphorus in PCl_5 require five hybrid sp^3d orbitals. (b) These orbitals combine to form a trigonal bipyramidal structure with each large lobe of the hybrid orbital pointing at a vertex. As before, there are also small lobes pointing in the opposite direction for each orbital (not shown for clarity).

Two images are shown and labeled “a” and “b.” Image a depicts a ball-and-stick model in a trigonal bipyramidal arrangement. Image b depicts the hybrid orbitals in the same arrangement and each is labeled, “s p superscript three d.”

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 PCl_6^-, the iodine atom in the interhalogens IF_6^+, IF_5, ICl_4^-, IF_4^- and the xenon atom in XeF_4.

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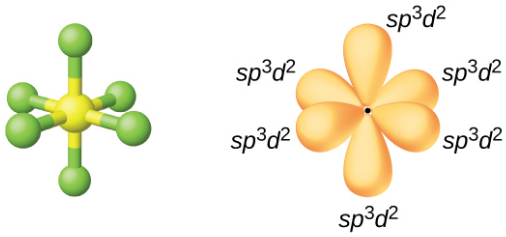


Figure 7.2.15: (a) Sulfur hexafluoride, SF_6, has an octahedral structure that requires sp^3d^2 hybridization. (b) The six sp^3d^2 orbitals form an octahedral structure around sulfur. Again, the minor lobe of each orbital is not shown for clarity.

Two images are shown and labeled “a” and “b.” Image a depicts a ball-and-stick model in an octahedral arrangement. Image b depicts the hybrid orbitals in the same arrangement and each is labeled, “s p superscript three d superscript two.”

7.2.5: 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 7.2.16. 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 7.2.16 that corresponds to this geometry.

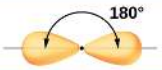
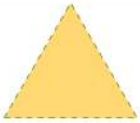
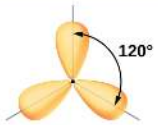
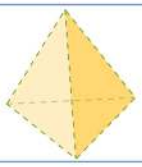
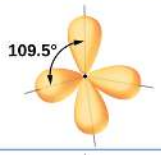
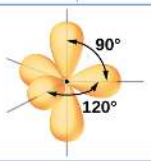
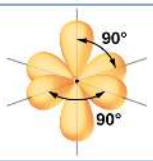
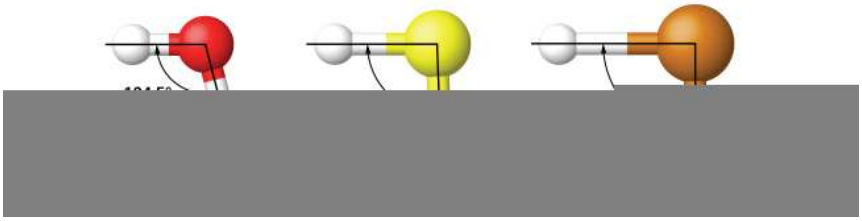
Regions of Electron Density	Arrangement		Hybridization	
2		linear	*sp*	
3		trigonal planar	sp^2	
4		tetrahedral	sp^3	
5		trigonal bipyramidal	sp^3d	
6		octahedral	sp^3d^2	

Figure 7.2.16: 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.

A table is shown that is composed of five columns and six rows. The header row contains the phrases, “Regions of electron density,” “Arrangement,” (which has two columns below it), and “Hybridization,” (which has two columns below it). The first column contains the numbers “2,” “3,” “4,” “5,” and “6.” The second column contains images of a line, a triangle, a three sided pyramid, a trigonal bipyramid, and an eight-faced ocatahedron. The third column contains the terms, “Linear,” “Trigonal planar,” “Tetrahedral,” “Trigonal bipyramidal,” and “Octahedral.” The fourth column contains the terms “s p,” “s p superscript 2,” “s p superscript 3,” “s p superscript 3 d,” and “s p superscript 3 d superscript 2.” The last column contains drawings of the molecules beginning with a peanut-shaped structure marked with an angle of “180 degrees.” The second structure is made up of three equal-sized, rounded structures connected at one point with an angle of “120 degrees,” while the third structure is a three-dimensional arrangement of four equal-sized, rounded structures labeled as “109.5 degrees.” The fourth structure is made up of five equal-sized, rounded structures connected at “120 and 90 degrees,” while the fifth structure has six equal-sized, rounded structures connected at “90 degrees.”

> *It is important to remember that hybridization was devised to rationalize experimentally observed molecular geometries, not the other way around.*

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.



Three Lewis structures are shown. The left structure shows an oxygen atom with two lone pairs of electrons single bonded to two hydrogen atoms. The middle structure is made up of a sulfur atom with two lone pairs of electrons single bonded to two hydrogen atoms. The right structure is made up of a tellurium atom with two lone pairs of electrons single bonded to two hydrogen atoms. From left to right, the bond angles of each molecule decrease.

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 7.2.1: Assigning Hybridization

Ammonium sulfate is important as a fertilizer. What is the hybridization of the sulfur atom in the sulfate ion, SO_4^{2-}?

Solution

The Lewis structure of sulfate shows there are four regions of electron density.

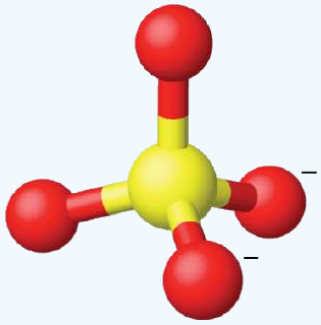
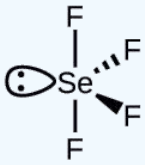


Figure 7.2.16).

A structure is shown in which a sulfur atom is bonded to four oxygen atoms in a tetrahedral arrangement. Two of the oxygen atoms have a negative charge.

Exercise 7.2.1

What is the hybridization of the selenium atom in SeF_4?



A Lewis structure is shown in which four fluorine atoms are each attached to one sulfur atom. Two of the attached fluorine atoms are vertically attached up and down, while two are attached into and out of the page to the right. The sulfur also has one lone pair of electrons attached to the left of the structure.

Answer

The selenium atom is sp^3d hybridized.

Example 7.2.2: Assigning Hybridization

Urea, $NH_2C(O)NH_2$, is sometimes used as a source of nitrogen in fertilizers. What is the hybridization of each nitrogen and carbon atom in urea?

Solution

The Lewis structure of urea is

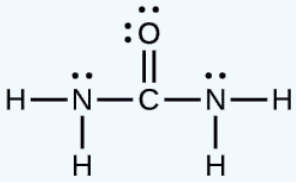


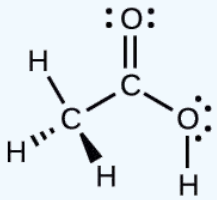
Figure 7.2.16). This is the hybridization of the nitrogen atoms in urea.

A Lewis structure is shown in which a carbon atom is double bonded to an oxygen atom that has two lone pairs of electrons. The carbon atom forms single bonds to two nitrogen atoms. Each nitrogen is single bonded to two hydrogen atoms, and each nitrogen atoms has one lone pair of electrons.

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 7.2.16), which is the hybridization of the carbon atom in urea.

Exercise 7.2.1

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?



A Lewis structure is shown in which a carbon atom is double bonded to an oxygen atom that has two lone pairs of electrons and single bonded to another oxygen atom that is single boned to a hydrogen atom. This second oxygen atom has two lone pairs of electrons. The carbon is also single bonded to a carbon atom that is single bonded to three hydrogen atoms.

Answer

$H_3\underline{C}$, sp^3; $\underline{C}(O)OH$, sp^2

Summary

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).

7.2.5.1: Footnotes

1. Note 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.

7.2.5.2: Glossary

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

***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

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7.3: Multiple Bonding and Molecular Orbitals

Learning Objectives

- To explain resonance structures using molecular orbitals.

So far in our valence bond orbital descriptions we have not dealt with polyatomic systems with multiple bonds. To do so, we can use an approach in which we describe σ bonding using localized electron-pair bonds formed by hybrid atomic orbitals, and π bonding using **molecular orbitals** formed by unhybridized *np* atomic orbitals.

Multiple Bonding

We begin our discussion by considering the bonding in ethylene (C_2H_4). Experimentally, we know that the H–C–H and H–C–C angles in ethylene are approximately 120°. This angle suggests that the carbon atoms are sp^2 hybridized, which means that a singly occupied sp^2 orbital on one carbon overlaps with a singly occupied *s* orbital on each H and a singly occupied sp^2 lobe on the other C. The sp^2 hybridization can be represented as follows:

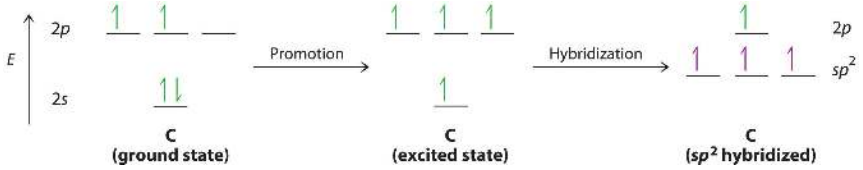


Figure 7.3.1). These two singly occupied $2p_z$ orbitals can overlap in a side-to-side fashion to form a π bond. The orbitals overlap both above and below the plane of the molecule but form just one bonding orbital space. The C–C π bond plus the hybridized C–C σ bond together form a double bond.

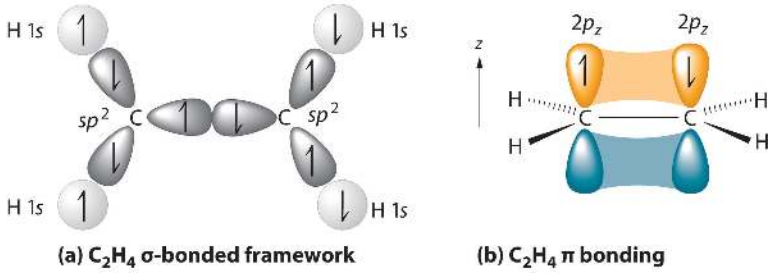
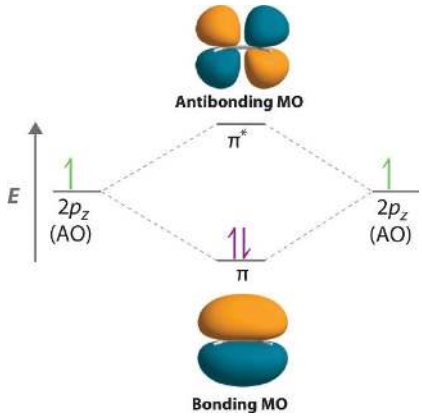


Figure 7.3.1: Bonding in Ethylene. (a) The σ-bonded framework is formed by the overlap of two sets of singly occupied carbon sp^2 hybrid orbitals and four singly occupied hydrogen 1*s* orbitals to form electron-pair bonds. This uses 10 of the 12 valence electrons to form a total of five σ bonds (four C–H bonds and one C–C bond). (b) One singly occupied unhybridized $2p_z$ orbital remains on each carbon atom to form a carbon–carbon π bond. (Note: by convention, in planar molecules the axis perpendicular to the molecular plane is the *z*-axis.)

When considering multiple bonds, we can introduce the more sophisticated **molecular orbital theory** to better understand how orbital overlap creates bonding orbitals. Recall that atomic orbitals represent *electron wavefunctions*; this implies that "orbital overlap" actually involves the combination of those wavefunctions, which can occur via both constructive and destructive interference. Thus, when the two singly occupied $2p_z$ orbitals in ethylene overlap, they actually create both a π bonding orbital (constructive combination) and a π^* antibonding orbital (destructive combination), which produces the energy-level diagram shown in Figure 7.3.2. With the formation of a π bonding orbital, electron density increases in the plane between the carbon nuclei. Electrons occupying this orbital lower the potential energy of the combination and tend to hold the two nuclei together (i.e., they form a bond.) The π^* orbital lies outside the internuclear region and has a nodal plane perpendicular to the internuclear axis; electrons in this orbital would tend to push the nuclei apart, so it is called an antibonding orbital. Because each $2p_z$ orbital has a single electron, there are only two electrons, enough to fill only the bonding (π) level, leaving the π^* orbital empty. Consequently, the C–C bond in ethylene consists of a σ bond and a π bond, which together give a C=C double bond. Our model is supported by the facts that the measured carbon–carbon bond is shorter than that in ethane (133.9 pm versus 153.5 pm) and the bond is stronger (728 kJ/mol versus 376 kJ/mol in ethane). The two CH_2 fragments are coplanar, which maximizes the overlap of the two singly occupied $2p_z$ orbitals.



IFigure 7.3.2: Molecular Orbital Energy-Level Diagram for π Bonding in Ethylene. As in the diatomic molecules discussed previously, the singly occupied $2p_z$ orbitals in ethylene can overlap to form a bonding/antibonding pair of π molecular orbitals. The two electrons remaining are enough to fill only the bonding π orbital. With one σ bond plus one π bond, the carbon–carbon bond order in ethylene is 2.

Triple bonds, as in acetylene (C_2H_2), can also be explained using a combination of hybrid atomic orbitals and molecular orbitals. The four atoms of acetylene are collinear, which suggests that each carbon is *sp* hybridized. If one *sp* lobe on each carbon atom is used to form a C–C σ bond and one is used to form the C–H σ bond, then each carbon will still have two unhybridized 2*p* orbitals (a $2p_{x,y}$ pair), each with one electron (part (a) in Figure 7.3.3).

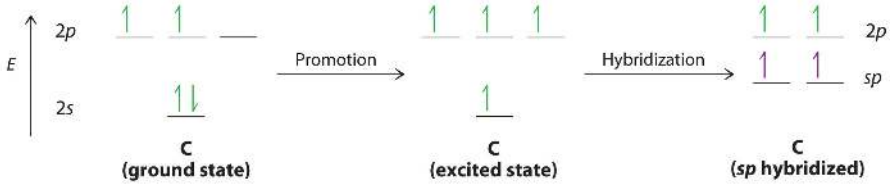


Figure 7.3.2). Because each of the unhybridized 2*p* orbitals has a single electron, four electrons are available for π bonding, which is enough to occupy only the bonding molecular orbitals. Acetylene must therefore have a carbon–carbon triple bond, which consists of a C–C σ bond and two mutually perpendicular π bonds. Acetylene does in fact have a shorter carbon–carbon bond (120.3 pm) and a higher bond energy (965 kJ/mol) than ethane and ethylene, as we would expect for a triple bond.

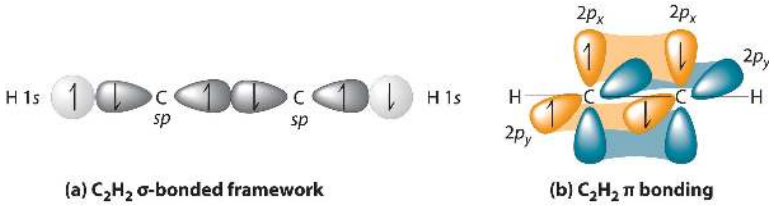


Figure 7.3.3: Bonding in Acetylene (a) In the formation of the σ-bonded framework, two sets of singly occupied carbon *sp* hybrid orbitals and two singly occupied hydrogen 1*s* orbitals overlap. (b) In the formation of two carbon–carbon π bonds in acetylene, two singly occupied unhybridized $2p_{x,y}$ orbitals on each carbon atom overlap. With one σ bond plus two π bonds, the carbon–carbon bond order in acetylene is 3.

In complex molecules, *hybrid orbitals* and *valence bond theory* can be used to describe σ bonding, and unhybridized π orbitals and *molecular orbital theory* can be used to describe π bonding.

Example 7.3.1

Describe the bonding in HCN using a combination of hybrid atomic orbitals and molecular orbitals. The HCN molecule is linear.

Given: chemical compound and molecular geometry

Asked for: bonding description using hybrid atomic orbitals and molecular orbitals

Strategy:

A. From the geometry given, predict the hybridization in HCN. Use the hybrid orbitals to form the σ-bonded framework of the molecule and determine the number of valence electrons that are used for σ bonding.

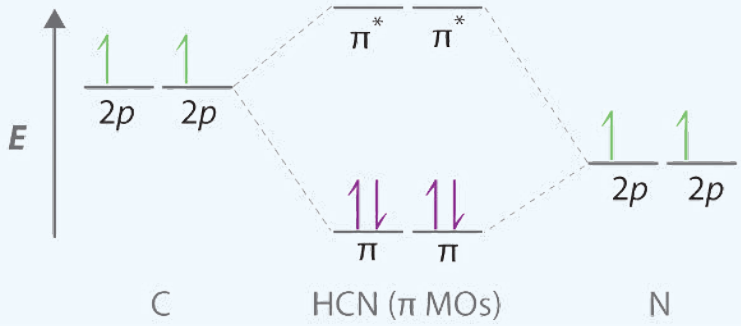
B. Determine the number of remaining valence electrons. Use any remaining unhybridized *p* orbitals to form π and π^* orbitals.
C. Fill the orbitals with the remaining electrons in order of increasing energy. Describe the bonding in HCN.

Solution:

A Because HCN is a linear molecule, it is likely that the bonding can be described in terms of *sp* hybridization at carbon. Because the nitrogen atom can also be described as *sp* hybridized, we can use one *sp* hybrid on each atom to form a C–N σ bond. This leaves one *sp* hybrid on each atom to either bond to hydrogen (C) or hold a lone pair of electrons (N). Of 10 valence electrons (5 from N, 4 from C, and 1 from H), 4 are used for σ bonding:



B We are now left with 2 electrons on N (5 valence electrons minus 1 bonding electron minus 2 electrons in the lone pair) and 2 electrons on C (4 valence electrons minus 2 bonding electrons). We have two unhybridized 2*p* atomic orbitals left on carbon and two on nitrogen, each occupied by a single electron. These four 2*p* atomic orbitals can be combined to give four molecular orbitals: two π (bonding) orbitals and two π^* (antibonding) orbitals. **C** With 4 electrons available, only the π orbitals are filled. The overall result is a triple bond (1 σ and 2 π) between C and N.



? Exercise 7.3.1

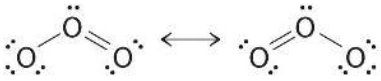
Describe the bonding in formaldehyde ($H_2C{=}O$), a trigonal planar molecule, using a combination of hybrid atomic orbitals and molecular orbitals.

Answer

- σ-bonding framework: Carbon and oxygen are sp^2 hybridized. Two sp^2 hybrid orbitals on oxygen have lone pairs, two sp^2 hybrid orbitals on carbon form C–H bonds, and one sp^2 hybrid orbital on C and O forms a C–O σ bond.
- π bonding: Unhybridized, singly occupied 2*p* atomic orbitals on carbon and oxygen interact to form π (bonding) and π^* (antibonding) molecular orbitals. With two electrons, only the π (bonding) orbital is occupied.

Molecular Orbitals and Resonance Structures

Resonance structures can be used to describe the bonding in molecules such as ozone (O_3) and the nitrite ion (NO_2^-). Ozone can be represented by either of these Lewis electron structures:



Although the VSEPR model correctly predicts that both species are bent, it gives no information about their bond orders.

Experimental evidence indicates that ozone has a bond angle of 117.5°. Because this angle is close to 120°, it is likely that the central oxygen atom in ozone is trigonal planar and sp^2 hybridized. If we assume that the terminal oxygen atoms are also sp^2 hybridized, then we obtain the σ-bonded framework shown in Figure 7.3.4. Two of the three sp^2 lobes on the central O are used to form O–O sigma bonds, and the third has a lone pair of electrons. Each terminal oxygen atom has two lone pairs of electrons that

are also in sp^2 lobes. In addition, each oxygen atom has one unhybridized 2*p* orbital perpendicular to the molecular plane. The σ bonds and lone pairs account for a total of 14 electrons (five lone pairs and two σ bonds, each containing 2 electrons). Each oxygen atom in ozone has 6 valence electrons, so O_3 has a total of 18 valence electrons. Subtracting 14 electrons from the total gives us 4 electrons that must occupy the three unhybridized 2*p* orbitals.

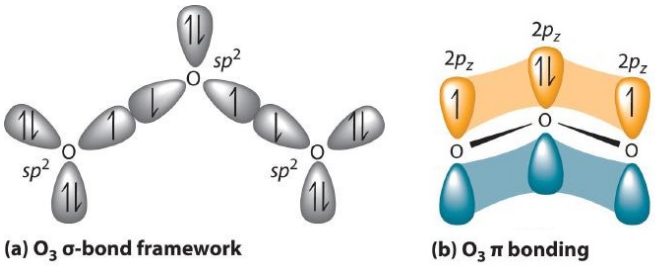


Figure 7.3.4: Bonding in Ozone. (a) In the formation of the σ-bonded framework, three sets of oxygen sp^2 hybrid orbitals overlap to give two O–O σ bonds and five lone pairs, two on each terminal O and one on the central O. The σ bonds and lone pairs account for 14 of the 18 valence electrons of O_3. (b) One unhybridized $2p_z$ orbital remains on each oxygen atom that is available for π bonding. The unhybridized $2p_z$ orbital on each terminal O atom has a single electron, whereas the unhybridized $2p_z$ orbital on the central O atom has 2 electrons.

With a molecular orbital approach to describe the π bonding, three 2*p* atomic orbitals give us three molecular orbitals, as shown in Figure 7.3.5. One of the molecular orbitals is a π bonding molecular orbital, which is shown as a banana-shaped region of electron density above and below the molecular plane. This region has *no* nodes perpendicular to the O_3 plane. The molecular orbital with the highest energy has two nodes that bisect the O–O σ bonds; it is a π* antibonding orbital. The third molecular orbital contains a single node that is perpendicular to the O_3 plane and passes through the central O atom; because the orbital nodes do not directly touch, this is a *nonbonding* molecular orbital. Because electrons in nonbonding orbitals are neither bonding nor antibonding, they are ignored in calculating bond orders.

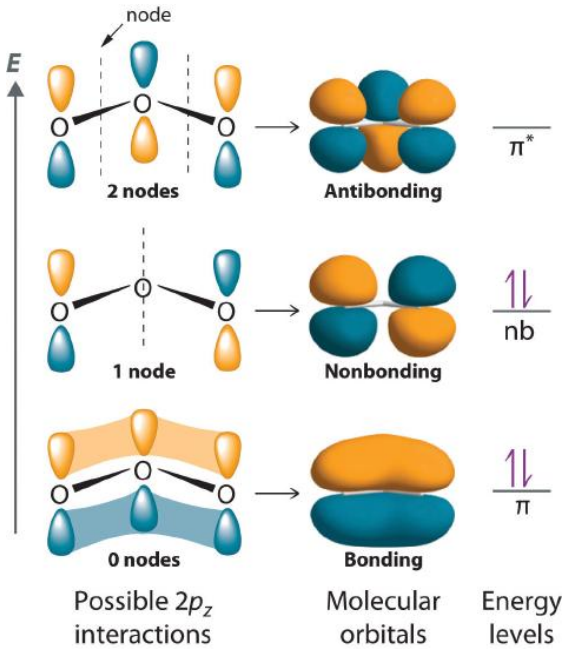


Figure 7.3.5: π Bonding in Ozone. The three unhybridized $2p_z$ atomic orbitals interact with one another to form three molecular orbitals: one π bonding orbital at lower energy, one π* antibonding orbital at higher energy, and a nonbonding orbital in between. Placing four electrons in this diagram fills the bonding and nonbonding orbitals. With one filled π bonding orbital holding three atoms together, the net π bond order is ½ per O–O bond. The combined σ/π bond order is thus 1 ½) for each O–O bond.

We can now place the remaining four electrons in the three energy levels shown in Figure 7.3.5, thereby filling the π bonding and the nonbonding levels. The result is a single π bond holding three oxygen atoms together, or ½π bond per O–O. We therefore predict the overall O–O bond order to be ½π bond plus 1 σ bond), just as predicted using resonance structures. The molecular orbital description, however, makes it more clear that resonance really means that electrons are *delocalized* over all three atoms at once. The molecular orbital approach also shows that the π nonbonding orbital is localized on the terminal O atoms, which

suggests that they are more electron rich than the central O atom (corresponding to the "extra" lone pair seen on one of the terminal O atoms in the Lewis resonance structures). The reactivity of ozone is consistent with the predicted charge localization.

> *Resonance structures are a crude way of describing molecular orbitals that extend over more than two atoms.*

Example 7.3.2

Describe the bonding in the nitrite ion in terms of a combination of hybrid atomic orbitals and molecular orbitals. Lewis dot structures and the VSEPR model predict that the NO_2^- ion is bent.

Given: chemical species and molecular geometry

Asked for: bonding description using hybrid atomic orbitals and molecular orbitals

Strategy:

A. Calculate the number of valence electrons in NO_2^-. From the structure, predict the type of atomic orbital hybridization in the ion.

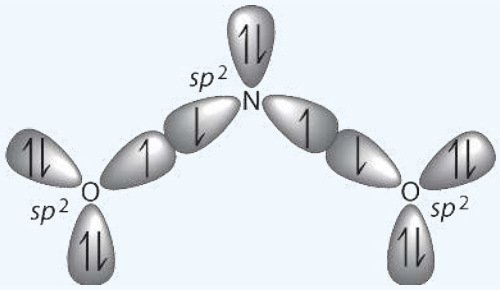
B. Predict the number and type of molecular orbitals that form during bonding. Use valence electrons to fill these orbitals and then calculate the number of electrons that remain.

C. If there are unhybridized orbitals, place the remaining electrons in these orbitals in order of increasing energy. Calculate the bond order and describe the bonding.

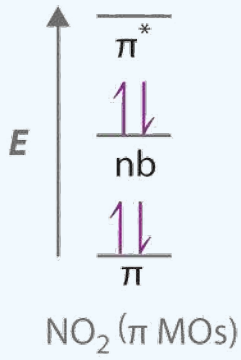
Solution:

A The lone pair of electrons on nitrogen and a bent structure suggest that the bonding in NO_2^- is similar to the bonding in ozone. This conclusion is supported by the fact that nitrite also contains 18 valence electrons (5 from N and 6 from each O, plus 1 for the −1 charge). The bent structure implies that the nitrogen is sp^2 hybridized.

B If we assume that the oxygen atoms are sp^2 hybridized as well, then we can use two sp^2 hybrid orbitals on each oxygen and one sp^2 hybrid orbital on nitrogen to accommodate the five lone pairs of electrons. Two sp^2 hybrid orbitals on nitrogen form σ bonds with the remaining sp^2 hybrid orbital on each oxygen. The σ bonds and lone pairs account for 14 electrons. We are left with three unhybridized 2*p* orbitals, one on each atom, perpendicular to the plane of the molecule, and 4 electrons. Just as with ozone, these three 2*p* orbitals interact to form bonding, nonbonding, and antibonding π molecular orbitals. The bonding molecular orbital is spread over the nitrogen and both oxygen atoms.



C Placing 4 electrons in the energy-level diagram fills both the bonding and nonbonding molecular orbitals and gives a π bond order of 1/2 per N–O bond. The overall N–O bond order is $1\ \frac{1}{2}$, consistent with a resonance structure.



NO_2 (π MOs)

Exercise 7.3.2

Describe the bonding in the formate ion (HCO_2^-), in terms of a combination of hybrid atomic orbitals and molecular orbitals.

Answer

Like nitrite, formate is a planar polyatomic ion with 18 valence electrons. The σ bonding framework can be described in terms of sp^2 hybridized carbon and oxygen, which account for 14 electrons. The three unhybridized 2*p* orbitals (on C and both O atoms) form three π molecular orbitals, and the remaining 4 electrons occupy both the bonding and nonbonding π molecular orbitals. The overall C–O bond order is therefore $frac32$

The Chemistry of Vision

Hydrocarbons in which two or more carbon–carbon double bonds are directly linked by carbon–carbon single bonds (called *conjugated* structures) are generally more stable than expected because of resonance. Because the double bonds are close enough to interact electronically with one another, the π electrons are shared over all the carbon atoms, as illustrated for 1,3-butadiene in Figure 7.3.6. As the number of interacting atomic orbitals increases, the number of molecular orbitals increases, the energy spacing between molecular orbitals decreases, and the systems become more stable (Figure 7.3.7). Thus as a chain of alternating double and single bonds becomes longer, the energy required to excite an electron from the highest-energy occupied (bonding) orbital to the lowest-energy unoccupied (antibonding) orbital decreases. If the chain is long enough, the amount of energy required to excite an electron corresponds to the energy of visible light. For example, vitamin A is yellow because its chain of five alternating double bonds is able to absorb violet light. Many of the colors we associate with dyes result from this same phenomenon; most dyes are organic compounds with alternating double bonds.

Figure 7.3.6: π Bonding in 1,3-Butadiene. (a) If each carbon atom is assumed to be sp^2 hybridized, we can construct a σ-bonded framework that accounts for the C–H and C–C single bonds, leaving *four* singly occupied $2p_z$ orbitals, one on each carbon atom. (b) As in ozone, these orbitals can interact, in this case to form *four* molecular orbitals. The molecular orbital at lowest energy is a bonding orbital with 0 nodes, the one at highest energy is antibonding with 3 nodes, and the two in the middle have 1 node and 2 nodes and are somewhere between bonding or antibonding and nonbonding, respectively. The energy of the molecular orbital increases with the number of nodes. With four electrons, only the two bonding orbitals are filled, consistent with the presence of two π bonds.

As the number of atomic orbitals increases, the difference in energy between the resulting molecular orbital energy levels decreases, which allows light of lower energy to be absorbed. As a result, organic compounds with long chains of carbon atoms and alternating single and double bonds tend to become more deeply colored as the number of double bonds increases.

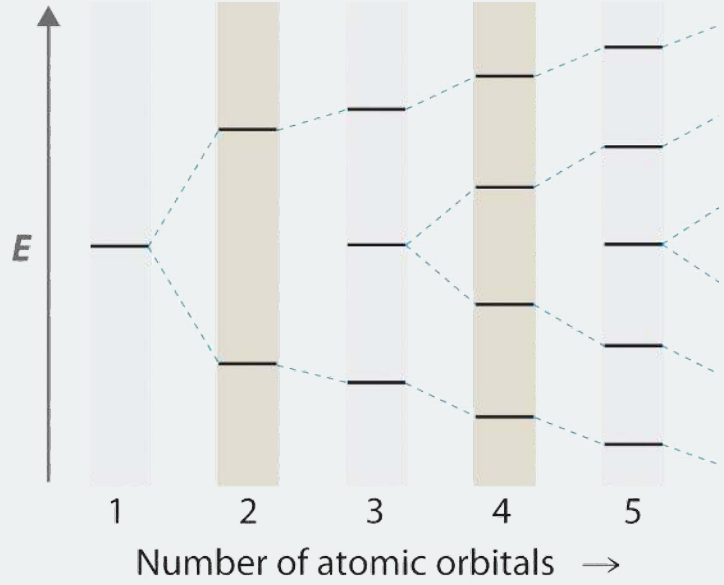


Figure 7.3.7: Molecular Orbital Energy-Level Diagrams for a Chain of n Like Orbitals That Interact ($n \leq 5$).

> As the number of interacting atomic orbitals increases, the energy separation between the resulting molecular orbitals steadily decreases.

A derivative of vitamin A called *retinal* is used by the human eye to detect light and has a structure with alternating C=C double bonds. When visible light strikes retinal, the energy separation between the molecular orbitals is sufficiently close that the energy absorbed corresponds to the energy required to change one double bond in the molecule from *cis*, where like groups are on the same side of the double bond, to *trans*, where they are on opposite sides, initiating a process that causes a signal to be sent to the brain. If this mechanism is defective, we lose our vision in dim light. Once again, a molecular orbital approach to bonding explains a process that cannot be explained using any of the other approaches we have described.

Summary

Polyatomic systems with multiple bonds can be described using hybrid atomic orbitals for σ bonding and molecular orbitals to describe π bonding. To describe the bonding in more complex molecules with multiple bonds, we can use an approach that uses hybrid atomic orbitals to describe the σ bonding and molecular orbitals to describe the π bonding. In this approach, unhybridized *np* orbitals on atoms bonded to one another are allowed to interact to produce bonding, antibonding, or nonbonding combinations. For π bonds between two atoms (as in ethylene or acetylene), the resulting molecular orbitals are virtually identical to the π molecular orbitals in diatomic molecules such as O_2 and N_2. Applying the same approach to π bonding between three or four atoms requires combining three or four unhybridized *np* orbitals on adjacent atoms to generate π bonding, antibonding, and nonbonding molecular orbitals extending over all of the atoms. Filling the resulting energy-level diagram with the appropriate number of electrons explains the bonding in molecules or ions that previously required the use of resonance structures in the Lewis electron-pair approach.

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CHAPTER OVERVIEW

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8: Valence Bond and MO Ligand Field (needs addition)
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12: The Effect of Ligands and the Spectrochemical Series
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1: Nomenclature

Learning Objectives

- To learn the basis for complex ion and compound nomenclature

Coordination complexes have their own classes of isomers, different magnetic properties and colors, and various applications (photography, cancer treatment, etc), so it makes sense that they would have a naming system as well. Consisting of a metal and ligands, their formulas follow the pattern [Metal ligands]$^{\pm Charge}$, while names are written Prefix Ligands Metal (Oxidation State).

Introduction

According to the Lewis Acid-Base theory, ligands are Lewis bases since they can donate electrons to the central metal atom. The metals, in turn, are Lewis acids since they accept electrons. **Coordination complexes** consist of a ligand and a metal center cation and their charge can be positive, negative, or neutral. **Coordination compounds** are neutral compounds that contain at least one complex ions. Example of coordination complexes and compounds are:

- Complex Cation: $[Co(NH_3)_6]^{3+}$
- Complex Anion: $[CoCl_4(NH_3)_2]^-$
- Neutral Complex: $[CoCl_3(NH_3)_3]$
- Coordination Compound: $K_4[Fe(CN)_6]$

A ligand can be an anion or a neutral molecule that *donates an electron pair* to the complex (NH_3, H_2O, Cl^-). The number of ligands that attach to a metal depends on whether the ligand is **monodentate** or **polydentate**.

Rules to Complex Ion Nomenclature

To begin naming coordination complexes, here are some things to keep in mind.

1. Ligands are named first in alphabetical order.
2. The name of the metal comes next.
3. The oxidation state of the metal follows, noted by a Roman numeral in parentheses (II, IV).

Rule 1: Anionic Ligands

Ligands that act as anions which end in "-ide" are replaced with an ending "-o" (e.g., Chloride → Chloro). Anions ending with "-ite" and "-ate" are replaced with endings "-ito" and "-ato" respectively (e.g., Nitrite → Nitrito, Nitrate → Nitrato).

Table 1.1: Anionic Monodentate Ligands

Molecular Formula	Ligand Name	Molecular Formula	Ligand Name
F^-	Fluoro	OH^-	Hydroxo
Cl^-	Chloro	SO_4^{2-}	Sulfato
Br^-	Bromo	$S_2O_3^{2-}$	Thiosulfato
I^-	Iodo	NO_2^-	Nitrito-N-; Nitro
O^{2-}	Oxo	ONO^-	Nitrito-O-; Nitrito
CN^-	Cyano	SCN^-	Thiocyanato-S-; Thiocyanato
NC^-	Isocyano	NCS^-	Thiocyanato-N-; Isothiocyanato

Rule 2: Neutral Ligands

Most neutral molecules that are ligands carry their normal name. The few exceptions are the first four on the chart: ammine, aqua, carbonyl, and nitrosyl.

Table 1.2: Select Neutral Monodentate Ligands. Note: Ammine is spelled with two m's when referring to a ligand. Amines are a class of organic nitrogen-containing compounds.

Molecular Formula of Ligand	Ligand Name
NH_3	Ammine
H_2O	Aqua
CO	Carbonyl
NO	Nitrosyl
CH_3NH_2	Methylamine
C_5H_5N	Pyridine

Polydentate ligands follow the same rules for anions and neutral molecules.

Table 1.3: Select Polydentate ligands

Short name	Extended name
en	Ethylenediamine
ox^{2-}	Oxalato
$EDTA^{4-}$	Ethylenediaminetetraacetato

Rule 3: Ligand Multiplicity

The number of ligands present in the complex is indicated with the prefixes di, tri, etc. The exceptions are polydentates that have a prefix already in their name (en and $EDTA^{4-}$ are the most common). When indicating how many of these are present in a coordination complex, put the ligand's name in parentheses and use *bis* (for two ligands), *tris* (for three ligands), and *tetrakis* (for four ligands).

Table 1.4: Prefixes for indicating number of ligands in a complex.

Number of Ligands	Monodentate Ligands	Polydentate Ligands
1	mono	-
2	di	bis
3	tri	tris
4	tetra	tetrakis
5	penta	pentakis
6	hexa	hexakis

Prefixes always go before the ligand name; they are not taken into account when putting ligands in alphabetical order. Note that "mono" often is not used. For example, $[FeCl(CO)_2(NH_3)_3]^{2+}$ would be called triamminedicarbonylchloroiron(III) ion. Remember that ligands are always named first, before the metal is.

Example 1.1

What is the name of this complex ion: $[CrCl_2(H_2O)_4]^+$?

Solution

Let's start by identifying the ligands. The ligands here are Cl and H_2O. Therefore, we will use the monodentate ligand names of "chloro" and "aqua". Alphabetically, aqua comes before chloro, so this will be their order in the complex's name. There are 4 aqua's and 2 chloro's, so we will add the number prefixes before the names. Since both are monodentate ligands, we will say "tetra[aqua]di[chloro]".

Now that the ligands are named, we will name the metal itself. The metal is Cr, which is chromium. Therefore, this coordination complex is called tetraaquadichlorochromium(III) ion. See the next section for an explanation of the (III).

? Exercise 1.1

What is the name of this complex ion: $[CoCl_2(en)_2]^+$?

Answer

We take the same approach. There are two chloro and ethylenediamine ligands. The metal is Co, cobalt. We follow the same steps, except that *en* is a polydentate ligand with a prefix in its name (ethylene**di**amine), so "bis" is used instead of "di", and parentheses are added. Therefore, this coordination complex is called dichlorobis(ethylenediamine)cobalt(III) ion.

Rule 4: The Metals

When naming the metal center, you must know the formal metal name and the oxidation state. To show the oxidation state, we use Roman numerals inside parenthesis. For example, in the problems above, chromium and cobalt have the oxidation state of +3, so that is why they have (III) after them. Copper, with an oxidation state of +2, is denoted as copper(II). If the overall coordination complex is an anion, the ending "-ate" is attached to the metal center. Some metals also change to their Latin names in this situation. Copper +2 will change into cuprate(II). The following change to their Latin names when part of an anion complex:

Table 1.5: Latin terms for Select Metal Ion

Transition Metal	Latin
Iron	Ferrate
Copper	Cuprate
Tin	Stannate
Silver	Argentate
Lead	Plumbate
Gold	Aurate

The rest of the metals simply have -ate added to the end (cobaltate, nickelate, zincate, osmate, cadmate, platinate, mercurate, etc. Note that the -ate tends to replace -um or -ium, if present).

Finally, when a complex has an overall charge, "ion" is written after it. This is not necessary if it is neutral or part of a coordination compound (Example 1.3). Here are some examples with determining oxidation states, naming a metal in an anion complex, and naming coordination compounds.

✓ Example 1.2

What is the name of $[Cr(OH)_4]^-$?

Solution

Immediately we know that this complex is an anion. There is only one monodentate ligand, hydroxide. There are four of them, so we will use the name "tetrahydroxo". The metal is chromium, but since the complex is an anion, we will have to use the "-ate" ending, yielding "chromate". The oxidation state of the metal is 3 (x+(-1)4=-1). Write this with Roman numerals and parentheses (III) and place it after the metal to get tetrahydroxochromate(III) ion.

? Exercise 1.2

What is the name of $[CuCl_4]^{2-}$?

Answer

tetrachlorocuprate(II) ion

A last little side note: when naming a coordination compound, it is important that you name the cation first, then the anion. You base this on the charge of the ligand. Foe xample, for NaCl. The the positive Na cation comes first and the negative Cl^- anion follows.

Example 1.3

What is the name of $[\mathrm{Pt(NH_3)_4}][\mathrm{Pt(Cl)_4}]$?

Solution

NH_3 is neutral, making the first complex positively charged overall. Cl has a -1 charge, making the second complex the anion. Therefore, you will write the complex with NH_3 first, followed by the one with Cl (the same order as the formula). This coordination compound is called tetraammineplatinum(II) tetrachloroplatinate(II).

Exercise 1.3: The Nitro/Nitrito Ambidentate Ligand

What is the name of $[\mathrm{CoCl(NO_2)(NH_3)_4}]^+$?

Answer

This coordination complex is called tetraamminechloronitrito-N-cobalt(III). N comes before the O in the symbol for the nitrite ligand, so it is called nitrito-N. If an O came first, as in $[CoCl(ONO)(NH_3)_4]^+$, the ligand would be called nitrito-O, yielding the name tetraamminechloronitrito-O-cobalt(III).

Nitro (for NO_2) and nitrito (for ONO) can also be used to describe the nitrite ligand, yielding the names tetraamminechloronitrocobalt(III) and tetraamminechloronitritocobalt(III).

Writing Formulas of Coordination Complexes

While chemistry typically follow the nomenclature rules for naming complexes and compounds, there is disagreement with the rules for constructing formulas of inorganic complexes. For example, the order of ligand names in their formula has been ambiguous with different conventions being used (charged vs neutral, number of each ligand, etc.). In 2005, IUPAC adopted the recommendation that all ligand names in formulas be listed **alphabetically** (in the same way as in the naming convention) irrespective of the charge or number of each ligand type.

However, this rule is not adhered to in many chemistry laboratories. For practice, the order of the ligands in chemical formulas does not matter as long as you write the transition metal first, which is the stance taken here.

Examples 1.4

Write the chemical formulas for:

a. Amminetetraaquachromium(II) ion
b. Amminesulfatochromium(II)

Solution

a. Amminetetraaquachromium(II) ion could be written as $[\mathrm{Cr(H_2O)_4(NH_3)}]^{+2}$ or $[\mathrm{Cr(NH_3)(H_2O)_4}]^{+2}$.
b. Amminesulfatochromium (II) could be written as $[\mathrm{Cr(SO_4)(NH_3)}]$ or $[\mathrm{Cr(NH_3)(SO_4)}]$.

Exercise 1.4

Write the chemical formulas for

a. Amminetetraaquachromium (II) sulfate
b. Potassium hexacyanoferrate (III)

Answer

a. Amminetetraaquachromium (II) sulfate can be written as $[Cr(H_2O)_4(NH_3)]SO_4$. Although $[Cr(NH_3)(H_2O)_4]SO_4$ is also acceptable.
b. Potassium hexacyanoferrate (III) is be written as $K_3[Fe(CN)_6]$

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2: Oxidation States of Transition Metals

The oxidation state of an element is related to the number of electrons that an atom loses, gains, or appears to use when joining with another atom in compounds. It also determines the ability of an atom to oxidize (to lose electrons) or to reduce (to gain electrons) other atoms or species. Almost all of the transition metals have multiple oxidation states experimentally observed.

Introduction

Filling atomic orbitals requires a set number of electrons. The s-block is composed of elements of Groups I and II, the alkali and alkaline earth metals (sodium and calcium belong to this block). Groups XIII through XVIII comprise of the p-block, which contains the nonmetals, halogens, and noble gases (carbon, nitrogen, oxygen, fluorine, and chlorine are common members). Transition metals reside in the d-block, between Groups III and XII. If the following table appears strange, or if the orientations are unclear, please review the section on atomic orbitals.

Table 2.1

s Orbital	p Orbitals	d Orbitals
1 orbital, 2 electrons	3 orbitals: p_x, p_y, p_z; 6 electrons	5 orbitals: $d_{x^2-y^2}$, d_{z^2}, d_{xy}, d_{yz}, d_{xz}; 10 electrons
	Highest energy orbital for a given quantum number n	Degenerate with s-orbital of quantum number n+1

The key thing to remember about electronic configuration is that the most stable noble gas configuration is ideal for any atom. Forming bonds are a way to approach that configuration. In particular, the transition metals form more lenient bonds with anions, cations, and neutral complexes in comparison to other elements. This is because the d orbital is rather diffused (the f orbital of the lanthanide and actinide series more so).

Neutral-Atom Electron Configurations

Counting through the periodic table is an easy way to determine which electrons exist in which orbitals. As mentioned before, by counting protons (atomic number), you can tell the number of electrons in a neutral atom. Organizing by block quickens this process. For example, if we were interested in determining the electronic organization of **Vanadium** (atomic number 23), we would start from hydrogen and make our way down the the Periodic Table).

1s (H, He), 2s (Li, Be), 2p (B, C, N, O, F, Ne), 3s (Na, Mg), 3p (Al, Si, P, S, Cl, Ar), 4s (K, Ca), 3d (Sc, Ti, V).

If you do not feel confident about this counting system and how electron orbitals are filled, please see the section on electron configuration.

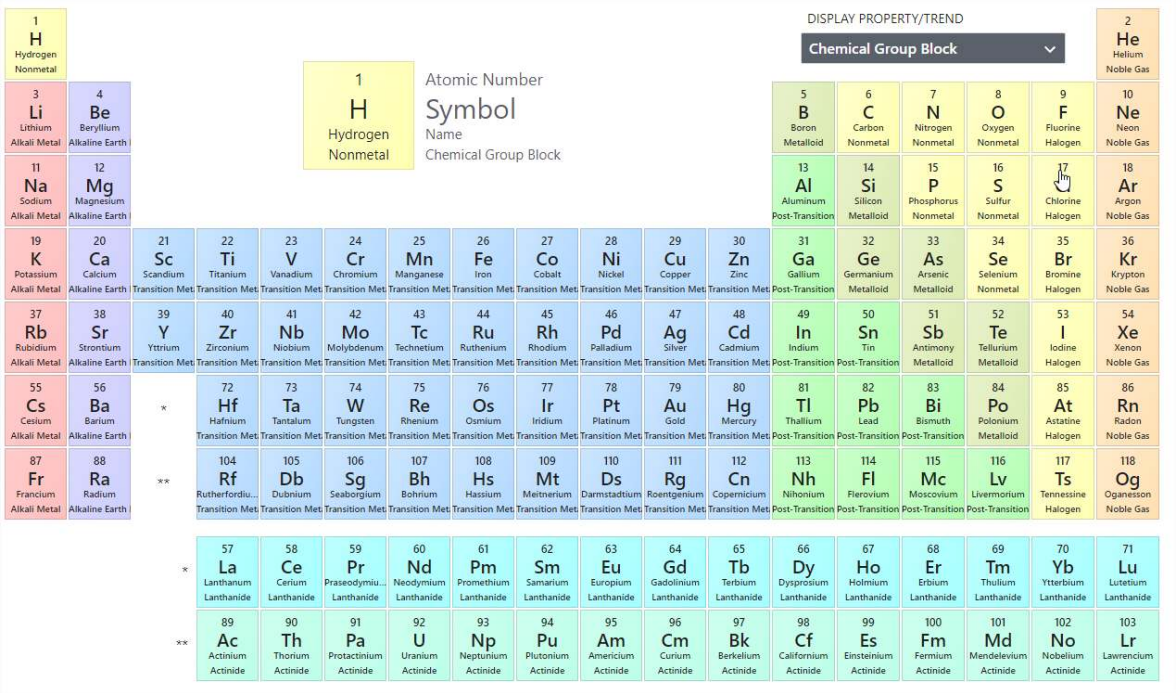


Figure 2.1: Periodic Table (Public Domain; PubChem)

Referring to the periodic table below confirms this organization. We have three elements in the 3d orbital. Therefore, we write in the order the orbitals were filled.

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^3$$

or

$$[Ar]\ 4s^2\ 3d^3.$$

The neutral atom configurations of the fourth period transition metals are in Table 2.2.

Table 2.2

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
[Ar] $4s^2 3d^1$	[Ar] $4s^2 3d^2$	[Ar] $4s^2 3d^3$	~~[Ar] $4s^2 3d^4$~~	[Ar] $4s^2 3d^5$	[Ar] $4s^2 3d^6$	[Ar] $4s^2 3d^7$	[Ar] $4s^2 3d^8$	~~[Ar] $4s^2 3d^9$~~	[Ar] $4s^2 3d^{10}$
			[Ar] $4s^1 3d^5$					[Ar] $4s^1 3d^{10}$	

Chromium and copper appear anomalous. Take a brief look at where the element **Chromium** (atomic number 24) lies on the Periodic Table (Figure 2.1). The electronic configuration for chromium is not [Ar] $4s^2 3d^4$ but instead it is [Ar] $4s^1 3d^5$. This is because the half-filled 3d manifold (with one 4s electron) is more stable than a partially filled d-manifold (and a filled 4s manifold). You will notice from Table 2.2 that the copper exhibits a similar phenomenon, although with a fully filled d-manifold.

Oxidation States of Transition Metal Ions

When considering ions, we add or subtract negative charges from an atom. Keeping the atomic orbitals when assigning oxidation numbers in mind helps in recognizing that transition metals pose a special case, but not an exception to this convenient method. An atom that accepts an electron to achieve a more stable configuration is assigned an oxidation number of -1. The donation of an electron is then +1. When a transition metal loses electrons, it tends to lose it's s orbital electrons before any of its d orbital electrons. For more discussion of these compounds form, see formation of coordination complexes.

Example 2.1

Write the electronic configurations of:

a. neutral iron,
b. iron(II) ion, and
c. iron(III) ion.

Answer

The atomic number of iron is 26 so there are 26 protons in the species.

a. Fe: [Ar] $4s^2$ $3d^6$
b. Fe^{2+}: [Ar] $3d^6$
c. Fe^{3+}: [Ar] $3d^5$

Note that the s-orbital electrons are lost **first**, then the d-orbital electrons.

Example 2.2

Determine the more stable configuration between the following pair:

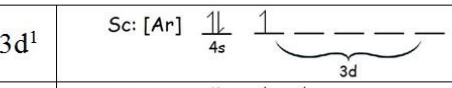
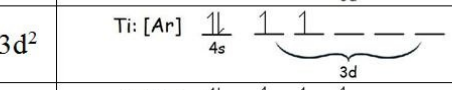
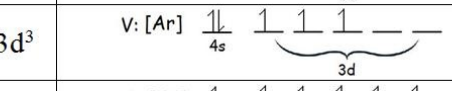
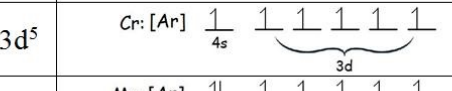
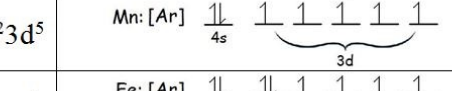
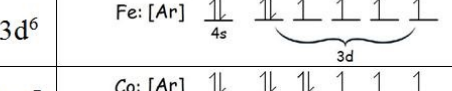
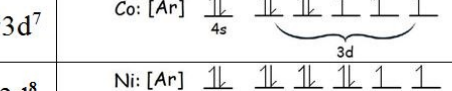
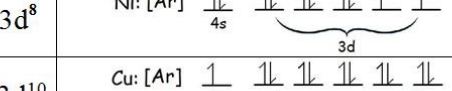
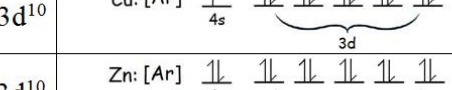
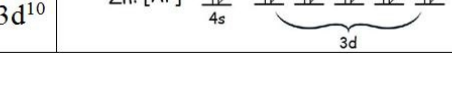
a. [Kr] $5s^2$ $4d^6$ vs. [Kr] $5s^1$ $4d^7$
b. Ag^{1+} vs. Ag^{2+}

Answer

a. This describes Ruthenium. There is only one 5s electron.
b. Once-oxidized silver ([Kr] $4d^{10}$) is more stable than twice- ([Kr] $4d^9$).

Multiple Oxidation States

Most transition metals have multiple oxidation states, since it is relatively easy to lose electron(s) for transition metals compared to the alkali metals and alkaline earth metals. Alkali metals have one electron in their valence s-orbital and their ions almost always have oxidation states of +1 (from losing a single electron). Similarly, alkaline earth metals have two electrons in their valences s-orbitals, resulting in ions with a +2 oxidation state (from losing both). However, transitions metals are more complex and exhibit a range of observable oxidation states due primarily to the removal of d-orbital electrons. The following chart describes the most common oxidation states of the period 3 elements.

Element Name and Symbol	Atomic Number	Common Oxidation States	Electron Configuration	
Scandium (Sc)	21	+3	Sc: [Ar] $4s^2 3d^1$	
Titanium (Ti)	22	+4	Ti: [Ar] $4s^2 3d^2$	
Vanadium (V)	23	+2, +3, +4, +5	V: [Ar] $4s^2 3d^3$	
Chromium (Cr)	24	+2, +3, +6	Cr: [Ar] $4s^1 3d^5$	
Manganese (Mn)	25	+2, +3, +4, +6, +7	Mn: [Ar] $4s^2 3d^5$	
Iron (Fe)	26	+2, +3	Fe: [Ar] $4s^2 3d^6$	
Cobalt (Co)	27	+2, +3	Co: [Ar] $4s^2 3d^7$	
Nickel (Ni)	28	+2	Ni: [Ar] $4s^2 3d^8$	
Copper (Cu)	29	+1,+2	Cu: [Ar] $4s^1 3d^{10}$	
Zinc (Zn)	30	+2	Zn: [Ar] $4s^2 3d^{10}$	

Scandium is one of the two elements in the first transition metal period which has only one oxidation state (zinc is the other, with an oxidation state of +2). All the other elements have at least two different oxidation states. Manganese, which is in the middle of the period, has the highest number of oxidation states, and indeed the highest oxidation state in the whole period since it has five unpaired electrons (see table below).

To help remember the stability of higher oxidation states for transition metals it is important to know the trend: the stability of the higher oxidation states progressively increases down a group. For example, in group 6, (chromium) Cr is most stable at a +3 oxidation state, meaning that you will not find many stable forms of Cr in the +4 and +5 oxidation states. By contrast, there are many stable forms of molybdenum (Mo) and tungsten (W) at +4 and +5 oxidation states.

Example 2.3

What makes zinc stable as Zn^{2+}? What makes scandium stable as Sc^{3+}?

Answer

Zinc has the neutral configuration $[Ar]4s^2 3d^{10}$. Losing 2 electrons does not alter the complete d orbital. Neutral scandium is written as $[Ar]4s^2 3d^1$. Losing 3 electrons brings the configuration to the noble state with valence $3p^6$.

Example 2.4

Why is iron almost always Fe^{2+} or Fe^{3+}?

Answer

Iron is written as $[Ar]4s^2 3d^6$. Losing 2 electrons from the s-orbital ($3d^6$) or 2 s- and 1 d-orbital ($3d^5$) electron are fairly stable oxidation states.

Example 2.5

Write manganese oxides in a few different oxidation states. Which ones are possible and/or reasonable?

Answer

Although Mn^{+2} is the most stable ion for manganese, the d-orbital can be made to remove 0 to 7 electrons. Compounds of manganese therefore range from Mn(0) as $Mn_{(s)}$, Mn(II) as MnO, Mn(II,III) as Mn_3O_4, Mn(IV) as MnO_2, or manganese dioxide, Mn(VII) in the permanganate ion MnO_4^-, and so on.

Oxidation State of Transition Metals in Compounds

When given an ionic compound such as $AgCl$, you can easily determine the oxidation state of the transition metal. In this case, you would be asked to determine the oxidation state of silver (Ag). Since we know that chlorine (Cl) is in the halogen group of the periodic table, we then know that it has a charge of -1, or simply Cl^-. In addition, by seeing that there is no overall charge for $AgCl$, (which is determined by looking at the top right of the compound, i.e., $AgCl^{\#}$, where # represents the overall charge of the compound) we can conclude that silver (Ag) has an oxidation state of +1. This gives us Ag^+ and Cl^-, in which the positive and negative charge cancels each other out, resulting with an overall neutral charge; therefore +1 is verified as the oxidation state of silver (Ag).

Example 2.6

Determine the oxidation state of cobalt in $CoBr_2$.

Answer

Similar to chlorine, bromine (Br) is also a halogen with an oxidation charge of -1 (Br^-). Since there are two bromines each with a charge of -1. In addition, we know that $CoBr_2$ has an overall neutral charge, therefore we can conclude that the cation (cobalt), Co must have an oxidation state of +2 to neutralize the -2 charge from the two bromine anions.

Example 2.7

What is the oxidation state of zinc in $ZnCO_3$. (Note: the CO_3 anion has a charge state of -2)

Answer

Knowing that CO_3 has a charge of -2 and knowing that the overall charge of this compound is neutral, we can conclude that zinc has an oxidation state of +2. This gives us Zn^{2+} and CO_3^{-2}, in which the positive and negative charges from zinc and carbonate will cancel with each other, resulting in an overall neutral charge expected of a compound.

Polyatomic Transition Metal Ions

Consider the manganese (Mn) atom in the permanganate (MnO_4^-) ion. Since oxygen has an oxidation state of -2 and we know there are four oxygen atoms. In addition, this compound has an overall charge of -1; therefore the overall charge is not neutral in this example. Thus, since the oxygen atoms in the ion contribute a total oxidation state of -8, and since the overall charge of the ion is -1, the sole manganese atom must have an oxidation state of +7. This gives us Mn^{7+} and 4 O^{2-}, which will result as MnO_4^-.

> *This example also shows that manganese atoms can have an oxidation state of +7, which is the highest possible oxidation state for the fourth period transition metals.*

Manganese: A Case Study

Manganese is widely studied because it is an important reducing agent in chemical analysis and is also studied in biochemistry for catalysis and in metallurgy in fortifying alloys. In plants, manganese is required in trace amounts; stronger doses begin to react with enzymes and inhibit some cellular function. Due to manganese's flexibility in accepting many oxidation states, it becomes a good example to describe general trends and concepts behind electron configurations.



Figure 2.2: (left) A rough fragment of lustrous silvery metal (CC BY-SA 3.0; Tomihahndorf via Wikipedia) (right) Some of the Lascaux cave paintings use manganese-based pigments. (Public Domain; Prof saxx via Wikipedia)

Electron configurations of unpaired electrons are said to be **paramagnetic** and respond to the proximity of magnets. Fully paired electrons are **diamagnetic** and do not feel this influence. Manganese, in particular, has paramagnetic and diamagnetic orientations depending on what its oxidation state is.

Mn_2O_3 is manganese(III) oxide with manganese in the +3 state. 4 unpaired electrons means this complex is paramagnetic.

$$[\mathrm{Ar}]4s^0 3d^4$$

MnO_2 is manganese(IV) oxide, where manganese is in the +4 state. 3 unpaired electrons means this complex is less paramagnetic than Mn^{3+}.

$$[\mathrm{Ar}]4s^0 3d^3$$

$KMnO_4$ is potassium permanganate, where manganese is in the +7 state with no electrons in the 4s and 3d orbitals.

$$[\mathrm{Ar}]4s^0 3d^0$$

Since the 3p orbitals are all paired, this complex is diamagnetic.

Summary

Oxidation states of transition metals follow the general rules for most other ions, except for the fact that the d orbital is degenerated with the s orbital of the higher quantum number. Transition metals achieve stability by arranging their electrons accordingly and are oxidized, or they lose electrons to other atoms and ions. These resulting cations participate in the formation of coordination complexes or synthesis of other compounds.

Questions

Determine the oxidation states of the transition metals found in these neutral compounds. Note: The transition metal is underlined in the following compounds.

(A) Copper(I) Chloride: $\underline{Cu}Cl$	(B) Copper(II) Nitrate: $\underline{Cu}(NO_3)_2$	(C) Gold(V) Fluoride: $\underline{Au}F_5$
(D) Iron(II) Oxide: $\underline{Fe}O$	(E) Iron(III) Oxide: $\underline{Fe}_2O_3$	(F) Lead(II) Chloride: $\underline{Pb}Cl_2$
(G) Lead(II) Nitrate: $\underline{Pb}(NO_3)_2$	(H) Manganese(II) Chloride: $\underline{Mn}Cl_2$	(I) Molybdenum trioxide: $\underline{Mo}O_3$
(J) Nickel(II) Hydroxide: $\underline{Ni}(OH)_2$	(K) Platinum(IV) Chloride: $\underline{Pt}Cl_4$	(L) Silver Sulfide: $\underline{Ag}_2S$
(M) Tungsten(VI) Fluoride: $\underline{W}F_6$	(N) Vanadium(III) Nitride: $\underline{V}N$	(O) Zirconium Hydroxide: $\underline{Zr}(OH)_4$

1. Determine the oxidation state of the transition metal for an overall non-neutral compound: Manganate ($\underline{Mn}O_4^{2-}$)
2. Why do transition metals have a greater number of oxidation states than main group metals (i.e. alkali metals and alkaline earth metals)?
3. Which transition metal has the most number of oxidation states?
4. Why does the number of oxidation states for transition metals increase in the middle of the group?

5. What two transition metals have only one oxidation state?

References

1. Oxtoby D, Gillis H P, Campion, A. *Principles of Modern Chemistry, 6th ed.* Thomson Brooks/Cole, Belmont. 2008; 313-318.
2. Audi A, Sherwood, P. *Valence-band x-ray photoelectron spectroscopic studies of manganese and its oxides interpreted by cluster and band structure calculations*; Surf. Interface Anal.; 2002; 33; 274-282.
3. Reaney S, Kwik-Uribe C, Smith D. *Manganese Oxidation State and Its Implications for Toxicity.* Chem. Res. Toxicol.; 2002; 15; 1119-1126.
4. *CRC Handbook, 88th ed. Sct. 1, Prt. 1 Electron Configuration and Ionization Energy of Neutral Atoms in the Ground State*; 13-14.
5. *CRC Handbook, 88th ed. Sct. 4, Prt. 1 Melting, Boiling, Triple, and Critical Point Temperatures of the Elements*; 133-134.

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3: History of Coordination compounds

Learning Objectives

- To know the most common structures observed for metal complexes.
- To predict the relative stabilities of metal complexes with different ligands

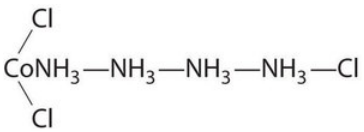
One of the most important properties of metallic elements is their ability to act as Lewis acids that form complexes with a variety of Lewis bases. A metal complex consists of a central metal atom or ion that is bonded to one or more ligands (from the Latin ligare, meaning “to bind”), which are ions or molecules that contain one or more pairs of electrons that can be shared with the metal. Metal complexes can be neutral, such as $Co(NH_3)_3Cl_3$; positively charged, such as $[Nd(H_2O)_9]^{3+}$; or negatively charged, such as $[UF_8]^{4-}$. Electrically charged metal complexes are sometimes called *complex ions*. A *coordination compound* contains one or more metal complexes.

Coordination compounds are important for at least three reasons. First, most of the elements in the periodic table are metals, and almost all metals form complexes, so metal complexes are a feature of the chemistry of more than half the elements. Second, many industrial catalysts are metal complexes, and such catalysts are steadily becoming more important as a way to control reactivity. For example, a mixture of a titanium complex and an organometallic compound of aluminum is the catalyst used to produce most of the polyethylene and polypropylene “plastic” items we use every day. Finally, transition-metal complexes are essential in biochemistry. Examples include hemoglobin, an iron complex that transports oxygen in our blood; cytochromes, iron complexes that transfer electrons in our cells; and complexes of Fe, Zn, Cu, and Mo that are crucial components of certain enzymes, the catalysts for all biological reactions.

History of the Coordination Compounds

Coordination compounds have been known and used since antiquity; probably the oldest is the deep blue pigment called Prussian blue: $KFe_2(CN)_6$. The chemical nature of these substances, however, was unclear for a number of reasons. For example, many compounds called “double salts” were known, such as $AlF_3 \cdot 3\,KF$, $Fe(CN)_2 \cdot 4\,KCN$, and $ZnCl_2 \cdot 2\,CsCl$, which were combinations of simple salts in fixed and apparently arbitrary ratios. Why should $AlF_3 \cdot 3\,KF$ exist but not $AlF_3 \cdot 4\,KF$ or $AlF_3 \cdot 2\,KF$? And why should a 3:1 KF:AlF3 mixture have different chemical and physical properties than either of its components? Similarly, adducts of metal salts with neutral molecules such as ammonia were also known—for example, $CoCl_3 \cdot 6\,NH_3$, which was first prepared sometime before 1798. Like the double salts, the compositions of these adducts exhibited fixed and apparently arbitrary ratios of the components. For example, $CoCl_3 \cdot 6\,NH_3$, $CoCl_3 \cdot 5\,NH_3$, $CoCl_3 \cdot 4\,NH_3$, and $CoCl_3 \cdot 3\,NH_3$ were all known and had very different properties, but despite all attempts, chemists could not prepare $CoCl_3 \cdot 2\,NH_3$ or $CoCl_3 \cdot NH_3$.

Although the chemical composition of such compounds was readily established by existing analytical methods, their chemical nature was puzzling and highly controversial. The major problem was that what we now call valence (i.e., the oxidation state) and coordination number were thought to be identical. As a result, highly implausible (to modern eyes at least) structures were proposed for such compounds, including the “Chattanooga choo-choo” model for $CoCl_3 \cdot 4NH_3$ shown here.



$CoCl_3 \cdot 4NH_3$

The modern theory of coordination chemistry is based largely on the work of Alfred Werner (1866–1919; Nobel Prize in Chemistry in 1913). In a series of careful experiments carried out in the late 1880s and early 1890s, he examined the properties of several series of metal halide complexes with ammonia. For example, five different “adducts” of ammonia with $PtCl_4$ were known at the time: $PtCl_4 \cdot nNH_3$ (n = 2–6). Some of Werner’s original data on these compounds are shown in Table 3.1. The electrical conductivity of aqueous solutions of these compounds was roughly proportional to the number of ions formed per mole, while the number of chloride ions that could be precipitated as AgCl after adding $Ag^+(aq)$ was a measure of the number of “free” chloride ions present. For example, Werner’s data on $PtCl_4 \cdot 6NH_3$ in Table 3.1 showed that all the chloride ions were present as free chloride. In contrast, $PtCl_4 \cdot 2NH_3$ was a neutral molecule that contained no free chloride ions.

Alfred Werner (1866–1919)

Werner, the son of a factory worker, was born in Alsace. He developed an interest in chemistry at an early age, and he did his first independent research experiments at age 18. While doing his military service in southern Germany, he attended a series of chemistry lectures, and he subsequently received his PhD at the University of Zurich in Switzerland, where he was appointed professor of chemistry at age 29. He won the Nobel Prize in Chemistry in 1913 for his work on coordination compounds, which he performed as a graduate student and first presented at age 26. Apparently, Werner was so obsessed with solving the riddle of the structure of coordination compounds that his brain continued to work on the problem even while he was asleep. In 1891, when he was only 25, he woke up in the middle of the night and, in only a few hours, had laid the foundation for modern coordination chemistry.

Table 3.1: Werner's Data on Complexes of Ammonia with $PtCl_4$

Complex	Conductivity (ohm^{-1})	Number of Ions per Formula Unit	Number of Cl^- Ions Precipitated by Ag^+
$PtCl_4 \cdot 6NH_3$	523	5	4
$PtCl_4 \cdot 5NH_3$	404	4	3
$PtCl_4 \cdot 4NH_3$	299	3	2
$PtCl_4 \cdot 3NH_3$	97	2	1
$PtCl_4 \cdot 2NH_3$	0	0	0

These data led Werner to postulate that metal ions have two different kinds of valence: (1) a primary valence (**oxidation state**) that corresponds to the positive charge on the metal ion and (2) a secondary valence (**coordination number**) that is the total number of ligand-metal bonds bound to the metal ion. If Pt had a primary valence of 4 and a secondary valence of 6, Werner could explain the properties of the $PtCl_4 \cdot NH_3$ adducts by the following reactions, where the metal complex is enclosed in square brackets:

$$[Pt(NH_3)_6]Cl_4 \rightarrow [Pt(NH_3)_6]^{4+}(aq) + 4Cl^-(aq)$$
$$[Pt(NH_3)_5Cl]Cl_3 \rightarrow [Pt(NH_3)_5Cl]^{3+}(aq) + 3Cl^-(aq)$$
$$[Pt(NH_3)_4Cl_2]Cl_2 \rightarrow [Pt(NH_3)_4Cl_2]^{2+}(aq) + 2Cl^-(aq)$$
$$[Pt(NH_3)_3Cl_3]Cl \rightarrow [Pt(NH_3)_3Cl_3]^{+}(aq) + Cl^-(aq)$$
$$[Pt(NH_3)_2Cl_4] \rightarrow [Pt(NH_3)_2Cl_4]^{0}(aq)$$

Further work showed that the two missing members of the series—$[Pt(NH_3)Cl_5]^-$ and $[PtCl_6]^{2-}$—could be prepared as their mono- and dipotassium salts, respectively. Similar studies established coordination numbers of 6 for Co^{3+} and Cr^{3+} and 4 for Pt^{2+} and Pd^{2+}.

Werner's studies on the analogous Co^{3+} complexes also allowed him to propose a structural model for metal complexes with a coordination number of 6. Thus he found that $[Co(NH_3)_6]Cl_3$ (yellow) and $[Co(NH_3)_5Cl]Cl_2$ (purple) were 1:3 and 1:2 electrolytes. Unexpectedly, however, two different $[Co(NH_3)_4Cl_2]Cl$ compounds were known: one was red, and the other was green (Figure 3.1*a*). Because both compounds had the same chemical composition and the same number of groups of the same kind attached to the same metal, there had to be something different about the arrangement of the ligands around the metal ion. Werner's key insight was that the six ligands in $[Co(NH_3)_4Cl_2]Cl$ had to be arranged at the vertices of an octahedron because that was the only structure consistent with the existence of two, and only two, arrangements of ligands (Figure 3.1*b*. His conclusion was corroborated by the existence of only two different forms of the next compound in the series: $Co(NH_3)_3Cl_3$.

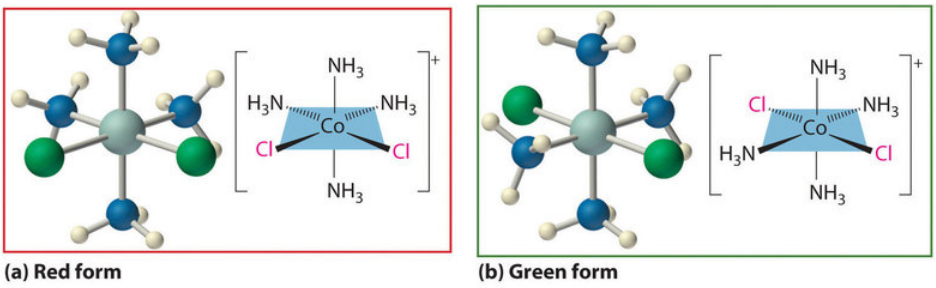


Figure 3.1: Complexes with Different Arrangements of the Same Ligands Have Different Properties. The $[Co(NH_3)_4Cl_2]^+$ ion can have two different arrangements of the ligands, which results in different colors: if the two Cl^- ligands are next to each other, the complex is red (a), but if they are opposite each other, the complex is green (b).

Example 3.1

In Werner's time, many complexes of the general formula MA_4B_2 were known, but no more than two different compounds with the same composition had been prepared for any metal. To confirm Werner's reasoning, calculate the maximum number of different structures that are possible for six-coordinate MA_4B_2 complexes with each of the three most symmetrical possible structures: a hexagon, a trigonal prism, and an octahedron. What does the fact that no more than two forms of any MA_4B_2 complex were known tell you about the three-dimensional structures of these complexes?

Given: three possible structures and the number of different forms known for MA_4B_2 complexes

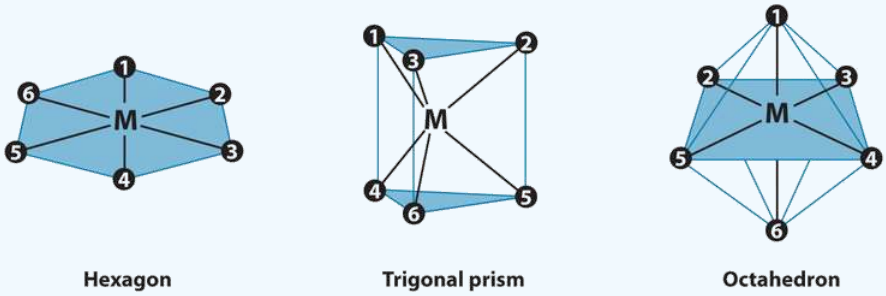
Asked for: number of different arrangements of ligands for MA_4B_2 complex for each structure

Strategy:

Sketch each structure, place a B ligand at one vertex, and see how many different positions are available for the second B ligand.

Solution

The three regular six-coordinate structures are shown here, with each coordination position numbered so that we can keep track of the different arrangements of ligands. For each structure, all vertices are equivalent. We begin with a symmetrical MA_6 complex and simply replace two of the A ligands in each structure to give an MA_4B_2 complex:



For the hexagon, we place the first B ligand at position 1. There are now three possible places for the second B ligand: at position 2 (or 6), position 3 (or 5), or position 4. These are the only possible arrangements. The (1, 2) and (1, 6) arrangements are chemically identical because the two B ligands are adjacent to each other. The (1, 3) and (1, 5) arrangements are also identical because in both cases the two B ligands are separated by an A ligand.

Turning to the trigonal prism, we place the first B ligand at position 1. Again, there are three possible choices for the second B ligand: at position 2 or 3 on the same triangular face, position 4 (on the other triangular face but adjacent to 1), or position 5 or 6 (on the other triangular face but not adjacent to 1). The (1, 2) and (1, 3) arrangements are chemically identical, as are the (1, 5) and (1, 6) arrangements.

In the octahedron, however, if we place the first B ligand at position 1, then we have only two choices for the second B ligand: at position 2 (or 3 or 4 or 5) or position 6. In the latter, the two B ligands are at opposite vertices of the octahedron, with the metal lying directly between them. Although there are four possible arrangements for the former, they are chemically identical because in all cases the two B ligands are adjacent to each other.

The number of possible MA_4B_2 arrangements for the three geometries is thus: hexagon, 3; trigonal prism, 3; and octahedron, 2. The fact that only two different forms were known for all MA_4B_2 complexes that had been prepared suggested that the correct structure was the octahedron but did not prove it. For some reason one of the three arrangements possible for the other two structures could have been less stable or harder to prepare and had simply not yet been synthesized. When combined with analogous results for other types of complexes (e.g., MA_3B_3), however, the data were best explained by an octahedral structure for six-coordinate metal complexes.

? Exercise 3.1

Determine the maximum number of structures that are possible for a four-coordinate MA_2B_2 complex with either a square planar or a tetrahedral symmetrical structure.

Answer

square planar, 2; tetrahedral, 1

Structures of Metal Complexes

The coordination numbers of metal ions in metal complexes can range from 2 to at least 9. In general, the differences in energy between different arrangements of ligands are greatest for complexes with low coordination numbers and decrease as the coordination number increases. Usually only one or two structures are possible for complexes with low coordination numbers, whereas several different energetically equivalent structures are possible for complexes with high coordination numbers ($n > 6$). The following presents the most commonly encountered structures for coordination numbers 2–9. Many of these structures should be familiar to you from our discussion of the valence-shell electron-pair repulsion (VSEPR) model because they correspond to the lowest-energy arrangements of n electron pairs around a central atom.

> *Compounds with low coordination numbers exhibit the greatest differences in energy between different arrangements of ligands.*

Coordination Number 2

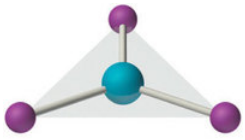
Although it is rare for most metals, this coordination number is surprisingly common for d^{10} metal ions, especially Cu^+, Ag^+, Au^+, and Hg^{2+}. An example is the $[Au(CN)_2]^-$ ion, which is used to extract gold from its ores. As expected based on VSEPR considerations, these complexes have the linear L–M–L structure shown here.



Linear ML_2

Coordination Number 3

Although it is also rare, this coordination number is encountered with d^{10} metal ions such as Cu^+ and Hg^{2+}. Among the few known examples is the HgI_3^- ion. Three-coordinate complexes almost always have the trigonal planar structure expected from the VSEPR model.

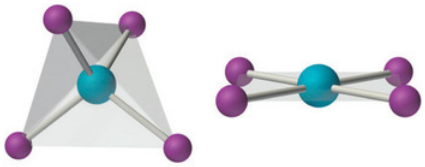


Trigonal planar ML_3

Coordination Number 4

Two common structures are observed for four-coordinate metal complexes: tetrahedral and square planar. The tetrahedral structure is observed for all four-coordinate complexes of nontransition metals, such as $[BeF_4]^{2-}$, and d^{10} ions, such as $[ZnCl_4]^{2-}$. It is also found for four-coordinate complexes of the first-row transition metals, especially those with halide ligands (e.g., $[FeCl_4]^-$ and $[FeCl_4]^{2-}$). In contrast, square planar structures are routinely observed for four-coordinate complexes of second- and third-row

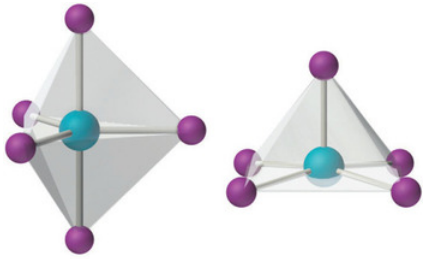
transition metals with d^8 electron configurations, such as Rh^+ and Pd^{2+}, and they are also encountered in some complexes of Ni^{2+} and Cu^{2+}.



Tetrahedral and square planar ML_4

Coordination Number 5

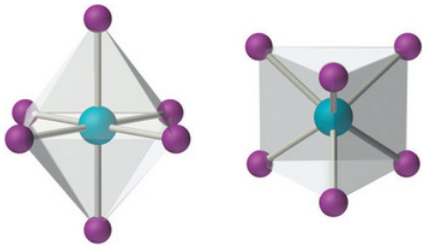
This coordination number is less common than 4 and 6, but it is still found frequently in two different structures: trigonal bipyramidal and square pyramidal. Because the energies of these structures are usually rather similar for most ligands, many five-coordinate complexes have distorted structures that lie somewhere between the two extremes.



Trigonal bipyramidal and square pyramidal ML_5

Coordination Number 6

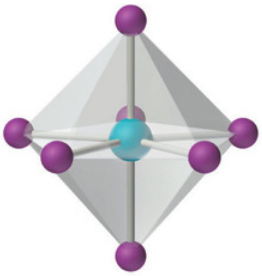
This coordination number is by far the most common. The six ligands are almost always at the vertices of an octahedron or a distorted octahedron. The only other six-coordinate structure is the trigonal prism, which is very uncommon in simple metal complexes.



Octahedral and trigonal prismatic ML_6

Coordination Number 7

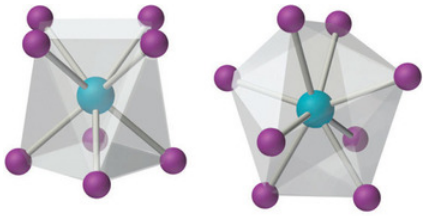
This relatively uncommon coordination number is generally encountered for only large metals (such as the second- and third-row transition metals, lanthanides, and actinides). At least three different structures are known, two of which are derived from an octahedron or a trigonal prism by adding a ligand to one face of the polyhedron to give a “capped” octahedron or trigonal prism. By far the most common, however, is the pentagonal bipyramid.



Pentagonal bipyramidal ML_7

Coordination Number 8

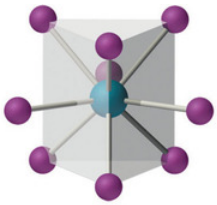
This coordination number is relatively common for larger metal ions. The simplest structure is the cube, which is rare because it does not minimize interligand repulsive interactions. Common structures are the square antiprism and the dodecahedron, both of which can be generated from the cube.



Square antiprismatic and trigonal dodecahedral ML_8

Coordination Number 9

This coordination number is found in larger metal ions, and the most common structure is the tricapped trigonal prism, as in $[Nd(H_2O)_9]^{3+}$.



Tricapped trigonal prismatic ML_9

Key Takeaways

- Coordination compounds are a major feature of the chemistry of over half the elements.
- Coordination compounds have important roles as industrial catalysts in controlling reactivity, and they are essential in biochemical processes.

Summary

Transition metals form metal complexes, polyatomic species in which a metal ion is bound to one or more ligands, which are groups bound to a metal ion. Complex ions are electrically charged metal complexes, and a coordination compound contains one or more metal complexes. Metal complexes with low coordination numbers generally have only one or two possible structures, whereas those with coordination numbers greater than six can have several different structures. Coordination numbers of two and three are common for d^{10} metal ions. Tetrahedral and square planar complexes have a coordination number of four; trigonal bipyramidal and square pyramidal complexes have a coordination number of five; and octahedral complexes have a coordination number of six. At least three structures are known for a coordination number of seven, which is generally found for only large metal ions. Coordination numbers of eight and nine are also found for larger metal ions.

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4: Coordination Number and Geometry

The total number of points of attachment to the central element is termed the **coordination number** and this can vary from 2 to as many as 16, but is usually 6. In simple terms, the coordination number of a complex is influenced by the relative sizes of the metal ion and the ligands and by electronic factors, such as charge which is dependent on the electronic configuration of the metal ion.

Introduction

Based on the radius ratio, it can be seen that the bigger the charge on the central ion, the more attraction there will be for negatively charged ligands, however at the same time, the bigger the charge the smaller the ion becomes which then limits the number of groups able to coordinate. It is important to recognize that every geometry has a specific coordination number, but every complex wish a specific coordination number will have a choice of several possible geometries (i.e., there is not a one-to-one correspondance between coordination number and geometry).

Coordination Number 2

This arrangement is not very common for first row transition metal ion complexes and some of the best known examples are for Silver(I). In this case we have a low charge and an ion at the right hand side of the d-block indicating smaller size

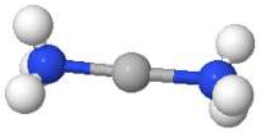


Figure 1: The linear $[Ag(NH_3)_2]^+$ ion

Coordination Number 3

Once again, this is not very common for first row transition metal ions. Examples with three different geometries have been identified:

- **Trigonal planar Geometry**: Well known for main group species like CO_3^{2-} etc., this geometry has the four atoms in a plane with the bond angles between the ligands at 120 degrees.

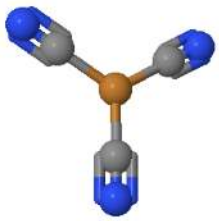


Figure 2: The Trigonal planar $[Cu(CN)_3]^{2-}$ system

- **Trigonal pyramid Geometry**: More common with main group ions.
- **T-shaped**: The first example of a rare T-shaped molecule was found in 1977.

Coordination Number 4

Two different geometries are possible. The tetrahedron is the more common while the square planar is found almost exclusively with metal ions having a d^8 electronic configuration.

- **Tetrahedral Geometry**: The chemistry of molecules centered around a tetrahedral C atom is covered in organic courses. To be politically correct, please change all occurrences of C to Co. There are large numbers of tetrahedral Cobalt(II) complexes known.

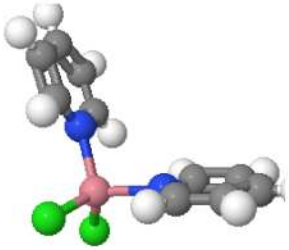


Figure 3: $CoCl_2pyr_2$

- **Square Planar Geometry:** This is fairly rare and is included only because some extremely important molecules exist with this shape.

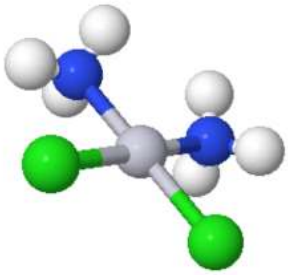


Figure 4: cisplatin - cis-$PtCl_2(NH_3)_2$

Coordination Number 5

- **Square pyramid Geometry:** Oxovanadium salts (Vanadyl, VO^{2+}) often show square pyramidal geometry, for example, $VO(acac)_2$. Note that the Vanadium(IV) can be considered coordinatively unsaturated and addition of pyridine leads to the formation of an octahedral complex.
- **Trigonal Bipyramid Geometry:** The structure of $[Cr(en)_3][Ni(CN)_5]$ 1.5 H_2O was reported in 1968 to be a remarkable example of a complex exhibiting both types of geometry in the same crystal. The reaction of cyanide ion with Ni^{2+} proceeds via several steps:

$$Ni^{2+} + 2CN^- \rightarrow Ni(CN)_2$$

$$Ni(CN)_2 + 2CN^- \rightarrow \underset{\text{orange-red}}{[Ni(CN)_4]^{2-}}$$

with $\log(\beta_4) = 30.1$

$$[Ni(CN)_4]^{2-} + CN^- \rightarrow \underset{\text{deep red}}{[Ni(CN)_5]^{3-}}$$

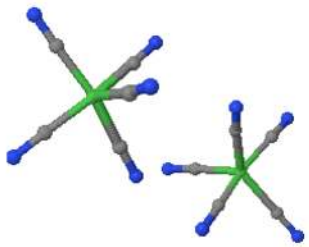


Figure 5: $[Ni(CN)_5]^{3-}$

Coordination Number 6

- **Hexagonal planar Geometry**: Unknown for first row transition metal ions, although the arrangement of six groups in a plane is found in some higher coordination number geometries.

- **Trigonal prism Geometry**: Most trigonal prismatic compounds have three bidentate ligands such as dithiolates or oxalates and few are known for first row transition metal ions.
- **Octahedral (Oh):** The most common geometry found for first row transition metal ions, including all aqua ions. In some cases distortions are observed and these can sometimes be explained in terms of the Jahn-Teller Theorem.

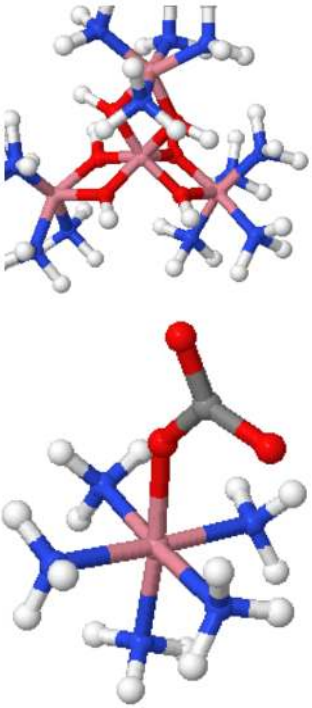


Figure 6: $[Co(en)_3]Cl_3$(left) and $[CoCO_3(NH_3)_5]^+$ (right)

Coordination Number 7

Not very common for 1st row complexes and the energy difference between the structures seems small and distortions occur so that prediction of the closest "idealized" shape is generally difficult. Three geometries are possible:

- **Capped octahedron (C_{3v}) Geometry**

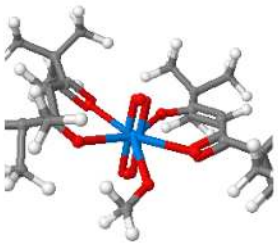


Figure 7: $K_3[NbOF_6]$

- **Capped trigonal prism (C_{2v})**
- **Pentagonal Bipyramid (D_{5h})**

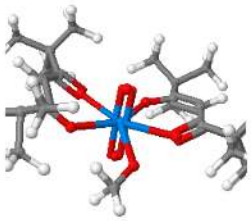


Figure 8: bis-(tert-butylacac)$_2$(DMSO)di-oxoUranium

Coordination Number 8

- **Dodecahedron (D_{2d}) Geometry**
- **Cube (O_h) Geometry**
- **Square antiprism (D_{4d}) Geometry**
- **Hexagonal bipyramid (D_{6h}) Geometry**

Coordination Number 9

- **Three-face centered trigonal prism (D_{3h}) Geometry**

Coordination Number 10

- **Bicapped square antiprism (D_{4d}) Geometry**

Coordination Number 11

- **All-faced capped trigonal prism (D_{3h}) Geometry: This is not a common stereochemistry.**

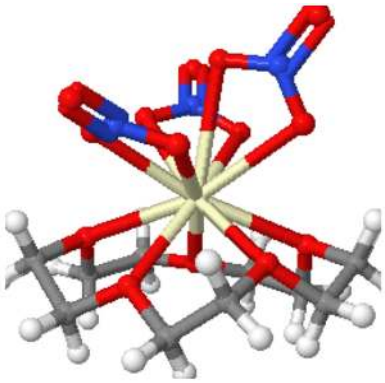


***Figure 9**: aqua-(12-crown-4)-tris(nitrato-O,O')-cerium(III) (12-crown-4) solvate and (15-crown-5)-tris(nitrato-O,O')-cerium(III) the Cerium ion is 11 coordinate.*

Coordination Number 12

- **cuboctahedron (O_h) Geometry**

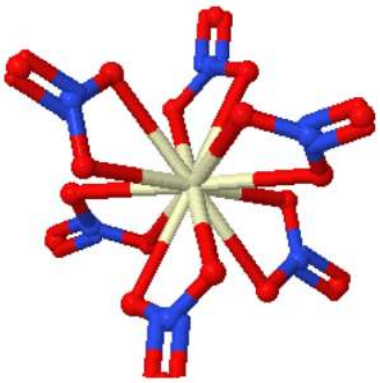


Figure 10: Ceric ammonium nitrate -$(NH_4)_2Ce(NO_3)_6$

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4.1: Isomers

This section will be about isomerism in coordination compounds. You may know isomerism already from your organic chemistry classes. Here, we will apply isomerism to coordination chemistry. Some forms of isomerism in organic and coordination chemistry are the same, but there are some forms of isomerism that only occur in coordination chemistry.

Let us first briefly review the definition of isomerism: Isomerism is when two or more compounds have identical empirical formulas but different structures.

Definition: Isomerism

When two or more compounds have identical empirical formulas but different structures they are called isomers.

We distinguish between two basic types of isomerisms: Constitutional isomerism and stereoisomerism. What is the difference? In constitutional isomerism the bonds are not between the same atoms.

Definition: Constitutional Isomers

In constitutional isomers the bonds are not between the same atoms.

In stereoisomerism, the bonds are between the same atoms, but ligands are at different coordination sites.

Definition: Stereoisomers

In stereoisomers, the bonds are between same atoms, but the ligands are at different coordination sites.

Forms of Constitutional Isomerism

Hydrate Isomerism

First, let us look more closely at hydrate isomerism. In hydrate isomerism, in one isomer a water ligand is in the first coordination sphere, and in the other isomer it is in the second coordination sphere. A water molecule in the second coordination sphere is only defined for the solid state, but not in solution. This is because in solution the water molecule would become part of the solvent. Here are a few examples for hydrate isomers.

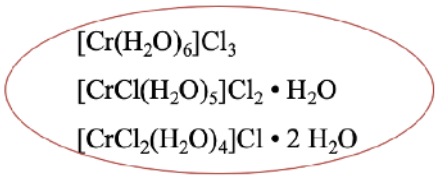


Figure 5.4.1 Two hydrate isomers of the complex $[Cr(H_2O)_6]Cl_3$

In the complex $[Cr(H_2O)_6]Cl_3$ there are six aqua ligands in the first coordination sphere (Fig. 5.4.1). In one hydrate isomer, there are only five water molecules in the first coordination sphere, the sixth one is in the second coordination sphere. One chloride anion has moved from the second to the first coordination sphere. There is a third hydrate isomer which has four aqua ligands in the first coordination sphere and two water molecules in the second coordination sphere. Two chloro ligands are now in the first coordination sphere, and one in the second coordination sphere. More hydrate isomers would be possible theoretically, but for some reason nature does not make them.

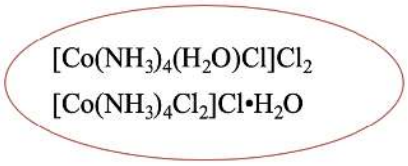


Figure 5.4.2 The hydrate isomers of the complex $[Co(NH_3)_4(H_2O)Cl]Cl_2$

Another example is $[Co(NH_3)_4(H_2O)Cl]Cl_2$. It has a hydrate isomer in which one aqua ligand has moved to the second coordination sphere, and one chloride anion has moved from the second to the first coordination sphere (Fig. 5.4.2).

Ionization Isomerism

A second form of isomerism is the ionization isomerism. In this case an ion moves from the first to the second coordination sphere and/or vice versa.

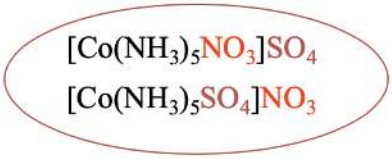


Figure 5.4.3 Two ionization isomers of the complex $[Co(NH_3)_5NO_3]SO_4$

For example, in the compound $[Co(NH_3)_5NO_3]SO_4$ there is a nitrate ion in the first coordination sphere, and a sulfate ion in the second coordination sphere (Fig. 5.4.3). There is an ionization isomer to this compound, in which the sulfate ion is now in the first coordination sphere, and the nitrate is in the second coordination sphere.

Coordination Isomerism

Another form of constitutional isomerism is coordination isomerism. In this isomerism, ligands are bound to different metal ions. Naturally, this implies that this form of isomerism can only exist if at least one isomer has two distinguishable metal ions.

For example, the compound $Pt(NH_3)_2Cl_2$ has two different coordination isomers. At first glance, they do not seem to be isomers at all. However, we can verify that they have the same empirical formula than the first compound (Fig. 5.4.4).

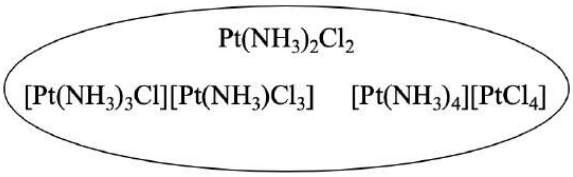


Figure 5.4.4 Two different coordination isomers for the complex $Pt(NH_3)_2Cl_2$

$[Pt(NH_3)_3Cl][Pt(NH_3)Cl_3]$ has two Pt atoms, four NH_3 units and four Cl atoms. That makes $Pt_2(NH_3)_4Cl_4$. This formula can be divided by 2 to to give $Pt(NH_3)_2Cl_2$. We can now easily see that the two compounds are isomers. The third isomer also has two Pt atoms, four NH_3 units, and four chloro atoms, so it must be an isomer as well.

Why are they coordination isomers? This is because in the first complex all ligands are bound to the same metal atom, whereas in the other two the ligands are bound to different metal atoms. In these compounds, one Pt atom belongs to a complex cation, and the other one to a complex anion. In the second isomer, three ammine ligands and one chloro ligand are bound to the first Pt atom, and one ammine and three chloro ligands are bound to the second Pt atom. In the third isomer, four ammine ligands are bound to the first platinum atom, and four chloro ligands belong to the second platinum atom.

Coordination isomerism is also possible for metal ions of different elements.

$$[Co(en)_3]Cr(CN)_6] \text{ and } [Cr(en)_3][Co(CN)_6]$$

Figure 5.4.5 Example of two coordination isomers with metal ions of different elements

In the example shown (Fig. 5.4.5), the first isomer has ethylenediamine bound to Co and cyanide bound to Cr, whereas in the second isomer ethylenediamine is bound to Cr and the cyano ligand is bound to Co.

$$[Pt(NH_3)]_4[PtCl_6] \text{ and } [Pt(NH_3)_4Cl_2][PtCl_4]$$

Pt(II) Pt(IV) Pt(IV) Pt(II)

Figure 5.4.6 Two coordination isomers with metal ions in different oxidation states (Oxidation states noted below each coordination sphere)

Further, in coordination isomers metal ions can be in different oxidation states. We can see that in the two depicted isomers there are complex cations, and complex anions with Pt in in different oxidation states (Fig. 5.4.6). In the first isomer Pt(II) makes the complex cation having four ammine ligands attached to it. Pt(IV) is part of the complex anion being surrounded by six chloro ligands. In the second isomer Pt(IV) forms the complex cation having four ammine and two chloro ligands in the first coordination sphere, and Pt(II) forms the complex anion having four chloro ligands.

Linkage isomerism

Linkage isomerism, also called ambidentate isomerism, is an isomerism that can be observed for ligands that have more than one reactive end. In two linkage isomers, the ligands will bind with different ends to the metal. Which end is reactive depends on the effective HOMO-LUMO interactions. Soft donor atoms tend to bind to soft metals, and hard donor atoms tend to bind to hard metals. Also the solvent can play a big role.

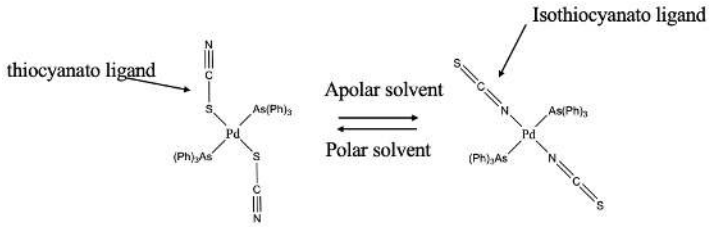


Figure 5.4.7 Two ambidentate isomers of thiocyanate

An example of an ambidentate ligand is the thiocyanate anion (Fig. 5.4.7). It can bind either with the sulfur or with the nitrogen end to a metal ion. When it binds with the S-end it is called the thiocyanato-ligand, when it binds with the N-end it is called the isothiocyanato ligand. Which atom binds to the metal can depend on the solvent. In the example shown, thiocyanate binds with S to Pd in polar solvents, but with N in apolar solvents. We could try to rationalize why. A possibility is that in polar solvents the more electronegative N atom can engage in hydrogen bonding which is not possible in apolar solvents. Steric arguments could also play a role. You can see that the triphenyl arsine ligands are fairly bulky. When the ligand binds with the nitrogen, then it binds in linear fashion avoiding steric interference with one of the arsine ligands. So it may be that in apolar solvents steric interactions dominate the behavior, while in polar solvents solvent-ligand interactions are in control.

It is even possible that two, same ambidentate ligands bind with opposite ends to the metal in one and the same molecule.

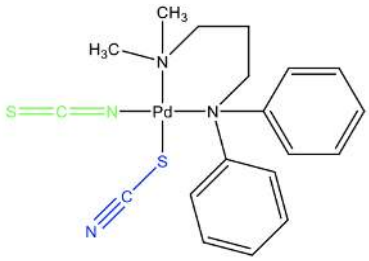


Figure 5.4.8 An example of two, same ambidentate ligands binding with opposite ends to the metal in one and the same molecule.

An example is the complex shown (Fig. 5.4.8). In this molecule, there is a thiocyanato and an isocyanato ligand binding to Pd. What arguments would we have to explain this ambidentate isomerism? Think about it for a moment. We can see that the two methyl groups are far less bulky than the two phenyl groups. When thiocyanate binds with the S-atom, then it can bend away from the two bulky phenyl groups. The second thiocyanate anion binds with the N atom because there is no significant interference between the methyl groups and the linear isothiocyanate ligand. This behavior indicates that thermodynamically, the Pd-N interaction is stronger, but only a little bit stronger because other factors such as steric interference can easily reverse the behavior.

Thio- and isothiocyanato ligands are not the only examples of ambidentate ligands.

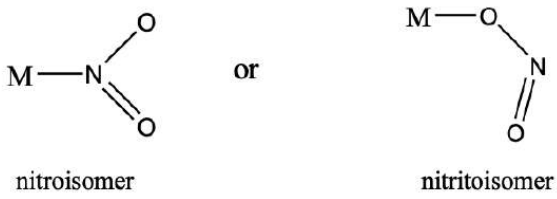


Figure 5.4.9 Two linkage isomers of the nitrite anion

Another example is the nitrite anion. It can either bind with the N- end or the O-end to a metal. In the first case it is called a nitroisomer, in the latter it is called a nitrito isomer (Fig. 5.4.9). Nitritoisomers are usually more stable.

Stereoisomers (Configuration Isomers)

Now let us discuss the second major type of isomerism: Stereisomerism. As mentioned previously, in stereoisomerism the bonds are between the same atoms, but the positions at which the ligands bind, the coordination sites, are different. There are two basic types of stereoisomerism: diastereomerism, and enantiomerism (Fig. 5.4.10).

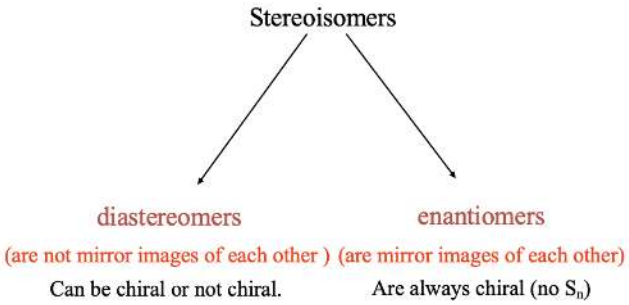


Figure 5.4.10 Types of stereoisomerism

In diastereomerism, the diastereomers are not mirror images to each other.

Definition: Diastereomers

Diastereomers are stereoisomers that are not mirror images of each other. They can be chiral or not chiral.

In enantiomerism, the enantiomers are mirror images to each others. Enantiomers are always chiral molecules.

Definition: Enantiomers

Stereoisomers that are mirror images of each other. They are always chiral.

Diastereomers can be chiral, but do not have to be chiral. Remember, a molecule is chiral when it does not have an improper rotational axis.

Example - Diastereomers and Enantiomers

Let us take an example from organic chemistry to illustrate the difference between enantiomerism and diastereomerism.

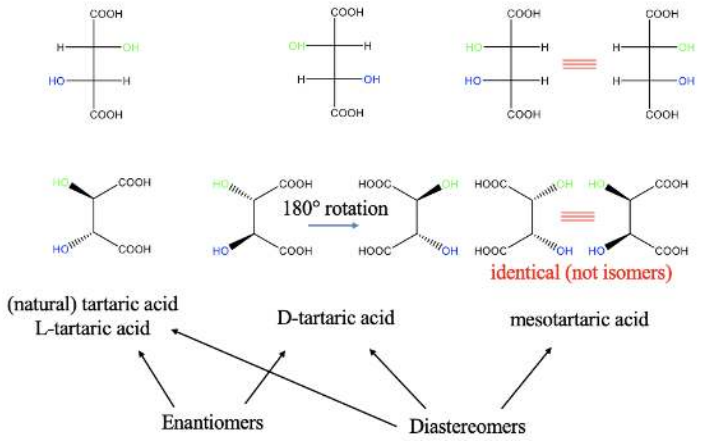


Figure 5.4.11 Example of diastereomers and enantiomers

Above (on the top left of Fig. 5.4.11) you see the Fischer projection an isomer of a compound called tartaric acid, it is called L-tartraric acid. The first OH group from the top points to the left, and the second one points to the right. This is the natural form of tartaric acid. The real structure of L-tartaric acid is depicted below (bottom left). You can see the the OH group that points to the right in the Fischer projection points toward us, while the other one, that points to the left in the Fischer projection, points away from us.

In the D-tartaric acid isomer, the first OH group in the Fischer projection points to the left, and the second one points to the right. For the real structure this means that the first OH-group points away from us, and the second one points toward us. These two isomers are mirror images to each other, and thus they are enantiomers. You may not immediately see in the real structure that the two are mirror images, but you can see it when you rotate the molecule around the C-C bond axis so that the carboxylic acid groups point to the the left (Fig. 5.4.11). Can you see it now?

There is a third isomer which is the so-called mesotartraric acid. We can draw its Fischer projection with both OH groups pointing to the right side (Fig. 5.4.11). In the real structure now both hydroxo groups point to the front. Is this molecule a mirror image of one of the two previous molecules? No, it is not! Therefore, it is a diasteromer relative to the other two. At first glance it seems that we can draw another molecule which is the mirror image of the mesotatraric acid. It would have two hydroxo groups pointing to the left in the Fischer projection, and two hydroxo groups pointing away from us in the real structure. However, the two molecules can be rotated so that they superimpose, and therefore they are not isomers, but identical molecules.

Cis-Trans Isomerism

Let us now discuss some common forms of stereoisomerism. The cis-trans isomerism is one very common stereoisomerism. It occurs when two, same ligands are in adjacent or opposite positions. For example, in a square planar complex two ligands can be adjacent or in opposite positions. When in adjacent position, the bond angle is 90° and we have a cis-isomer, when in opposite position, the bond angle is 180° and we have a trans-isomer.

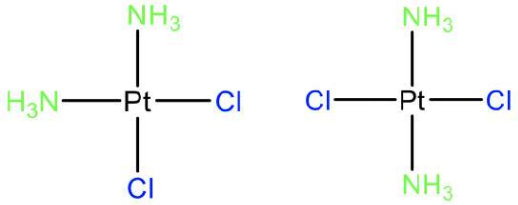


Figure 5.4.12 Cis-platinum and trans-platinum, respectively

The probably most well known example of a cis-isomer in coordination chemistry is cis-platinum which is an anti-cancer drug (Fig. 5.4.12). Its trans-isomers does not have these pharmaceutical properties showing that cis-trans isomerism can have a profound impact on the properties of a molecule. Overall cis-trans isomerism in Pt(II) complexes have been most intensely studied, but cis-trans isomerism is also known for other d^8 metal ions in square planar complexes. We can also ask if cis- and trans isomers are diastereomers or enantiomers. Let us look at the example of cis- and trans-platinum to answer this question. Clearly, these two isomers are not mirror images to each other, so they must be diasteromers. Generally, cis- and trans- isomers are diastereomers.

Cis-trans isomerism extends beyond square planar complexes, and is also known for other shapes, for example, the trigonal bipyramidal shape, and the octahedral shape. In the cis-isomer of an octahedral complex two ligands occupy positions on the same face of the octahedron, whereas in the trans-isomer they occupy opposite position of the octahedron.

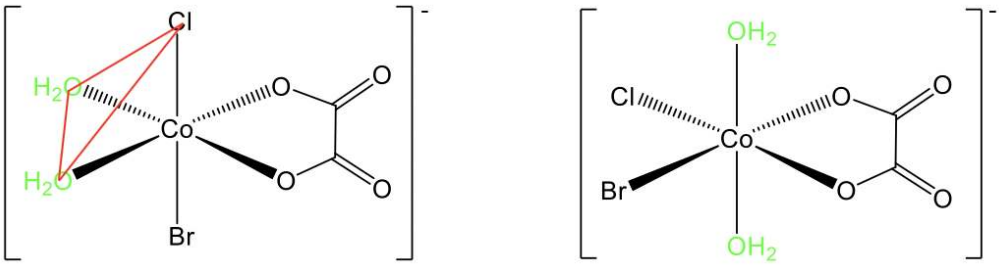


Figure 5.4.13 Cis and trans isomers of the diaquabromochlorooxalato cobalt(1-) complex, respectively

For example, in the complex diaquabromochlorooxalato cobalt(1-) there are cis and trans isomers known (Fig. 5.4.13). In the trans-isomer the two aqua-ligands stand in opposite position, and there is a 180° angle between them. In the cis-isomer they are in adjacent position, and the angle is 90°. We can see that the two ligands are on the same triangular face of the octahedron, shown in red.

Are there rules that can help us to decide if a cis- or a trans- complex will form? As you might suspect, the largest ligands usually go in trans-position due to steric repulsion arguments. Bidentate ligands usually form the cis-isomer because bidentate ligands are usually designed to make five- or six-membered rings with the metal ion. Are cis-trans isomers chiral? If the ligands are simple,

then they are usually not, but if they are more complicated, then they can be. In this context it needs to be said that ideal structures are rarely observed. For example, a square planar complex is rarely an ideal square plane e.g. because the bond angles may be somewhat distorted from the 90° angle due to the fact that the ligands have unequal steric requirements. A slight distortion actually can remove one or many symmetry elements, leading to chirality, however, such small deviations are usually ignored.

Fac-mer Isomerism

Another common type of stereoisomerism in coordination chemistry is fac-mer isomerism. Fac stands for facial and mer stands for meridional. In a fac-isomer the same ligands are on a common face of a polyhedral complex, in the mer isomer they are on a plane that bisects the polyhedron. This kind of isomerism is very common for octahedral complexes, but not restricted to those.



Figure 5.4.14 Fac- (left) and mer-isomers (right) of the triammine trichloro cobalt(III) complex.

For example the complex triammine trichloro cobalt(III) has a fac- and a mer-isomer. You can see that in the fac-isomer the identical ligands are on two opposite triangular faces of the octahedron. In the mer-isomers they lie on two planes that bisect the octahedron. We can again ask if they are diastereomers or enantiomers? The answer is: They are not mirror images to each other, so they are not enantiomers, but diastereomers.

Fac-mer Isomerism with Tridentate Ligands

Fac-mer isomerism is also common for octahedral complexes with tridentate ligands, for example the ligand diethylenetriamine (Fig. 5.4.15).

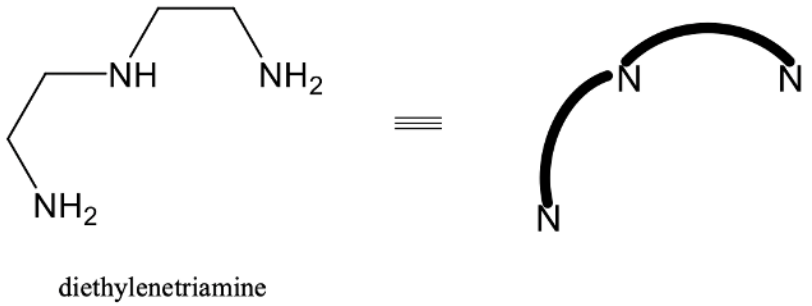


Figure 5.4.15 Diethylenetriamine

In this ligand two NH_2 groups and one NH group are interconnected by two ethylene units. For clarity reasons, in complexes with this ligand, often only the N donor atom of the NH_2 and NH groups is depicted, and the ethylene diammine units are simplified as bent lines interconnecting the N-atoms. We will use this simplification in the following (Fig. 5.4.16).

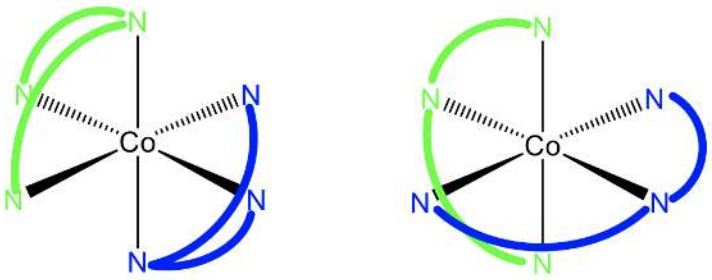


Figure 5.4.16 Fac-mer isomers of the bis(diethylenetriamine) cobalt complex.

Here is an example of bis(diethylenetriamine) cobalt complexes that are fac-mer isomers (Fig. 5.4.16). One ethylenediamine ligand is shown in green, the other one is shown in blue. You can see that the left isomer is the fac-isomer with all three donor atoms of a ligand placed on the same face of the octahedron. On the right side is the mer-isomer, with all donor atoms of the same ligand placed on planes that bisect the octahedron. Also in this case the two isomers are not mirror images and are diasteromers to each other.

Triethylenetetramine Complexes

There is isomerism similar to fac-mer isomerism in octahedral complexes with the tetradentate ligand triethylenetetramine (Fig. 5.4.17).

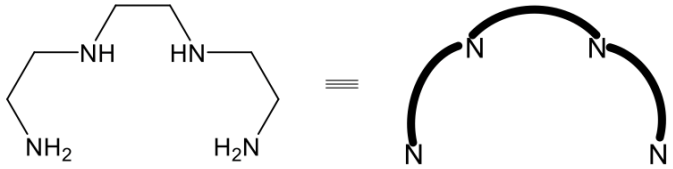


Figure 5.4.17 Triethylenetetramine

In this ligand, two NH and two NH_2 groups are bridged by four ethylene groups. We can again depict the ligand in a simplified way by just showing the N donor atoms, and by simplification of the ethylene groups as bent lines.

One possibility to realize an octahedral complex with triethylenetetraamine ligands is to orient all three rings in the same plane, we can also say we have an octahedral complex with three coplanar rings. This is shown below (Fig.5.4.18).

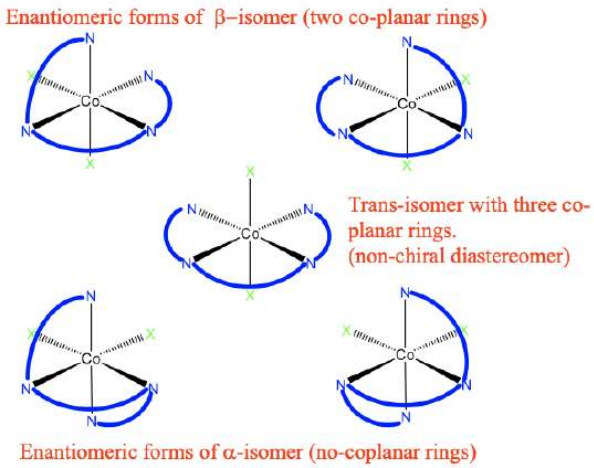


Figure 5.4.18 Octahedral complex with triethylenetertraamine ligands

The three ethylenediamine units make three five-membered rings which are co-planar to each other. The N-atoms occupy overall four vertices of the octahedron. There are two other generic ligands X located at to opposite vertices of the octahedron. Therefore, this isomer is called the trans-isomer.

We can ask if this molecule is chiral? The answer is no, because there is a mirror plane which is co-planar with the three five-membered rings. In addition to this trans-isomer, there are also two cis-isomers, one is called the α-isomer, the other one is called the β-isomer. In the β-isomer, there are now only two co-planar rings, the third one is now out of plane. The two ligands X are in cis-position relative to each other. Is the trans-isomer a diastereomer or enantiomer to the β -isomer? They are clearly not mirror images to each other, therefore they must be diasteromers. Is this β-isomer chiral? Yes, it is! There is no improper rotational axis. Therefore, an enantiomer must exist, and this enantiomer must be a mirror image of the β-form. Here it is! Naturally, it must also have two co-planar rings, and two ligands X in cis-position. It is therefore also considered a β-isomer.

Now let us discuss the α-isomerism. In an α-isomer no two ligands are co-planar any more. This isomer is a diasteromer to the trans- and the β-form because the isomers are not mirror images. Also the α-isomer is chiral. Therefore, there must be another α-isomer which is the mirror image to the first α-isomer. It is shown in the bottom right of **Figure 5.4.18**.

Nomenclature for Propeller Complexes

Complexes with two or more non-coplanar rings that are non-adjacent are always chiral and are called “propeller complexes”. There is a special nomenclature for propeller complexes that we will briefly discuss in the following.

Let us first understand why these complexes are propeller complexes? They are called like that because the non-coplanar rings are oriented relative to each other similarly to propeller blades. A propeller must have at least two blades, but can also have more than that. We distinguish between so-called left handed propellers and right-handed propellers. A left-handed propeller has the property to move away from you in a medium like air or water when rotated counter-clockwise.

Definition: Left-Handed Propeller

Counterclockwise rotation moves a left-handed propeller away

A right handed propeller moves away from you when rotated clock-wise.

Definition: Right-Handed Propeller

Clockwise rotation moves a right-handed propeller away

The tip of one blade of a left-handed propeller describes a left-handed helix as it moves away, the tip of a blade of a right-handed propeller describes are right-handed helix as it moves away.

Determining the Handedness of "Propeller Compexes"

How can we determine the handedness of a propeller molecule? Let us determine it using the example of the tris(oxalato) ferrate(III) anion. Fig. 5.4.19.

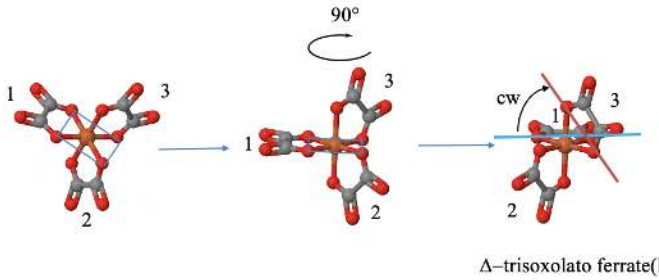


Figure 5.4.19 The tris(oxalato) ferrate(III) anion. The molecule is rotated in two steps so that ring 1 is oriented horizontally, and points to the back. The horizontal blue line needs to be rotated counter-clockwise to make it parallel to the brown line.

It is a three-bladed propeller molecule because it has three five-membered rings between the three oxolato ligands and the iron center. Each ring is considered a blade. None of the rings are co-planar and none of them are adjacent, meaning that the rings do not share a donor atom.

In order to determine the handedness, we can first rotate the molecule so that one of the rings is oriented horizontally and points to the back. Unless we have a three-dimensional model, we need to do this in our mind. Once that is accomplished we can draw a horizontal line between the two donor atoms of that ring. Next we can draw a line between two donor atoms of another ring. If

necessary, we extend the line so that the line crosses the horizontal line. Next, we determine the smallest angle between the two lines, and rotate the horizontal line until it becomes parallel to the other line. We can do this just in our mind. If we need to rotate anti-clockwise, the propeller is considered left-handed, we call it a Λ -isomer. If we need to rotate clock-wise, the the propeller is right-handed, we call it Δ-isomer.

Determining Handedness for Propeller Molecules Requiring More Than One Label

In some cases coordination compounds have multiple non-adjacent, non-coplanar ring combinations, and the handedness must be determined for each combination. Examples are octahedral EDTA complexes.

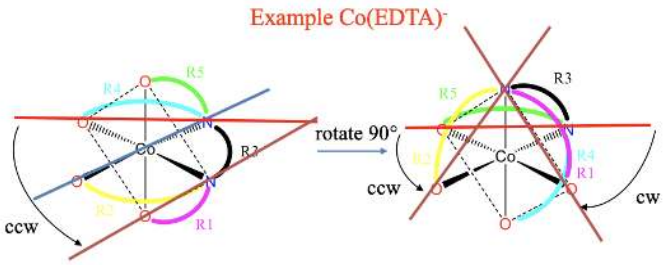


Figure 5.4.20 An octahedral EDTA Co complex. Rotation around the blue line moves the green ring into horizontal position, pointing to the back.

In those complexes there are overall five different rings which we can label R1 to R5. You can see the different rings in different colors (Fig. 5.4.20) For clarity we have abbreviated the linkers between the donor atoms by bent lines in different colors. Each color represents a different linker making a different ring.

We realize that ring R3 is shared with all other rings, therefore it is adjacent to all other rings and does not need to be considered. R1 is adjacent to R2, and R3, but not adjacent and not co-planar with R4 and R5. Therefore we need to consider the R1-R4 and R1-R5 combinations. Further, R2 is coplanar with R3 and R4, and adjacent to R3, but is not coplanar and not adjacent to R5. Therefore, we need to consider the R2-R5 combination as well. R4 and R5 are adjacent, so we do not need to consider this combination. We have found all combinations we need.

We now need to rotate the complex so that one relevant ring is oriented horizontally and points to the back. We can for example choose the ring R4. Luckily, is already correctly oriented. Next, we can connect the donor atoms of the ring R4 to produce a horizontal line. Now let us draw a line between the donor atoms of the ring R1. We see that we need to rotate the horizontal line counter-clockwise to make it parallel to this line, thus the R1-R4 ring combination is a Λ-configuration.

We can next determine the R1-R5 handedness by first reorienting the molecule so that R5 points to the back. R1 could also be chosen. However, R5 is part of two relevant ring combinations, and so we can kill two birds with one stone if we choose R5. We can move ring R5 to the back by rotating 90° counter-clockwise around the blue axis shown in Fig. 5.4.20. It goes through an O atom, the cobalt atom, and an N atom. This axis stands perpendicular to the square indicated by dotted lines. The square has four donor atoms on the four vertices, and these donor atoms move 90° counter-clockwise as the rotation is carried out. The orientation of the rings follow the movement of the donor atoms. The O-donor atom of the ring R5 moves so that R5 is now horizontal, and points to the back. Next we can interconnect the donor atoms of R5, and the donor atoms of R1 by lines. We can see that the horizontal line must be rotated clockwise so that it becomes parallel with the other one. Therefore, the R1-R5 configuration is a Δ-configuration.

For the determination of the combination R2-R5 the complex does not need to be reoriented again. We can directly draw a line through the donor atoms of R2, and determine the direction of rotation. This time we need to rotate counter-clockwise again, meaning the R2-R5 combination is in Λ-configuration.

Overall, we have a $\Lambda\Delta\Lambda$-(ethylenediamine tetracetato)cobaltate(III). Note that the order of designation is arbitrary, we could have named the molecule a $\Lambda\Lambda\Delta$-complex or a $\Delta\Lambda\Lambda$-complex also.

Exercise

Let us practice this by one more example.

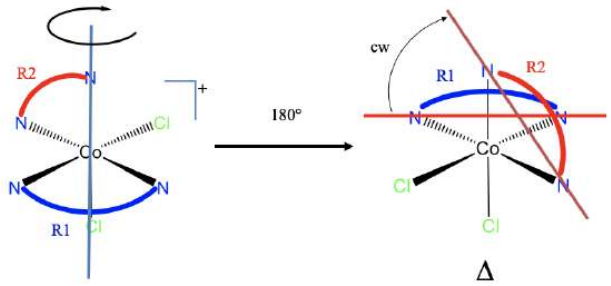


Figure 5.4.21 Example to determine handedness

What is the handedness of the complex shown? First of all: Does it meet the criteria for a propeller complex? The answer is yes. There are two rings, R1 and R2, and they are both not coplanar, and non-adjacent.

To determine handedness we need to first move the molecule so that one ring is oriented horizontally and points to the back. We could choose any of them, but it seems easier to rotate the ring R1 that points to the front and is oriented horizontally by 180° around an axis that is defined by one N and on Cl atom (shown in blue in Fig. 5.4.21)), and is oriented vertically. This rotation moves one of the donor atoms of the other ring by 180°, which defines the new orientation of the ring. Now we can draw a horizontal line through the donor atom of ring 1, and a line through the donor atoms of ring R2. We can see that we must rotate clock-wise, and the propeller complex is right-handed.

Ring Conformations

In addition to isomerism, also conformism has an influence on the structure of a coordination compound. There may be two or more conformers possible for a particular isomer. As an example, let us consider a ring between a metal ion and an ethylenediamine ligand (Fig. 5.4.22).

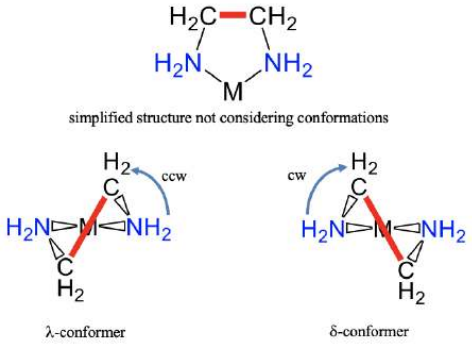


Figure 5.4.22 Ring structure between a metal ion and an ethylene diamine ligand

In contrast to simplified depictions often used, it is not planar, because of the sp^3-hybridization of the carbon and nitrogen atoms. There are two different conformations possible that differ in the orientation of the C-C bond within the ring. They are shown above (Fig. 5.4.22). In the conformation shown left we must rotate a thought horizontal line going through the two nitrogen donor atoms counterclockwise so that it becomes parallel to the C-C bond. For the other conformer, we need to rotate the thought horizontal line clockwise. We call the first conformer the λ-conformer, and the second one the δ-conformer. In this case we use lower case letters to indicate conformerism and not isomerism.

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

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5: Polydented Ligands

Ligands can be further characterized as monodentate, bidentate, tridentate etc. where the concept of teeth **(dent)** is introduced. Monodentate ligands bind through only one donor atom. Monodentate means "one-toothed." The halides, phosphines, ammonia and amines seen previously are monodentate ligands. Bidentate ligands bind through two donor sites. Bidentate means "two-toothed." An example of a bidentate ligand is ethylenediamine. It can bind to a metal via two donor atoms at once.



Figure 5.1: The hypothetical "lobster ligand" binds to the Ni^{2+} via two donor sites.

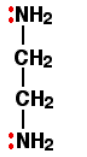
Bidentate binding allows a ligand to bind more tightly. Tridentate ligands, which bind through three donors, can bind even more tightly, and so on. This phenomenon is generally called the "**chelate effect**." This term comes from the Greek chelos, meaning "crab." A crab does not have any teeth at all, but it does have two claws for tightly holding onto something for a couple of reasons. A very simple analogy is that, if you are holding something with two hands rather than one, you are not as likely to drop it.

Complex metal ions containing more complicated ligands

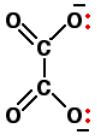
In the examples previously disccussed, each ligand only forms one bond with the central metal ion to give the complex ion. Such a ligand is said to be unidentate. That means literally that it only has one tooth! It only has one pair of electrons that it can use to bond to the metal - any other lone pairs are pointing in the wrong direction. Some ligands, however, have rather more teeth! These are known generally as multidentate or polydentate ligands, but can be broken down into a number of different types.

Bidentate ligands

Bidentate ligands have two lone pairs, both of which can bond to the central metal ion. The two commonly used examples are 1,2-diaminoethane (old name: ethylenediamine - often given the abbreviation "en"), and the ethanedioate ion (old name: oxalate).

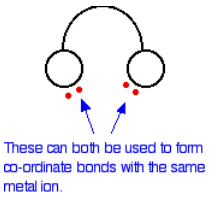


1,2-diaminoethane



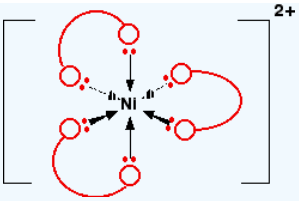
ethanedioate ion

In the ethanedioate ion, there are lots more lone pairs than the two shown, but these are the only ones we are interested in. You can think of these bidentate ligands rather as if they were a pair of headphones, carrying lone pairs on each of the "ear pieces". These will then fit snuggly around a metal ion.



Example 5.1: $Ni(NH_2CH_2CH_2NH_2)_3^{2+}$

You might find this abbreviated to $[Ni(en)_3]^{2+}$. The structure of the ion looks like this:



In this case, the "ear pieces" are the nitrogen atoms of the NH2 groups - and the "bit that goes over your head " is the $-CH_2CH_2-$ group. If you were going to draw this in an exam, you would obviously want to draw it properly - but for learning purposes, drawing all the atoms makes the diagram look unduly complicated!

Notice that the arrangement of the bonds around the central metal ion is exactly the same as it was with the ions with 6 water molecules attached. The only difference is that this time each ligand uses up two of the positions - at right angles to each other.

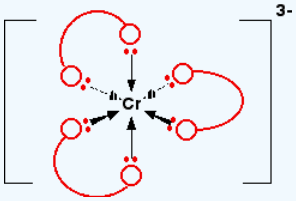
Because the nickel is forming 6 co-ordinate bonds, the coordination number of this ion is 6, despite the fact that it is only joined to 3 ligands. Coordination number counts the number of bonds, not the number of ligands.

Example 5: $Cr(C_2O_4)_3^{3-}$

This is the complex ion formed by attaching 3 ethanedioate (oxalate) ions to a chromium(III) ion. The shape is exactly the same as the previous nickel complex. The only real difference is the number of charges. The original chromium ion carried 3+ charges, and each ethanedioate ion carried -2, i.e.,

$$(+3) + (3 \times -2) = -3.$$

The structure of the ion looks like this:

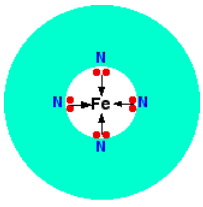


Again, if you drew this in an exam, you would want to show all the atoms properly. If you need to be able to do this, practice drawing it so that it looks clear and tidy! Refer back to the diagram of the ethanedioate ion further up the page to help you.

A Quadridentate Ligand

A quadridentate ligand has four lone pairs, all of which can bond to the central metal ion. An example of this occurs in haemoglobin (American: hemoglobin). The functional part of this is an iron(II) ion surrounded by a complicated molecule called heme. This is a sort of hollow ring of carbon and hydrogen atoms, at the center of which are 4 nitrogen atoms with lone pairs on them. Heme is one of a group of similar compounds called porphyrins. They all have the same sort of ring system, but with different groups attached to the outside of the ring. You aren't going to need to know the exact structure of the haem at this level.

We could simplify the heme with the trapped iron ion as:



Each of the lone pairs on the nitrogen can form a co-ordinate bond with the iron(II) ion - holding it at the center of the complicated ring of atoms. The iron forms 4 co-ordinate bonds with the heme, but still has space to form two more - one above and one below the plane of the ring. The protein globin attaches to one of these positions using a lone pair on one of the nitrogens in one of its amino acids. The interesting bit is the other position.

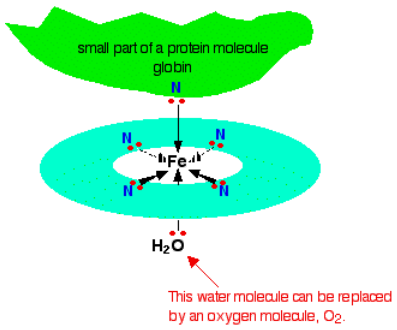


Figure 5.2: Overall, the complex ion has a co-ordination number of 6 because the central metal ion is forming 6 co-ordinate bonds.

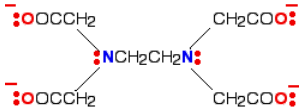
The water molecule which is bonded to the bottom position in the diagram is easily replaced by an oxygen molecule (again via a lone pair on one of the oxygens in O_2) - and this is how oxygen gets carried around the blood by the haemoglobin. When the oxygen gets to where it is needed, it breaks away from the haemoglobin which returns to the lungs to get some more.

Carbon Monoxide Poisoning

You probably know that carbon monoxide is poisonous because it reacts with hemeoglobin. It bonds to the same site that would otherwise be used by the oxygen - but it forms a very stable complex. The carbon monoxide doesn't break away again, and that makes that hemeoglobin molecule useless for any further oxygen transfer.

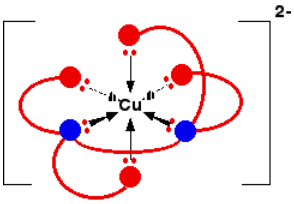
A Hexadentate Ligand

A hexadentate ligand has 6 lone pairs of electrons - all of which can form co-ordinate bonds with the same metal ion. The best example is EDTA. The diagram shows the structure of the ion with the important atoms and lone pairs picked out.



the $EDTA^{4-}$ ion

The EDTA ion entirely wraps up a metal ion using all 6 of the positions that we have seen before. The co-ordination number is again 6 because of the 6 co-ordinate bonds being formed by the central metal ion. The diagram below shows this happening with a copper(II) ion. Here is a simplified version. Make sure that you can see how this relates to the full structure above.



the $[Cu(EDTA)]^{2-}$ ion

The overall charge, of course, comes from the 2+ on the original copper(II) ion and the 4- on the $EDTA^{4-}$ ion.

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6: Hard and Soft Acids and Bases

The thermodynamic stability of a metal complex depends greatly on the properties of the ligand and the metal ion and on the type of bonding. Metal–ligand interaction is an example of a Lewis acid–base interaction. Lewis bases can be divided into two categories:

- hard bases contain small, relatively nonpolarizable donor atoms (such as N, O, and F), and
- soft bases contain larger, relatively polarizable donor atoms (such as P, S, and Cl).

Metal ions with the highest affinities for hard bases are hard acids, whereas metal ions with the highest affinity for soft bases are soft acids. Some examples of hard and soft acids and bases are given in Table 6.1. Notice that hard acids are usually cations of electropositive metals; consequently, they are relatively nonpolarizable and have higher charge-to-radius ratios. Conversely, soft acids tend to be cations of less electropositive metals; consequently, they have lower charge-to-radius ratios and are more polarizable. Chemists can predict the relative stabilities of complexes formed by the d-block metals with a remarkable degree of accuracy by using a simple rule: hard acids prefer to bind to hard bases, and soft acids prefer to bind to soft bases.

Table 6.1: Examples of Hard and Soft Acids and Bases

	Acids	Bases
hard	H^+	NH_3, RNH_2, N_2H_4
	Li^+, Na^+, K^+	H_2O, ROH, R_2O
	Be^{2+}, Mg^{2+}, Ca^{2+}, VO^{2+}	OH^-, F^-, Cl^-, $CH_3CO_2^-$
	Al^{3+}, Sc^{3+}, Cr^{3+}	CO_3^{2-}
	Ti^{4+}	PO_4^{3-}
soft	BF_3, Al_2Cl_6, CO_2, SO_3	
	Cu^+, Ag^+, Au^+, Tl^+, Hg_2^{2+}	H^-
	Pd^{2+}, Pt^{2+}, Hg^{2+}	CN^-, SCN^-, I^-, RS^-
	$GaCl_3$, $GaBr_3$, GaI_3	CO, R_2S

> *Hard acids prefer to bind to hard bases, and soft acids prefer to bind to soft bases.*

Because the interaction between hard acids and hard bases is primarily electrostatic in nature, the stability of complexes involving hard acids and hard bases increases as the positive charge on the metal ion increases and as its radius decreases. For example, the complex of Al^{3+} (r = 53.5 pm) with four fluoride ligands (AlF_4^-) is about 10^8 times more stable than InF_4^-, the corresponding fluoride complex of In^{3+} (r = 80 pm). In general, the stability of complexes of divalent first-row transition metals with a given ligand varies inversely with the radius of the metal ion, as shown in Table 6.2. The inversion in the order at copper is due to the anomalous structure of copper(II) complexes, which will be discussed shortly.

Table 6.2

complex stability	Mn^{2+}	$< Fe^{2+}$	$< Co^{2+}$	$< Ni^{2+}$	$< Cu^{2+}$	$> Zn^{2+}$
ionic radius (pm)	83	78	74.5	69	73	74

Because a hard metal interacts with a base in much the same way as a proton, by binding to a lone pair of electrons on the base, the stability of complexes of hard acids with hard bases increases as the ligand becomes more basic. For example, because ammonia is a stronger base than water, metal ions bind preferentially to ammonia. Consequently, adding ammonia to aqueous solutions of many of the first-row transition-metal cations results in the formation of the corresponding ammonia complexes.

In contrast, the interaction between soft metals (such as the second- and third-row transition metals and Cu^+) and soft bases is largely covalent in nature. Most soft-metal ions have a filled or nearly filled d subshell, which suggests that metal-to-ligand π

bonding is important. Complexes of soft metals with soft bases are therefore much more stable than would be predicted based on electrostatic arguments.

The hard acid–hard base/soft acid–soft base concept also allows us to understand why metals are found in nature in different kinds of ores. Recall that most of the first-row transition metals are isolated from oxide ores but that copper and zinc tend to occur naturally in sulfide ores. This is consistent with the increase in the soft character of the metals across the first row of the transition metals from left to right. Recall also that most of the second- and third-row transition metals occur in nature as sulfide ores, consistent with their greater soft character.

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7: Magnetic Moments

Magnetic moments are often used in conjunction with electronic spectra to gain information about the oxidation number and stereochemistry of the central metal ion in coordination complexes. A common laboratory procedure for the determination of the magnetic moment for a complex is the Gouy method which involves weighing a sample of the complex in the presence and absence of a magnetic field and observing the difference in weight. A template is provided for the calculations involved.

For first row transition metal ions in the free ion state, i.e. isolated ions in a vacuum, all 5 of the 3d orbitals are degenerate.

A simple crystal field theory approach to the bonding in these ions assumes that when they form octahedral complexes, the energy of the d orbitals are no longer degenerate but are split such that two orbitals, the d_{x2-y2} and the d_{z2} (e_g subset) are at higher energy than the d_{xy}, d_{xz}, d_{yz} orbitals (the t_{2g} subset).

For octahedral ions with between 4 and 7 d electrons, this gives rise to 2 possible arrangements called either high spin/weak field or low spin/strong field respectively. The energy gap is dependent on the position of the coordinated ligands in the SPECTROCHEMICAL SERIES.

Note

A good starting point is to assume that all Co(III), d^6 complexes are octahedral and LOW spin, i.e. t_{2g}^6.

In tetrahedral complexes, the energy levels of the orbitals are again split, such that the energy of two orbitals, the $d_{x^2-y^2}$ and the d_{z^2} (e subset) are now at lower energy (more favored) than the remaining three d_{xy}, d_{xz}, d_{yz} (the t_2 subset) which are destabilized.

> *Tetrahedral complexes are ALL high spin since the difference between the 2 subsets of energies of the orbitals is much smaller than is found in octahedral complexes.*

The usual relationship quoted between them is:

$$\Delta_{tet} \approx \frac{4}{9}\Delta_{oct}$$

Square planar complexes are less common than tetrahedral and d^8 e.g. Ni(II), Pd(II), Pt(II), etc, have a strong propensity to form square planar complexes. As with octahedral complexes, the energy gap between the d_{xy} and $d_{x^2-y^2}$ is Δ_{oct} and these are considered strong field / low spin hence they are all diamagnetic, μ=0 Bohr Magneton (B.M.)

The formula used to calculate the spin-only magnetic moment can be written in two forms; the first based on the number of unpaired electrons, n, and the second based on the electron spin quantum number, S. Since for each unpaired electron, $n = 1$ and $S = 1/2$ then the two formulae are clearly related and the answer obtained must be identical.

$$\mu_{so} = \sqrt{n(n+2)}$$

$$\mu_{so} = \sqrt{4S(S+1)}$$

Comparison of calculated spin-only magnetic moments with experimental data for some octahedral complexes

Ion	Config	μ_{so} / B.M.	μ_{obs} / B.M.
Ti(III)	d^1 (t_{2g}^1)	√3 = 1.73	1.6-1.7
V(III)	d^2 (t_{2g}^2)	√8 = 2.83	2.7-2.9
Cr(III)	d^3 (t_{2g}^3)	√15 = 3.88	3.7-3.9
Cr(II)	d^4 high spin (t_{2g}^3 e_g^1)	√24 = 4.90	4.7-4.9
Cr(II)	d^4 low spin (t_{2g}^4)	√8 = 2.83	3.2-3.3
Mn(II)/ Fe(III)	d^5 high spin (t_{2g}^3 e_g^2)	√35 = 5.92	5.6-6.1
Mn(II)/ Fe(III)	d^5 low spin (t_{2g}^5)	√3 = 1.73	1.8-2.1

Ion	Config	μ_{so} / B.M.	μ_{obs} / B.M.
Fe(II)	d^6 high spin ($t_{2g}^4\ e_g^2$)	$\sqrt{24} = 4.90$	5.1-5.7
Co(III)	d^6 low spin (t_{2g}^6)	0	0
Co(II)	d^7 high spin ($t_{2g}^5\ e_g^2$)	$\sqrt{15} = 3.88$	4.3-5.2
Co(II)	d^7 low spin ($t_{2g}^6\ e_g^1$)	$\sqrt{3} = 1.73$	1.8
Ni(II)	d^8 ($t_{2g}^6\ e_g^2$)	$\sqrt{8} = 2.83$	2.9-3.3
Cu(II)	d^9 ($t_{2g}^6\ e_g^3$)	$\sqrt{3} = 1.73$	1.7-2.2

Comparison of calculated spin-only magnetic moments with experimental data for some tetahedral complexes

Ion	Config	μ_{so} / B.M.	μ_{obs} / B.M.
Cr(V)	d^1 (e^1)	$\sqrt{3} = 1.73$	1.7-1.8
Cr(IV) / Mn(V)	d_2 (e^2)	$\sqrt{8} = 2.83$	2.6 - 2.8
Fe(V)	d^3 ($e^2\ t_2^1$)	$\sqrt{15} = 3.88$	3.6-3.7
-	d^4 ($e^2\ t_2^2$)	$\sqrt{24} = 4.90$	-
Mn(II)	d^5 ($e^2\ t_2^3$)	$\sqrt{35} = 5.92$	5.9-6.2
Fe(II)	d^6 ($e^3\ t_2^3$)	$\sqrt{24} = 4.90$	5.3-5.5
Co(II)	d^7 ($e^4\ t_2^3$)	$\sqrt{15} = 3.88$	4.2-4.8
Ni(II)	d^8 ($e^4\ t_2^4$)	$\sqrt{8} = 2.83$	3.7-4.0
Cu(II)	d^9 ($e^4\ t_2^5$)	$\sqrt{3} = 1.73$	-

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9: Crystal Field Theory

Learning Objectives

- To understand how crystal field theory explains the electronic structures and colors of metal complexes.

One of the most striking characteristics of transition-metal complexes is the wide range of colors they exhibit. In this section, we describe crystal field theory (CFT), a bonding model that explains many important properties of transition-metal complexes, including their colors, magnetism, structures, stability, and reactivity. The central assumption of CFT is that metal–ligand interactions are purely electrostatic in nature. Even though this assumption is clearly not valid for many complexes, such as those that contain neutral ligands like CO, CFT enables chemists to explain many of the properties of transition-metal complexes with a reasonable degree of accuracy. The Learning Objective of this Module is to understand how crystal field theory explains the electronic structures and colors of metal complexes.

d-Orbital Splittings

CFT focuses on the interaction of the five (n − 1)d orbitals with ligands arranged in a regular array around a transition-metal ion. We will focus on the application of CFT to octahedral complexes, which are by far the most common and the easiest to visualize. Other common structures, such as square planar complexes, can be treated as a distortion of the octahedral model. According to CFT, an octahedral metal complex forms because of the electrostatic interaction of a positively charged metal ion with six negatively charged ligands or with the negative ends of dipoles associated with the six ligands. In addition, the ligands interact with one other electrostatically. As you learned in our discussion of the valence-shell electron-pair repulsion (VSEPR) model, the lowest-energy arrangement of six identical negative charges is an octahedron, which minimizes repulsive interactions between the ligands.

We begin by considering how the energies of the d orbitals of a transition-metal ion are affected by an octahedral arrangement of six negative charges. Recall that the five d orbitals are initially degenerate (have the same energy). If we distribute six negative charges uniformly over the surface of a sphere, the d orbitals remain degenerate, but their energy will be higher due to repulsive electrostatic interactions between the spherical shell of negative charge and electrons in the d orbitals (Figure $9.1a$). Placing the six negative charges at the vertices of an octahedron does not change the average energy of the d orbitals, but it does remove their degeneracy: the five d orbitals split into two groups whose energies depend on their orientations. As shown in Figure $9.1b$, the d_{z^2} and $d_{x^2-y^2}$ orbitals point directly at the six negative charges located on the x, y, and z axes. Consequently, the energy of an electron in these two orbitals (collectively labeled the e_g orbitals) will be greater than it will be for a spherical distribution of negative charge because of increased electrostatic repulsions. In contrast, the other three d orbitals (d_{xy}, d_{xz}, and d_{yz}, collectively called the t_{2g} orbitals) are all oriented at a 45° angle to the coordinate axes, so they point between the six negative charges. The energy of an electron in any of these three orbitals is lower than the energy for a spherical distribution of negative charge.

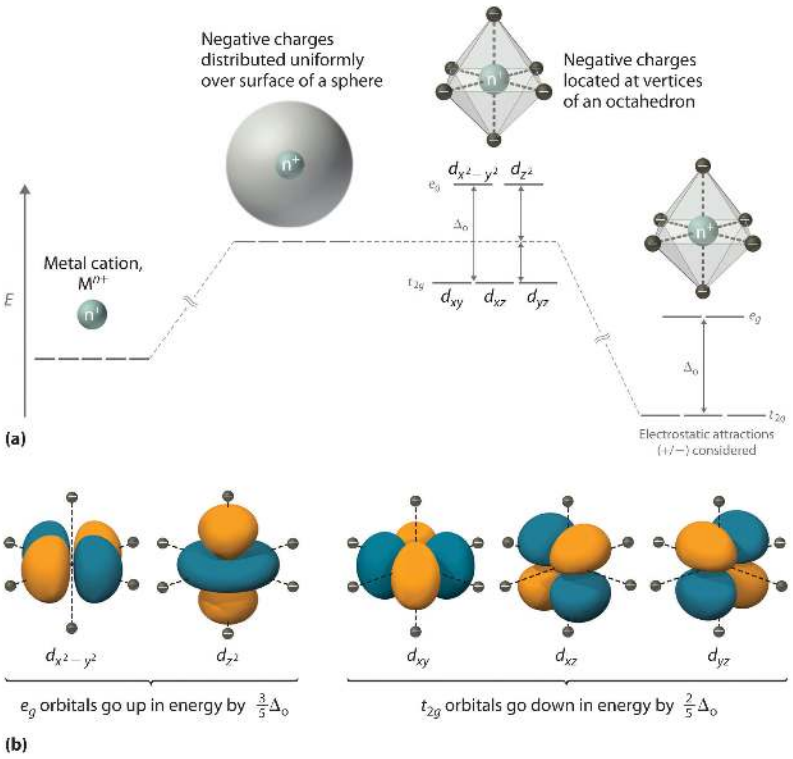


Figure 9.1: An Octahedral Arrangement of Six Negative Charges around a Metal Ion Causes the Five d Orbitals to Split into Two Sets with Different Energies. (a) Distributing a charge of −6 uniformly over a spherical surface surrounding a metal ion causes the energy of all five d orbitals to increase due to electrostatic repulsions, but the five d orbitals remain degenerate. Placing a charge of −1 at each vertex of an octahedron causes the d orbitals to split into two groups with different energies: the $d_{x^2-y^2}$ and d_{z^2} orbitals increase in energy, while the, d_{xy}, d_{xz}, and d_{yz} orbitals decrease in energy. The average energy of the five d orbitals is the same as for a spherical distribution of a −6 charge, however. Attractive electrostatic interactions between the negatively charged ligands and the positively charged metal ion (far right) cause all five d orbitals to decrease in energy but does not affect the splittings of the orbitals. (b) The two e_g orbitals (left) point directly at the six negatively charged ligands, which increases their energy compared with a spherical distribution of negative charge. In contrast, the three t_{2g} orbitals (right) point between the negatively charged ligands, which decreases their energy compared with a spherical distribution of charge.

The difference in energy between the two sets of d orbitals is called the crystal field splitting energy (Δ_o), where the subscript o stands for octahedral. As we shall see, the magnitude of the splitting depends on the charge on the metal ion, the position of the metal in the periodic table, and the nature of the ligands. (Crystal field splitting energy also applies to tetrahedral complexes: Δ_t.) It is important to note that the splitting of the d orbitals in a crystal field does not change the total energy of the five d orbitals: the two e_g orbitals increase in energy by $0.6\Delta_o$, whereas the three t_{2g} orbitals decrease in energy by $0.4\Delta_o$. Thus the total change in energy is

$$2(0.6\Delta_o) + 3(-0.4\Delta_o) = 0.$$

> *Crystal field splitting does not change the total energy of the d orbitals.*

Thus far, we have considered only the effect of repulsive electrostatic interactions between electrons in the d orbitals and the six negatively charged ligands, which increases the total energy of the system and splits the d orbitals. Interactions between the positively charged metal ion and the ligands results in a net stabilization of the system, which decreases the energy of all five d orbitals without affecting their splitting (as shown at the far right in Figure $9.1a$).

Electronic Structures of Metal Complexes

We can use the d-orbital energy-level diagram in Figure 9.1 to predict electronic structures and some of the properties of transition-metal complexes. We start with the Ti^{3+} ion, which contains a single d electron, and proceed across the first row of the transition metals by adding a single electron at a time. We place additional electrons in the lowest-energy orbital available, while keeping their spins parallel as required by Hund's rule. As shown in Figure 24.6.2, for d^1–d^3 systems—such as $[Ti(H_2O)_6]^{3+}$, $[V(H_2O)_6]^{3+}$, and $[Cr(H_2O)_6]^{3+}$, respectively—the electrons successively occupy the three degenerate t_{2g} orbitals with their spins parallel, giving

one, two, and three unpaired electrons, respectively. We can summarize this for the complex $[Cr(H_2O)_6]^{3+}$, for example, by saying that the chromium ion has a d^3 electron configuration or, more succinctly, Cr^{3+} is a d^3 ion.

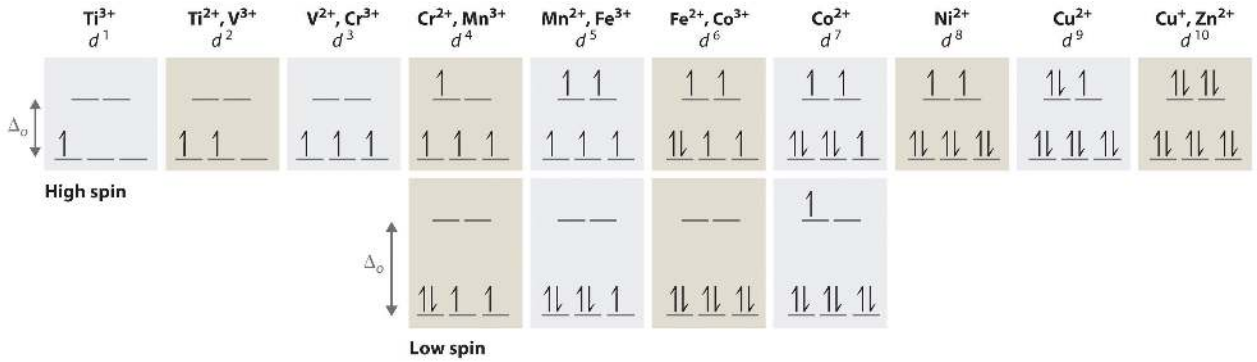


Figure 9.2: The Possible Electron Configurations for Octahedral d^n Transition-Metal Complexes (n = 1–10). Two different configurations are possible for octahedral complexes of metals with d^4, d^5, d^6, and d^7 configurations; the magnitude of Δ_o determines which configuration is observed.

When we reach the d^4 configuration, there are two possible choices for the fourth electron: it can occupy either one of the empty e_g orbitals or one of the singly occupied t_{2g} orbitals. Recall that placing an electron in an already occupied orbital results in electrostatic repulsions that increase the energy of the system; this increase in energy is called the spin-pairing energy (P). If Δ_o is less than P, then the lowest-energy arrangement has the fourth electron in one of the empty e_g orbitals. Because this arrangement results in four unpaired electrons, it is called a high-spin configuration, and a complex with this electron configuration, such as the $[Cr(H_2O)_6]^{2+}$ ion, is called a high-spin complex. Conversely, if Δ_o is greater than P, then the lowest-energy arrangement has the fourth electron in one of the occupied t_{2g} orbitals. Because this arrangement results in only two unpaired electrons, it is called a low-spin configuration, and a complex with this electron configuration, such as the $[Mn(CN)_6]^{3-}$ ion, is called a low-spin complex. Similarly, metal ions with the d^5, d^6, or d^7 electron configurations can be either high spin or low spin, depending on the magnitude of Δ_o.

In contrast, only one arrangement of d electrons is possible for metal ions with d^8–d^{10} electron configurations. For example, the $[Ni(H_2O)_6]^{2+}$ ion is d^8 with two unpaired electrons, the $[Cu(H_2O)_6]^{2+}$ ion is d^9 with one unpaired electron, and the $[Zn(H_2O)_6]^{2+}$ ion is d^{10} with no unpaired electrons.

> *If Δ_o is less than the spin-pairing energy, a high-spin configuration results. Conversely, if Δ_o is greater, a low-spin configuration forms.*

Factors That Affect the Magnitude of Δ_o

The magnitude of Δ_o dictates whether a complex with four, five, six, or seven d electrons is high spin or low spin, which affects its magnetic properties, structure, and reactivity. Large values of Δ_o (i.e., $\Delta_o > P$) yield a low-spin complex, whereas small values of Δ_o (i.e., $\Delta_o < P$) produce a high-spin complex. As we noted, the magnitude of Δ_o depends on three factors: the charge on the metal ion, the principal quantum number of the metal (and thus its location in the periodic table), and the nature of the ligand. Values of Δ_o for some representative transition-metal complexes are given in Table 9.1.

Table 9.1: Crystal Field Splitting Energies for Some Octahedral (Δ_o)* and Tetrahedral (Δ_t) Transition-Metal Complexes

Octahedral Complexes	Δ_o (cm^{-1})	Octahedral Complexes	Δ_o (cm^{-1})	Tetrahedral Complexes	Δ_t (cm^{-1})
$[Ti(H_2O)_6]^{3+}$	20,300	$[Fe(CN)_6]^{4-}$	32,800	VCl_4	9010
$[V(H_2O)_6]^{2+}$	12,600	$[Fe(CN)_6]^{3-}$	35,000	$[CoCl_4]^{2-}$	3300
$[V(H_2O)_6]^{3+}$	18,900	$[CoF_6]^{3-}$	13,000	$[CoBr_4]^{2-}$	2900
$[CrCl_6]^{3-}$	13,000	$[Co(H_2O)_6]^{2+}$	9300	$[CoI_4]^{2-}$	2700

*Energies obtained by spectroscopic measurements are often given in units of wave numbers (cm^{-1}); the wave number is the reciprocal of the wavelength of the corresponding electromagnetic radiation expressed in centimeters: 1 cm^{-1} = 11.96 J/mol.

Octahedral Complexes	Δ_o (cm^{-1})	Octahedral Complexes	Δ_o (cm^{-1})	Tetrahedral Complexes	Δ_t (cm^{-1})
$[Cr(H_2O)_6]^{2+}$	13,900	$[Co(H_2O)_6]^{3+}$	27,000		
$[Cr(H_2O)_6]^{3+}$	17,400	$[Co(NH_3)_6]^{3+}$	22,900		
$[Cr(NH_3)_6]^{3+}$	21,500	$[Co(CN)_6]^{3-}$	34,800		
$[Cr(CN)_6]^{3-}$	26,600	$[Ni(H_2O)_6]^{2+}$	8500		
$Cr(CO)_6$	34,150	$[Ni(NH_3)_6]^{2+}$	10,800		
$[MnCl_6]^{4-}$	7500	$[RhCl_6]^{3-}$	20,400		
$[Mn(H_2O)_6]^{2+}$	8500	$[Rh(H_2O)_6]^{3+}$	27,000		
$[MnCl_6]^{3-}$	20,000	$[Rh(NH_3)_6]^{3+}$	34,000		
$[Mn(H_2O)_6]^{3+}$	21,000	$[Rh(CN)_6]^{3-}$	45,500		
$[Fe(H_2O)_6]^{2+}$	10,400	$[IrCl_6]^{3-}$	25,000		
$[Fe(H_2O)_6]^{3+}$	14,300	$[Ir(NH_3)_6]^{3+}$	41,000		

*Energies obtained by spectroscopic measurements are often given in units of wave numbers (cm^{-1}); the wave number is the reciprocal of the wavelength of the corresponding electromagnetic radiation expressed in centimeters: 1 cm^{-1} = 11.96 J/mol.

Source of data: Duward F. Shriver, Peter W. Atkins, and Cooper H. Langford, Inorganic Chemistry, 2nd ed. (New York: W. H. Freeman and Company, 1994).

Charge on the Metal Ion

Increasing the charge on a metal ion has two effects: the radius of the metal ion decreases, and negatively charged ligands are more strongly attracted to it. Both factors decrease the metal–ligand distance, which in turn causes the negatively charged ligands to interact more strongly with the d orbitals. Consequently, the magnitude of Δ_o increases as the charge on the metal ion increases. Typically, Δ_o for a tripositive ion is about 50% greater than for the dipositive ion of the same metal; for example, for $[V(H_2O)_6]^{2+}$, Δ_o = 11,800 cm^{-1}; for $[V(H_2O)_6]^{3+}$, Δ_o = 17,850 cm^{-1}.

Principal Quantum Number of the Metal

For a series of complexes of metals from the same group in the periodic table with the same charge and the same ligands, the magnitude of Δ_o increases with increasing principal quantum number: Δ_o (3d) < Δ_o (4d) < Δ_o (5d). The data for hexaammine complexes of the trivalent group 9 metals illustrate this point:

$$[Co(NH_3)_6]^{3+}: \Delta_o = 22{,}900\ cm^{-1}$$

$$[Rh(NH_3)_6]^{3+}: \Delta_o = 34{,}100\ cm^{-1}$$

$$[Ir(NH_3)_6]^{3+}: \Delta_o = 40{,}000\ cm^{-1}$$

The increase in Δ_o with increasing principal quantum number is due to the larger radius of valence orbitals down a column. In addition, repulsive ligand–ligand interactions are most important for smaller metal ions. Relatively speaking, this results in shorter M–L distances and stronger d orbital–ligand interactions.

The Nature of the Ligands

Experimentally, it is found that the Δ_o observed for a series of complexes of the same metal ion depends strongly on the nature of the ligands. For a series of chemically similar ligands, the magnitude of Δ_o decreases as the size of the donor atom increases. For example, Δ_o values for halide complexes generally decrease in the order F^- > Cl^- > Br^- > I− because smaller, more localized charges, such as we see for F^-, interact more strongly with the d orbitals of the metal ion. In addition, a small neutral ligand with a highly localized lone pair, such as NH_3, results in significantly larger Δ_o values than might be expected. Because the lone pair points directly at the metal ion, the electron density along the M–L axis is greater than for a spherical anion such as F^-. The

experimentally observed order of the crystal field splitting energies produced by different ligands is called the spectrochemical series, shown here in order of decreasing Δ_o:

$$\underset{\text{strong-field ligands}}{CO \approx CN^- > NO_2^-} > en > NH_3 > \underset{\text{intermediate-field ligands}}{SCN^- > H_2O > \text{oxalate}^{2-}} > OH^- > F > \text{acetate}^- > \underset{\text{weak-field ligands}}{Cl^- > Br^- > I^-}$$

The values of Δ_o listed in Table 9.1 illustrate the effects of the charge on the metal ion, the principal quantum number of the metal, and the nature of the ligand.

> *The largest Δ_o splittings are found in complexes of metal ions from the third row of the transition metals with charges of at least +3 and ligands with localized lone pairs of electrons.*

Colors of Transition-Metal Complexes

The striking colors exhibited by transition-metal complexes are caused by excitation of an electron from a lower-energy d orbital to a higher-energy d orbital, which is called a d–d transition (Figure 24.6.3). For a photon to effect such a transition, its energy must be equal to the difference in energy between the two d orbitals, which depends on the magnitude of Δ_o.

Figure 9.3: A d–d Transition. In a d–d transition, an electron in one of the t_{2g} orbitals of an octahedral complex such as the $[Cr(H_2O)_6]^{3+}$ ion absorbs a photon of light with energy equal to Δ_o, which causes the electron to move to an empty or singly occupied e_g orbital.

Recall that the color we observe when we look at an object or a compound is due to light that is transmitted or reflected, not light that is absorbed, and that reflected or transmitted light is complementary in color to the light that is absorbed. Thus a green compound absorbs light in the red portion of the visible spectrum and vice versa, as indicated by the color wheel. Because the energy of a photon of light is inversely proportional to its wavelength, the color of a complex depends on the magnitude of Δ_o, which depends on the structure of the complex. For example, the complex $[Cr(NH_3)_6]^{3+}$ has strong-field ligands and a relatively large Δ_o. Consequently, it absorbs relatively high-energy photons, corresponding to blue-violet light, which gives it a yellow color. A related complex with weak-field ligands, the $[Cr(H_2O)_6]^{3+}$ ion, absorbs lower-energy photons corresponding to the yellow-green portion of the visible spectrum, giving it a deep violet color.

We can now understand why emeralds and rubies have such different colors, even though both contain Cr^{3+} in an octahedral environment provided by six oxide ions. Although the chemical identity of the six ligands is the same in both cases, the Cr–O distances are different because the compositions of the host lattices are different (Al_2O_3 in rubies and $Be_3Al_2Si_6O_{18}$ in emeralds). In ruby, the Cr–O distances are relatively short because of the constraints of the host lattice, which increases the d orbital–ligand interactions and makes Δ_o relatively large. Consequently, rubies absorb green light and the transmitted or reflected light is red, which gives the gem its characteristic color. In emerald, the Cr–O distances are longer due to relatively large $[Si_6O_{18}]^{12-}$ silicate rings; this results in decreased d orbital–ligand interactions and a smaller Δ_o. Consequently, emeralds absorb light of a longer wavelength (red), which gives the gem its characteristic green color. It is clear that the environment of the transition-metal ion, which is determined by the host lattice, dramatically affects the spectroscopic properties of a metal ion.



Gem-quality crystals of ruby and emerald. The colors of both minerals are due to the presence of small amounts of Cr^{3+} impurities in octahedral sites in an otherwise colorless metal oxide lattice.

Crystal Field Stabilization Energies

Recall that stable molecules contain more electrons in the lower-energy (bonding) molecular orbitals in a molecular orbital diagram than in the higher-energy (antibonding) molecular orbitals. If the lower-energy set of d orbitals (the t_{2g} orbitals) is selectively populated by electrons, then the stability of the complex increases. For example, the single d electron in a d^1 complex such as $[Ti(H_2O)_6]^{3+}$ is located in one of the t_{2g} orbitals. Consequently, this complex will be more stable than expected on purely electrostatic grounds by $0.4\Delta_o$. The additional stabilization of a metal complex by selective population of the lower-energy d orbitals is called its crystal field stabilization energy (CFSE). The CFSE of a complex can be calculated by multiplying the number of electrons in t_{2g} orbitals by the energy of those orbitals ($-0.4\Delta_o$), multiplying the number of electrons in e_g orbitals by the energy of those orbitals ($+0.6\Delta_o$), and summing the two. Table 9.2 gives CFSE values for octahedral complexes with different d electron

configurations. The CFSE is highest for low-spin d^6 complexes, which accounts in part for the extraordinarily large number of Co(III) complexes known. The other low-spin configurations also have high CFSEs, as does the d^3 configuration.

Table 9.2: CFSEs for Octahedral Complexes with Different Electron Configurations (in Units of Δo)

	High Spin		CFSE (Δ_o)	Low Spin		CFSE (Δ_o)
d^0			0			
d^1	↑		0.4			
d^2	↑ ↑		0.8			
d^3	↑ ↑ ↑		1.2			
d^4	↑ ↑ ↑	↑	0.6	↑↓ ↑ ↑		1.6
d^5	↑ ↑ ↑	↑ ↑	0.0	↑↓ ↑↓ ↑		2.0
d^6	↑↓ ↑ ↑	↑ ↑	0.4	↑↓ ↑↓ ↑↓		2.4
d^7	↑↓ ↑↓ ↑	↑ ↑	0.8	↑↓ ↑↓ ↑↓	↑	1.8
d^8	↑↓ ↑↓ ↑↓	↑ ↑	1.2			
d^9	↑↓ ↑↓ ↑↓	↑↓ ↑	0.6			
d^{10}	↑↓ ↑↓ ↑↓	↑↓ ↑↓	0.0			

CFSEs are important for two reasons. First, the existence of CFSE nicely accounts for the difference between experimentally measured values for bond energies in metal complexes and values calculated based solely on electrostatic interactions. Second, CFSEs represent relatively large amounts of energy (up to several hundred kilojoules per mole), which has important chemical consequences.

> *Octahedral d^3 and d^8 complexes and low-spin d^6, d^5, d^7, and d^4 complexes exhibit large CFSEs.*

Example 9.1

For each complex, predict its structure, whether it is high spin or low spin, and the number of unpaired electrons present.

a. $[CoF_6]^{3-}$
b. $[Rh(CO)_2Cl_2]^-$

Given: complexes

Asked for: structure, high spin versus low spin, and the number of unpaired electrons

Strategy:

a. From the number of ligands, determine the coordination number of the compound.
b. Classify the ligands as either strong field or weak field and determine the electron configuration of the metal ion.
c. Predict the relative magnitude of Δ_o and decide whether the compound is high spin or low spin.
d. Place the appropriate number of electrons in the d orbitals and determine the number of unpaired electrons.

Solution

a. A With six ligands, we expect this complex to be octahedral.

B The fluoride ion is a small anion with a concentrated negative charge, but compared with ligands with localized lone pairs of electrons, it is weak field. The charge on the metal ion is +3, giving a d^6 electron configuration.

C Because of the weak-field ligands, we expect a relatively small Δ_o, making the compound high spin.

D In a high-spin octahedral d^6 complex, the first five electrons are placed individually in each of the d orbitals with their spins parallel, and the sixth electron is paired in one of the t_{2g} orbitals, giving four unpaired electrons.

b. A This complex has four ligands, so it is either square planar or tetrahedral.

B C Because rhodium is a second-row transition metal ion with a d^8 electron configuration and CO is a strong-field ligand, the complex is likely to be square planar with a large Δ_o, making it low spin. Because the strongest d-orbital interactions are along the x and y axes, the orbital energies increase in the order $d_{z^2}$$d_{yz}$, and d_{xz} (these are degenerate); d_{xy}; and $d_{x^2-y^2}$.

D The eight electrons occupy the first four of these orbitals, leaving the $d_{x^2-y^2}$. orbital empty. Thus there are no unpaired electrons.

? Exercise 9.1

For each complex, predict its structure, whether it is high spin or low spin, and the number of unpaired electrons present.

a. $[Mn(H_2O)_6]^{2+}$
b. $[PtCl_4]^{2-}$

Answers

a. octahedral; high spin; five
b. square planar; low spin; no unpaired electrons

Summary

Crystal field theory, which assumes that metal–ligand interactions are only electrostatic in nature, explains many important properties of transition-metal complexes, including their colors, magnetism, structures, stability, and reactivity. Crystal field theory (CFT) is a bonding model that explains many properties of transition metals that cannot be explained using valence bond theory. In CFT, complex formation is assumed to be due to electrostatic interactions between a central metal ion and a set of negatively charged ligands or ligand dipoles arranged around the metal ion. Depending on the arrangement of the ligands, the d orbitals split into sets of orbitals with different energies. The difference between the energy levels in an octahedral complex is called the crystal field splitting energy (Δ_o), whose magnitude depends on the charge on the metal ion, the position of the metal in the periodic table, and the nature of the ligands. The spin-pairing energy (P) is the increase in energy that occurs when an electron is added to an already occupied orbital. A high-spin configuration occurs when the Δ_o is less than P, which produces complexes with the maximum number of unpaired electrons possible. Conversely, a low-spin configuration occurs when the Δ_o is greater than P, which produces complexes with the minimum number of unpaired electrons possible. Strong-field ligands interact strongly with the d orbitals of the metal ions and give a large Δ_o, whereas weak-field ligands interact more weakly and give a smaller Δ_o. The colors of transition-metal complexes depend on the environment of the metal ion and can be explained by CFT.

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10: Introduction to Ligand Field Theory (Octahedral complexes)

Concepts from molecular orbital (MO) theory are useful in understanding the reactivity of coordination compounds. One of the basic ways of applying MO concepts to coordination chemistry is in Ligand Field Theory (LFT). LFT is essentially a version of MO theory that focuses on how the d-orbitals of a metal ion interact with ligand orbitals to create bonding, antibonding, and non-bonding interactions. These interactions result in orbitals that are close in energy to the original d-orbitals of the metal. Due to their similarity to the metal d-orbitals, they are usually referred to as the metal d-orbitals even though they are actually molecular orbitals. The interactions of ligand orbitals with metal d-orbitals results in different splitting of the metal d-orbitals into sets of bonding, antibonding and non-bonding orbitals. In the octahedral case, the splitting of d-orbitals is the same in LFT as we saw previously in CFT. The main difference between the two theories is the explanation of how this splitting is derived. LFT also describes bonding, while CFT can't.

The symmetry of the central metal orbital and that of the ligand group orbitals (aka SALCs, symmetry adapted linear combinations of atomic orbitals) determines the relative eenergies (eg the splitting) of the d-oritals of the metal complex. The symmetry of the SALCs depends on the coordination geometry of the ligands and the specific type of orbitals involved (eg s vs p). For example, ligand s orbitals in a tetrahedral coordination sphere will have a different symmetries and different abilities to interact with the metal d-orbitals than orbitals in an octahedral coordination sphere because they will interact with the different d orbitals in different ways.

> *Ligand Field Theory looks at the effect of donor atoms on the energy of d orbitals in the metal complex.*
>
> *The effect depends on the coordination geometry of the ligands.*

A simple octahedral case

Let's start with an example of six ligand s-orbitals in an octahedral coordination structure. Assume the six ligands all lie along the x, y and z axes and that they interact with the metal using *just* their s orbitals (see Figure 10.1).

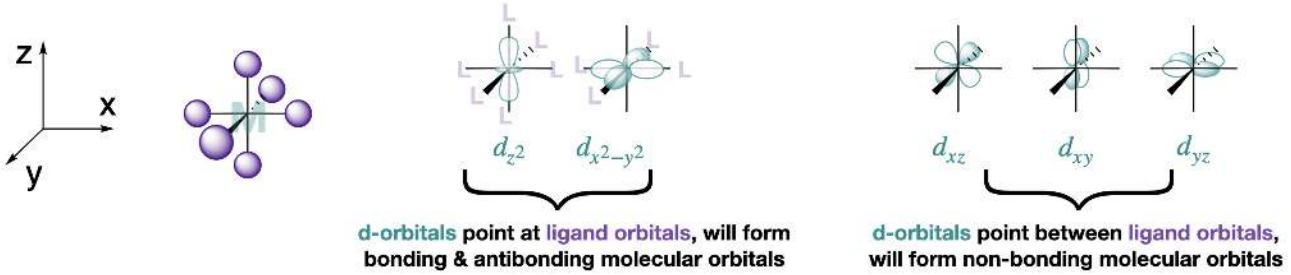


Figure 10.1: An octahedral arrangement of ligand s-orbitals (purple) around a central metal (teal). Two of the metal d-orbitals ($d_{x^2-y^2}$ and d_{z^2}) are compatible to bond with ligand s-orbitals, while the other three (d_{xy}, d_{xz}, d_{yz} cannot form productive interactions with ligand s-orbitals (CC-BY-NC-SA; Kathryn Haas).

Because the ligand s orbitals lie on the axes, there are two d orbitals that will form productive interactions with these ligands: the $d_{x^2-y^2}$ which has lobes that point directly along the x and y axes, and the d_{z^2}, which has lobes that point along the z axis and along the xy plane. The ligand s orbitals have two SALCs with appropriate symmetry to interact with these two metal d-orbitals. However, the remaining three orbitals, the d_{xy}, d_{xz}, and d_{yz}, cannot form productive interactions with ligand s-orbitals.

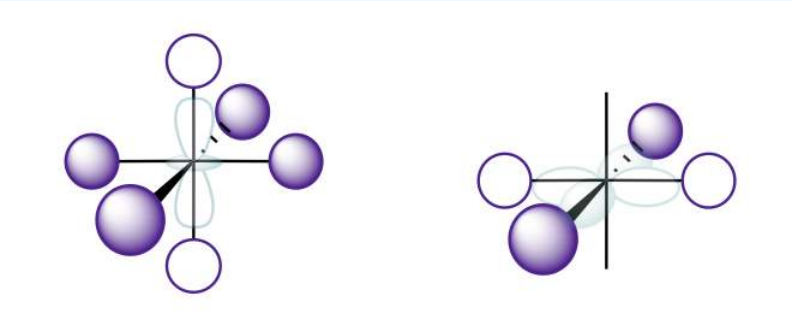
Exercise 10.1

Sketch the two ligand SALCs that would interact with the d-orbitals, as shown in Figure 10.1. What is the symmetry of these SALCs under the octahedral point group?

Answer

The sketches are shown below, where the purple lobes show the group orbital and the teal transparent orbital in the center is the d-orbital with compatible symmetry. These sketches were drawn simply by matching the symmetry of the central metal

orbital. A full explanation for how to systematically generate such sketches is described in a previous chapter. The octahedral character table tells us that the (d_{x^2-y^2}\) and d_{z^2} orbitals transform together with e_g symmetry. Thus, the two SALCs sketched below would also transform with e_g symmetry.



The metal $d_{x^2-y^2}$ and d_{z^2} will combine with the e_g SALCs (see exercise above) to form new bonding and antibonding molecular orbitals. A simplified drawing of this interaction, which forms bonding and antibonding molecular orbitals is shown below in Figure 10.2. There are also for other ligand SALCs that will interact with s and p orbitals, but for the moment we're not going to worry about them.

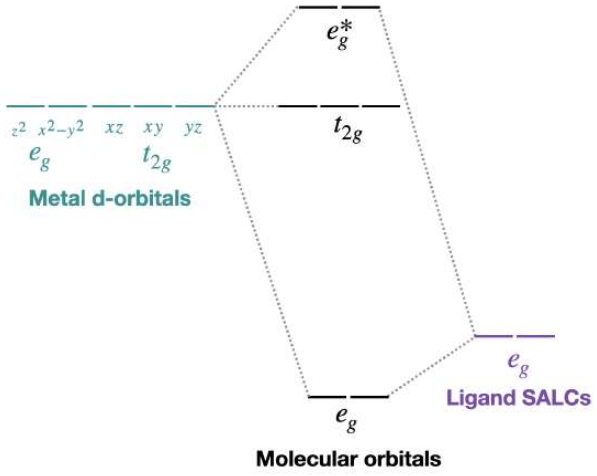


Figure 10.2: Diagram of metal d orbitals (left) and ligand e_g SALCs (right) along with their relative energies. The orbitals in the middle represent the molecular orbitals: there is a set of bonding e_g, a set of antibonding e_g^*, and set of non-bonding t_{2g} orbitals. The metal d-orbitals are considered to be "split" into the t_{2g} and e_g^* molecular orbitals, while the bonding e_g have mostly ligand character (this is all based on relative energies of molecular orbitals compared to metal and ligand atomic orbtials. Energy increases from bottom to top. (CC-BY-NC-SA; Kathryn Haas)

Now, remember that metals usually have d electrons that are much higher in energy than those on typical donor atoms (like oxygen, sulfur, nitrogen or phosphorus). That means the antibonding combinations will be much closer in energy to the original d orbitals, because both are relatively high in energy. The bonding combination will be much closer in energy to the original ligand orbitals, because these ones are all relatively low in energy.

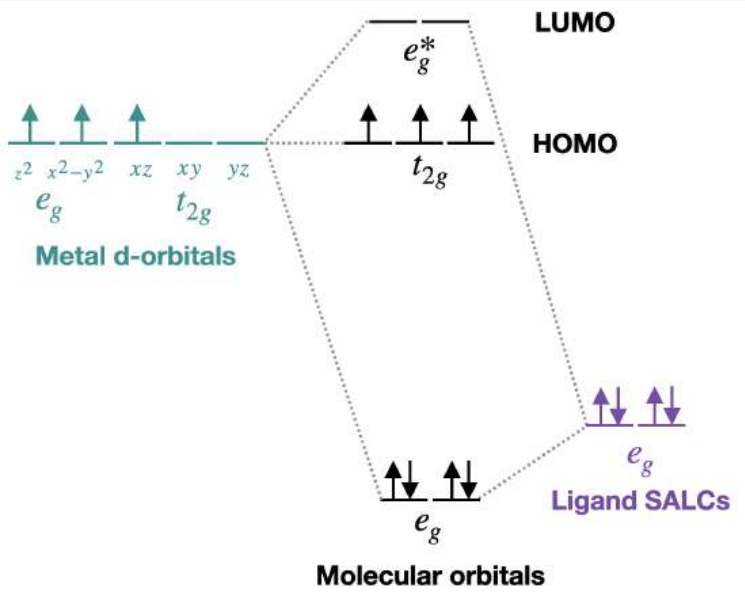
That energetic similarity generally translates into a similarity in shape and location as well. In other words, the antibonding combination between a d orbital and a ligand orbital is a lot like the original d orbital. The bonding combination is more like the original ligand orbital than the original d orbital. Because of those similarities, inorganic chemists often refer to those antibonding orbitals as if they were still the original d orbitals.

Exercise 10.1

Use the diagram in Figure 10.2. Fill in the diagram for a d^3 metal complex. Identify the froteir orbtials (the HOMO and the LUMO).

Answer

When filling in electrons to this diagram we assume that each ligand bonds to the metal by donating two electrons; two SALCs results in four ligand electrons to add to the system. The metal has three d orbitals according to the description. The molecular orbitals should then be filled starting with the lowest energy orbitals. The HOMO-LUMO gap is between the t_{2g} non-bonding and e_g^* antibonding orbitals:



Summary for simple octahedral case

- Assume the six ligands all lie along the x, y and z axes.
- The $d_{x^2-y^2}$ and the d_{z^2} orbitals point at the ligands along the axes.
- These two orbitals "become" antibonding orbitals and are thus "raised" relatively high in energy.
- These orbitals are called the "**e_g**" set of orbitals due to their symmetry under the octahedral point group.

On the other hand, the other three d orbitals, the d_{xy}, d_{xz} and d_{yz}, all lie *between* the donor ligands, rather than hitting them head-on. These orbitals will interact less strongly with the donor electrons.

- The d_{xy}, d_{xz} and d_{yz} orbitals all lie between the bond axes.
- These three orbitals will be changed in energy only a little.
- These orbitals are more like non-bonding orbitals.
- These orbitals are sometimes called the "**t_{2g}**" set of orbitals.

Remember, only the energy of the *electrons* affects the overall energy of the system. The unoccupied d orbitals are raised in energy, but the occupied orbitals go down in energy (or else stay the same).

Apart from the stabilization of the complex, there is another consequence of this picture. What we are left with is two distinct sets of d energy levels, one lower than the other. That will have an effect on the electron configuration at the metal atom in the complex. In other words, there will be cases where electrons could be paired or unpaired, depending on how these orbitals are occupied.

Take the case of the biologically important iron(II) ion. It has a d^6 valence electron configuration. In less formal parlance of inorganic chemistry, "iron(II) is d^6." In an iron(II) ion all alone in space, all the d orbitals would have the same energy level. We

would put one electron in each orbital, and have one left. The left over electron would need to pair up in one of the d orbitals (Notice that, in the chemistry of transition metal *ions*, the valence s and p orbitals are always assumed to be unoccupied).

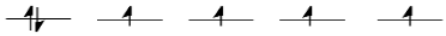


Figure 10.5:

Things are very different in an octahedral complex, like $K_4[Fe(CN)_6]$. In that case, the d orbitals are no longer at the same energy level. There are two possible configurations to consider.

In one case, one electron would go into each of the lower energy d orbitals. A choice would be made for the fourth electron. Does it go into the higher energy d orbital, or does it pair up with one of the lower energy d electrons? The choice depends on how much higher in energy the upper d orbitals are, compared to how much energy it costs to put two electrons in the same d orbital.

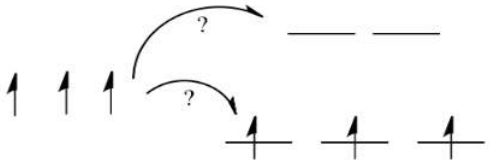


Figure 10.6:

If the "d orbital splitting energy" is pretty low, so that the two sets of d orbitals are still pretty similar in energy, the next electron can go into a higher orbital. Pairing would not be required until the final electron. Overall, that would leave four unpaired electrons, just like in the case of a lone metal ion in space. This is called the "high-spin" case, because electrons can easily go into the higher orbital.

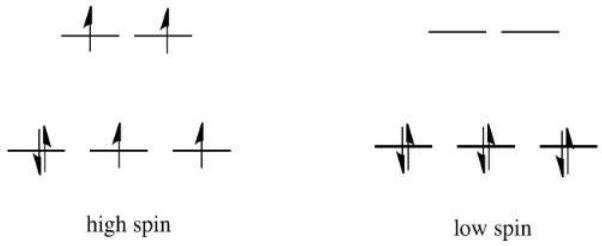


Figure 10.7:

If the d orbital splitting energy is too high, the next electron must pair up in a lower orbital. All three remaining electrons pair up, and so there are no unpaired electrons in the complex. This is called the "low-spin" case, because electrons more easily pair up in the orbital.

So the overall rule is that if the energy to pair up the electrons is greater than the energy needed to get to the next level, the electron will go ahead and occupy the next level.

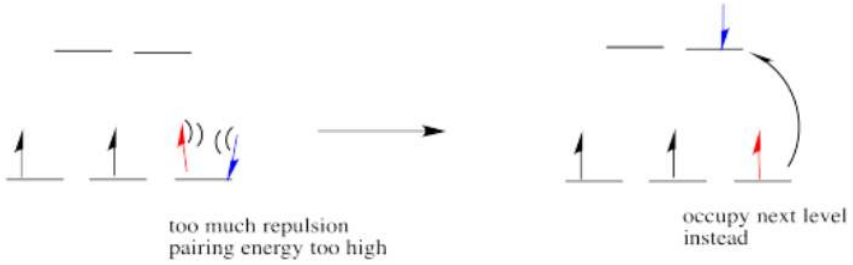


Figure 10.8:

However, if the energy it takes to get to the next level is more than it would cost to pair up, the electrons will just pair up instead.

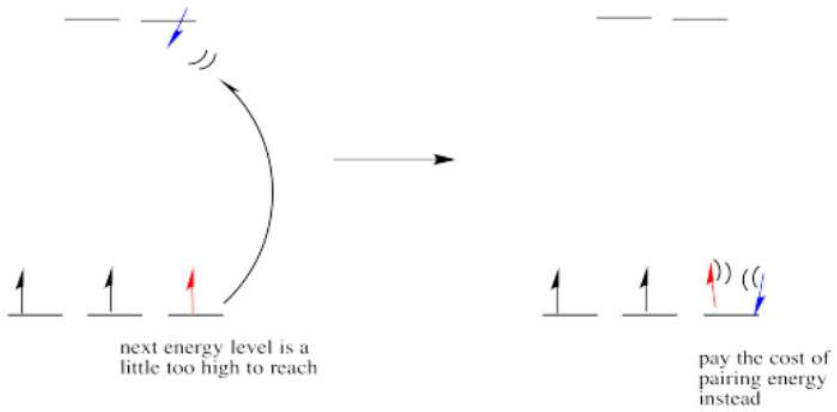


Figure 10.9:

> *The electron configuration can be "high spin" or "low-spin", depending on how large the energy splitting is between the two sets of d orbitals.*

The difference between the high-spin case and the low-spin case is significant because unpaired electrons affect the magnetic properties of a material. The low-spin case would be diamagnetic, resulting in no interaction with a magnetic field. However, the high-spin case would be paramagnetic, and would be attracted to a magnetic field.

It turns out $K_4[Fe(CN)_6]$ is diamagnetic. Thus, it is pretty clear that it is a low-spin complex. The energy difference between the two d orbital levels is relatively large in this case.

In addition to influencing magnetic properties, whether a complex is high- or low-spin also influences reactivity. Compounds with high-energy d electrons are generally more labile, meaning they let go of ligands more easily.

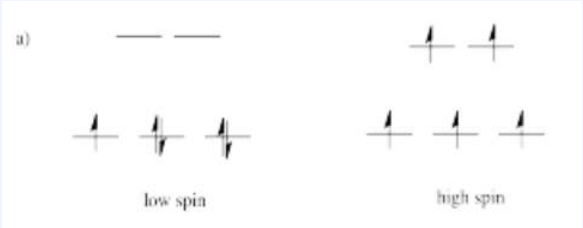
- electron configuration influences magnetic properties
- electron configuration influences lability (how easily ligands are released)

Exercise 10.1

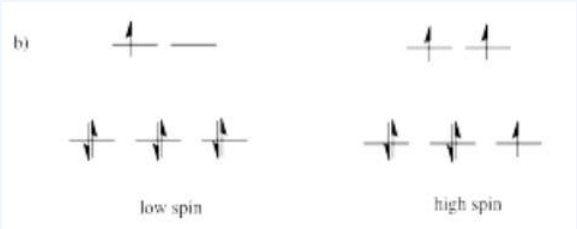
Draw both high spin and low spin d-orbital splitting diagrams for the following ions in an octahedral environment and determine the number of unpaired electrons in each case.

a) Mn^{2+} b) Co^{2+} c) Ni^{2+} d) Cu^{+} e) Fe^{3+} f) Cr^{2+} g) Zn^{2+}

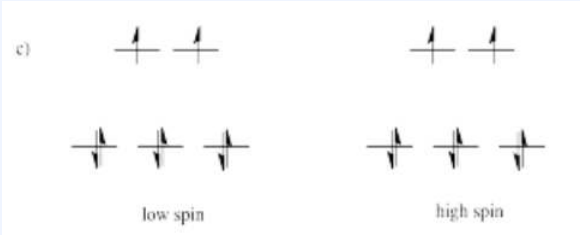
Answer a)



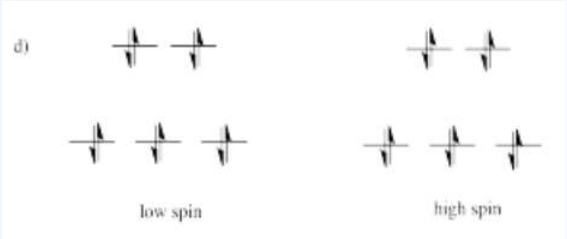
Answer b)



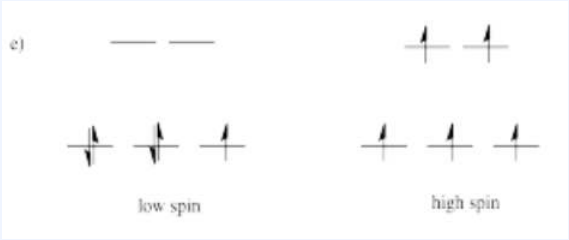
Answer c)



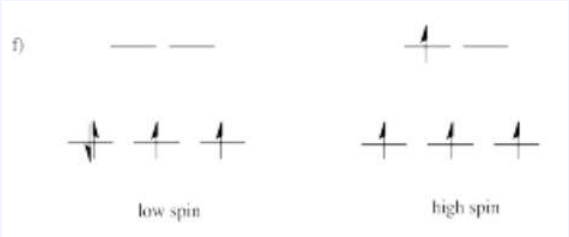
Answer d)



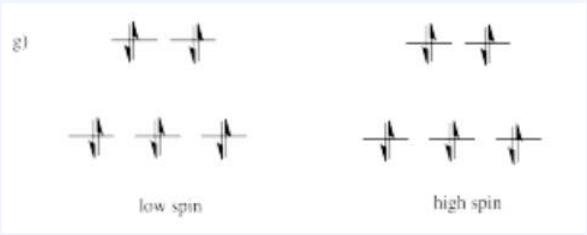
Answer e)



Answer f)



Answer g)



Exercise 10.2

The d orbital splitting diagram for a tetrahedral coordination environment is shown below. Given this diagram, and the axes in the accompanying picture, identify which d orbitals are found at which level. In the picture, the metal atom is at the center of the cube, and the circle represent the ligands.

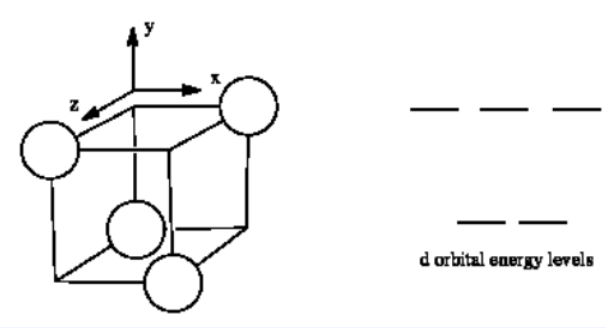
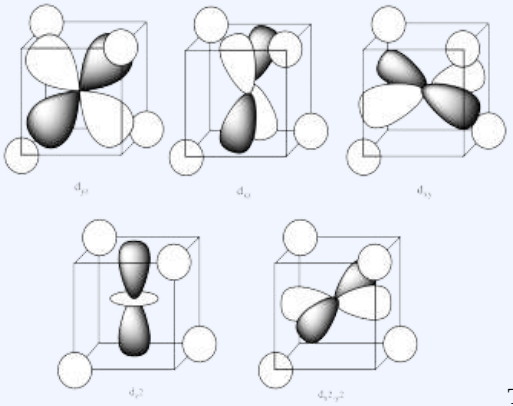


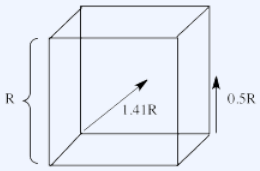
Figure 10.17:

Answer

The three orbitals shown above interact a little more strongly with the ligands. The three orbitals shown below interact a little more weakly.



The reason for the difference in the interaction has to do with how close the nearest lobe of a d orbital comes to a ligand. There are really two possible positions: the face of a cube or the edge of a cube. If the ligands are at alternating corners of the cube, then the orbitals pointing at the edges are a little closer than those pointing at the faces of the cube.



$$\sqrt{R^2 + R^2} = 0.5\sqrt{2R^2} = 0.705R$$

Exercise 10.3

Typically, the d orbital splitting energy in the tetrahedral case is only about 4/9 as large as the splitting energy in the analogous octahedral case. Explain why it is smaller for the tetrahedral case.

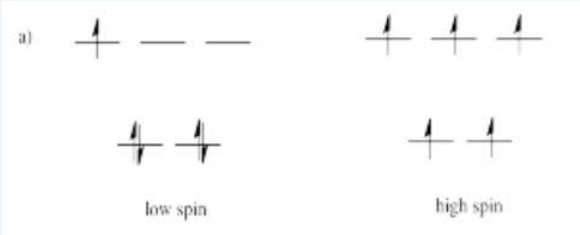
Answer

The ligands do not overlap with the d orbitals as well in tetrahedral complexes as they do in octahedral complexes. Thus, there is a weaker bonding interaction in the tetrahedral case. That means the antibonding orbital involving the d electrons is not raised as high in energy, so the splitting between the two d levels is smaller.

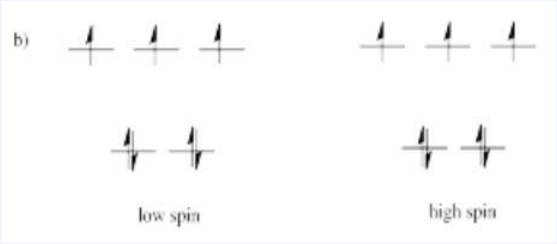
Exercise 10.4

Suppose each of the ions in Exercise 10.1 (CC8.1) were in tetrahedral, rather than octahedral, coordination environments. Draw the d orbital diagrams for the high spin and the low spin case for each ion.

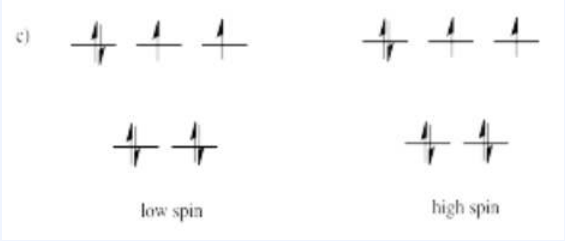
Answer a)



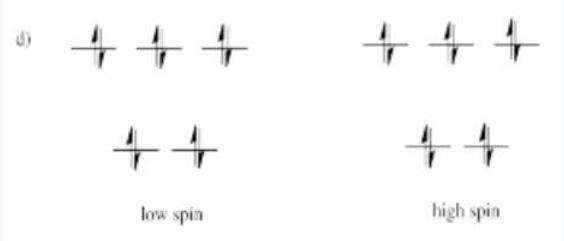
Answer b)



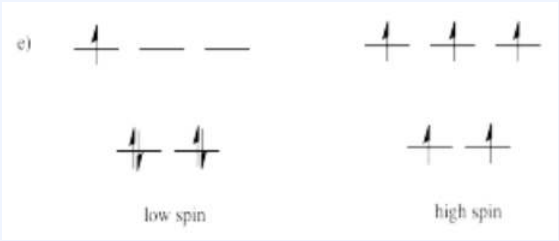
Answer c)



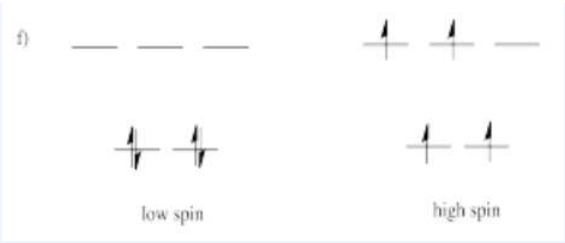
Answer d)



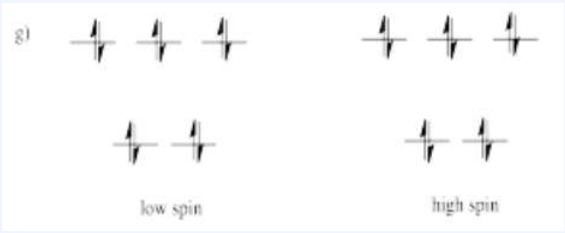
Answer e)



Answer f)



Answer g)



Exercise 10.5

Usually, tetrahedral ions are high spin rather than low spin. Explain why.

Answer

Because the d orbital splitting is much smaller in the tetrahedral case, it is likely that the energy required to pair two electrons in the same orbital will be greater than the energy required to promote an electron to the next energy level. In most cases, the complex will be high spin.

Exercise 10.6

The d orbital splitting diagram for a square planar environment is shown below. Given this diagram, and the axes in the accompanying picture, identify which d orbitals are found at which level.

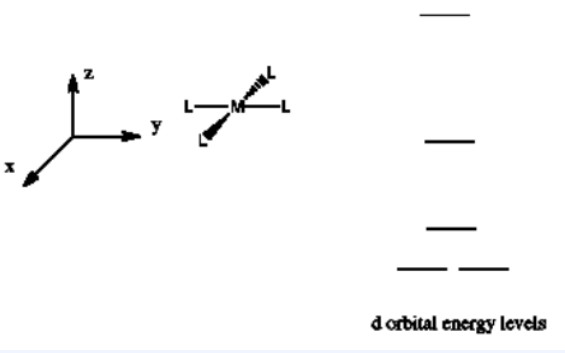
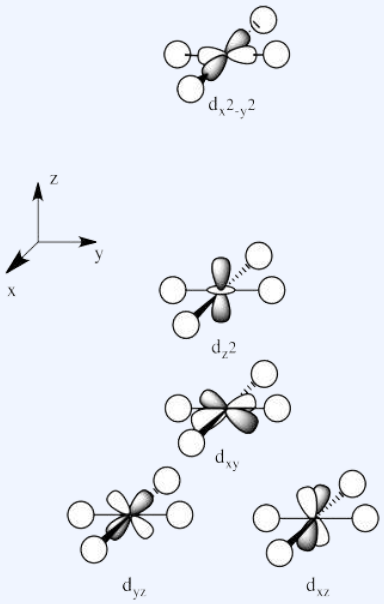


Figure 10.18:

Answer

The orbitals are shown in order of energy.



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Chris P Schaller, Ph.D., (College of Saint Benedict / Saint John's University)

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10.1: Tetrahedral and Octahedral Geometries

Until this point, we have focused on one of the most common cases for metal complexes, the 6-coordinate octahedral ligand field geometry. Now, we will examine other geometries, with a focus on 4-coordinate ligand fields. Almost everything you have already learned about octahedrons can be applied to 4-coordinate metal complexes (effects of metal and ligands on Δ); the main difference is the splitting pattern of d-orbitals is different in each 4-coordinate complex than it was in the octahedral cases. Also, the magnitudes of splitting are different in important ways.

Since CFT is simpler than LFT, let's use CFT to describe and derive these "new-to-you" splitting patterns. Now is a good time to go back and recall how CFT was used to derive the splitting of d-orbitals in an octahedral field so that you can use that as a launching pad for deriving the tetrahedron (harder) and square planar geometries:

? Exercise 10.1.1

The d orbital splitting diagram for a tetrahedral coordination environment is shown below. Given this diagram, and the axes in the accompanying picture, identify which d orbitals are found at which level. In the picture, the metal atom is at the center of the cube, and the circle represent the ligands.

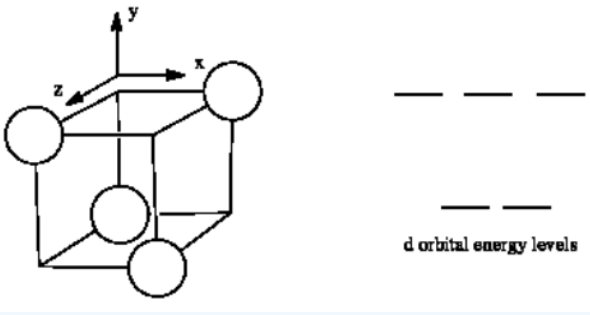
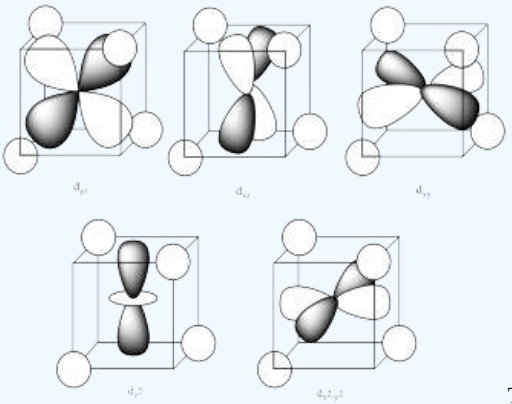


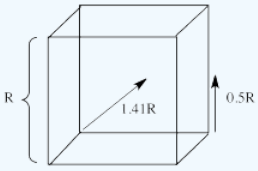
Figure 10.1.1:

Answer

The three upper orbitals (dy, dx, dz) interact a little more strongly with the ligands. The two lower orbitals (dz^2 and dx^2-y^2) interact a little more weakly.



The reason for the difference in the interaction has to do with how close the nearest lobe of a d orbital comes to a ligand. There are really two possible positions: the face of a cube or the edge of a cube. If the ligands are at alternating corners of the cube, then the orbitals pointing at the edges are a little closer than those pointing at the faces of the cube.



$$\sqrt{R^2 + R^2} = 0.5\sqrt{2R^2} = 0.705R$$

? Exercise 10.1.2

Typically, the d orbital splitting energy in the tetrahedral case is only about 4/9 as large as the splitting energy in the analogous octahedral case. Explain why it is smaller for the tetrahedral case.

Answer

The ligands do not overlap with the d orbitals as well in tetrahedral complexes as they do in octahedral complexes. Thus, there is a weaker bonding interaction in the tetrahedral case. That means the antibonding orbital involving the d electrons is not raised as high in energy, so the splitting between the two d levels is smaller.

Exercise 10.1.3

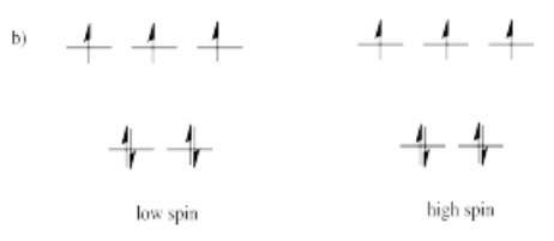
Suppose each of the ions below were in tetrahedral coordination environments. Draw the d orbital diagrams for the high-spin and the low-spin case for each ion. Which one (high-spin or low-spin) is more likely?

a) Mn^{2+} b) Co^{2+} c) Ni^{2+} d) Cu^{+} e) Fe^{3+} f) Cr^{2+} g) Zn^{2+}

Answer a)

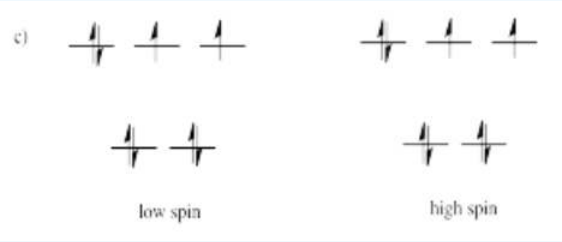
High spin is more likely for tetrahedral coordination geometry due to weak interactions between ligand orbitals and metal d-orbitals.

Answer b)



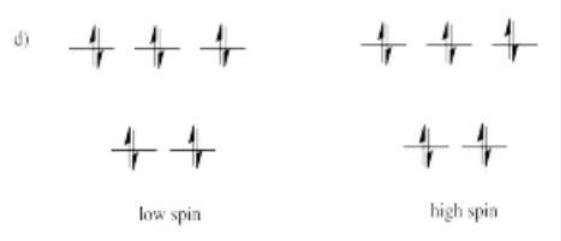
High spin is more likely for tetrahedral coordination geometry due to weak interactions between ligand orbitals and metal d-orbitals.

Answer c)



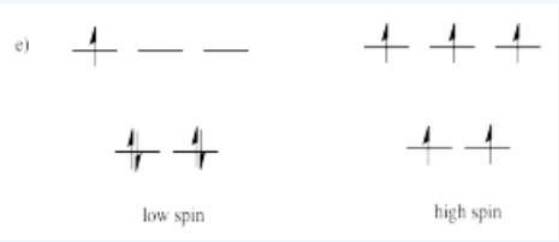
High spin is more likely for tetrahedral coordination geometry due to weak interactions between ligand orbitals and metal d-orbitals.

Answer d)



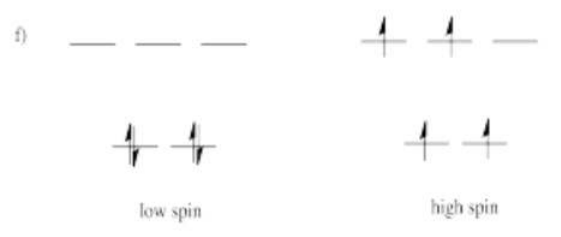
High spin is more likely for tetrahedral coordination geometry due to weak interactions between ligand orbitals and metal d-orbitals.

Answer e)



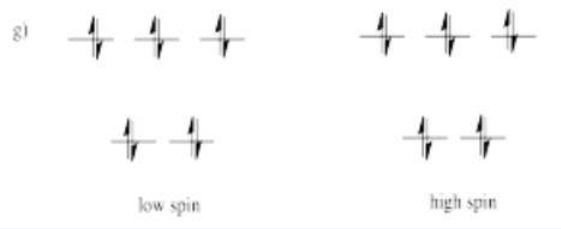
High spin is more likely for tetrahedral coordination geometry due to weak interactions between ligand orbitals and metal d-orbitals.

Answer f)



High spin is more likely for tetrahedral coordination geometry due to weak interactions between ligand orbitals and metal d-orbitals.

Answer g)



High spin is more likely for tetrahedral coordination geometry due to weak interactions between ligand orbitals and metal d-orbitals.

? Exercise 10.1.4

Usually, tetrahedral ions are high spin rather than low spin. Explain why.

Answer

Because the d orbital splitting is much smaller in the tetrahedral case, it is likely that the energy required to pair two electrons in the same orbital will be greater than the energy required to promote an electron to the next energy level. In most cases, the complex will be high spin.

? Exercise 10.1.5

The d orbital splitting diagram for a square planar environment is shown below. Given this diagram, and the axes in the accompanying picture, identify which d orbitals are found at which level.

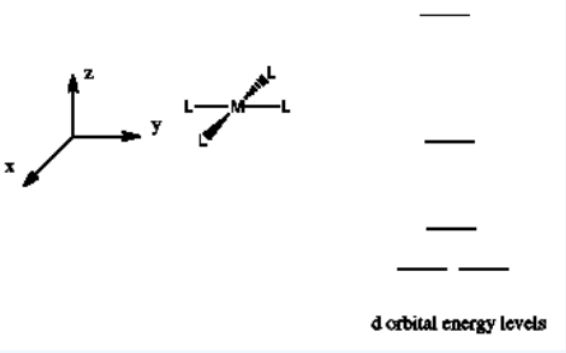
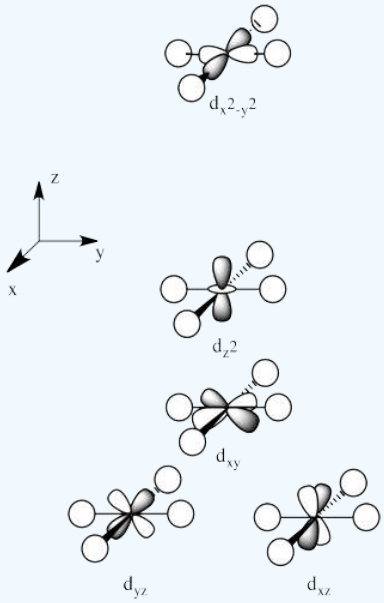


Figure 10.1.18:

Answer

The orbitals are shown in order of energy.



Exercise 10.1.6

Predict whether each compound will be square planar or tetrahedral.

a. $[Zn(NH_3)_4]^{2+}$

b. $[NiCl_4]^{2+}$

c. $[Ni(CN)_4]^{2-}$

d. $[Ir(CO)(OH)(PCy_3)_2]^{2+}$; Cy = cyclohexyl

e. $[Ag(dppb)_2]^+$; dppb = 1,4-bis(diphenylphosphino)butane

f. $PtCl_2(NH_3)_2$

g. $PdCl_2(NH_3)_2$

h. $[CoCl_4]^{2-}$

i. $Rh(PPh_3)_3Cl$

Answer a)

$[Zn(NH_3)4]^{2+}$ 3d metal, d^{10}, sigma donor ligand → tetrahedral

Answer b)

$[NiCl_4]^{2+}$ 3d metal, d^8, pi donor ligand → tetrahedral

Answer c)

$[Ni(CN)_4]^{2-}$ 3d metal, d^8, pi acceptor ligand → square planar

Answer d)

$[Ir(CO)(OH)(PCy_3)_2]^{2+}$ 5d metal, d^8 → square planar

Answer e)

$[Ag(dppb)_2]^{1+}$ 4d metal, d^{10}, sigma donor ligand → tetrahedral

Answer f)

$[PtCl_2(NH_3)_2]$ 5d metal, d^8 → square planar

Answer g)

$[PdCl_2(NH_3)_2]$ 4d metal, d^8, M^{+2}, sigma donor ligand → square planar

Answer h)

$[CoCl_4]^{2-}$ 3d metal, d^7, sigma donor ligand → tetrahedral

Answer i)

$[Rh(PPh_3)_3Cl]$ 5d metal, d^8 → square planar

LFSE and SE for Other Geometries

Just like in the case of octahedral metal complexes, we can apply CFT (or LFT) to calculate LFSE and SE of 4-coordinate (or any-coordinate) metal complexes. Once again, in terms of the d orbital splitting diagram, the results are similar to what we see from molecular orbital theory. For tetrahedral geometry, which is the most common geometry when the coordination number is four, we get a set of two high-lying orbitals and three lower ones.

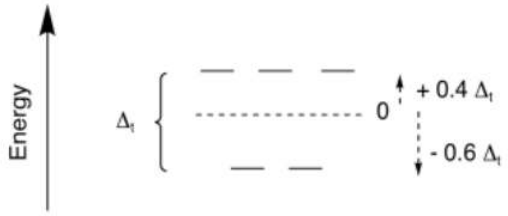


Figure 10.1.11:

The overall splitting is expressed as Δ_t; the t stands for tetrahedral. However, sometimes it is useful to compare different geometries. In crystal field theory, it can be shown that the amount of splitting in a tetrahedral field is much smaller than in an octahedral field. In general, $\Delta_t = 4/9\ \Delta_o$.



Figure 10.1.12:

Which geometries are most likely?

We wouldn't usually use crystal field theory to decide whether a metal is more likely to adopt a tetrahedral or an octahedral geometry. In most cases, the outcome is more strongly dependent on factors other than the d orbital energies. For example, maybe a complex would be too crowded with six ligands, so it only binds four; it becomes tetrahedral rather than octahedral. Or maybe a metal does not have enough electrons in its valence shell, so it binds a couple more ligands; it becomes octahedral rather than tetrahedral.

However, this comparison between Δ_o and Δ_t does help to explain why tetrahedral complexes are much more likely than octahedral complexes to adopt high-spin configurations. The splitting is smaller in tetrahedral geometry, so pairing energy is more likely to become the deciding factor there than it is in octahedral cases.

? Exercise 10.1.1

Tetrahedral complexes are pretty common for high-spin d^6 metals, even though the 18-electron rule suggests octahedral complexes should form. In contrast, low-spin d^6 complexes do not usually form tetrahedral complexes. Use calculations of stabilisation energies to explain why.

Answer

high-spin d^6



octahedral

$SE = [2(0.6) -4(0.4)]\Delta_o + PE$

$SE = -0.4\Delta_o + PE$

tetrahedral

$SE = [3(0.4) - 3(0.6](4/9)\Delta_o + PE$

$SE = -0.6\Delta_o + PE$

$\Delta SE = SE_{oh} - SE_{td} = -0.4\Delta_o + PE -(-0.6\Delta_o + PE) = +0.2\Delta_o$

This is a slight preference for tetrahedral.

low-spin d^6



octahedral

$SE = [0(0.6) -6(0.4)]\Delta_o + 3PE$

$SE = -2.4\Delta_o + 3PE$

tetrahedral

$SE = [2(0.4) - 4(0.6](4/9)\Delta_o + 2PE$

$SE = -1.6\Delta_o + PE$

$\Delta SE = SE_{oh} - SE_{td} = -2.4\Delta_o + 3PE - (-1.6\Delta_o + 2PE) = -0.8\Delta_o + PE$

This is a preference for octahedral, although it would be offset by the pairing energy.

Crystal field theory has also been used to determine the splitting between the orbitals in a square planar geometry. That is a much more complicated case, because there are four different levels. Once again, the energy levels are often expressed in terms of Δ_o.

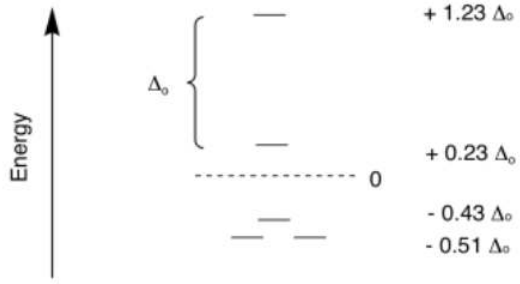


Figure 10.1.13:

We could use a calculation of stabilisation energy to predict whether a particular complex is likely to adopt a tetrahedral or a square planar geometry. Both geometries are possible, so it would be useful to be able to predict which geometry occurs in which case. However, just as in the case of comparing octahedral and tetrahedral gemoetries, there is another factor that is often more important.

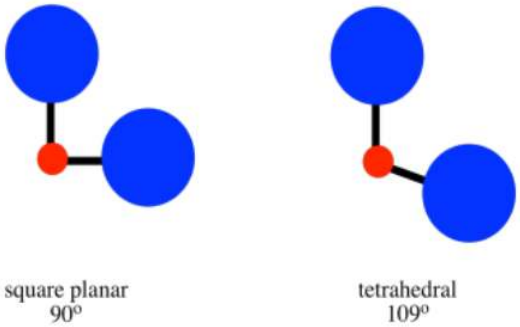


Figure 10.1.14:

That factor is steric crowding. In a tetrahedron, all the ligands are 109° from each other. In a square planar geometry, the ligands are only 90° away from each other. Tetrahedral geometry is always less crowded than square planar, so that factor always provides a bias toward tetrahedral geometry. As a result, we might expect square planar geometry to occur only when sterics is heavily outweighed by ligand field stabilisation energy.

? Exercise 10.1.2

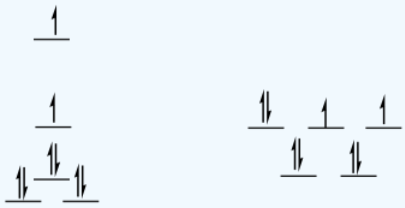
The most common examples of square planar complexes have metals that are d^8. Use calculations of the stabilisation energy to explain why if the complex is:

(a) low-spin

(b) high-spin

Answer a)

high-spin d^8



square planar

$SE = [1.23 + 0.23 - 2(0.43) -4(0.51)]\Delta_o + 3PE$

$SE = -1.44\Delta_o + 3PE$

tetrahedral

$SE = [4(0.4) - 4(0.6](4/9)\Delta_o + 3PE$

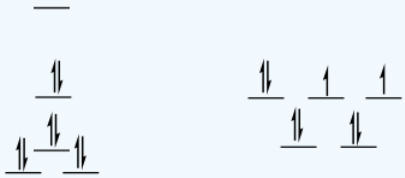
$SE = -0.36\Delta_o + 3PE$

$\Delta SE = SE_{sq} - SE_{td} = -1.44\Delta_o + 3PE -(-0.36\Delta_o + 3PE) = -1.08\Delta_o$

This is an appreciable preference for square planar.

Answer b)

low-spin d^8



square planar

$SE = [0 + 2(0.23) - 2(0.43) -4(0.51)]\Delta_o + 4PE$

$SE = -2.44\Delta_o + 4PE$

tetrahedral = same as before (ls = hs for d^8 tetrahedral)

$\Delta SE = SE_{sq} - SE_{td} = -2.44\Delta_o + 3PE -(-0.36\Delta_o + 3PE) = -2.08\Delta_o + PE$

This is an even more appreciable preference for square planar, although it is offset by pairing energy. Pairing energy would have to be twice as big as Δ_o in order to completely offset the LFSE.

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11: Ligand Field Stabilisation Energy (LFSE)

There is a variation on how to think about d orbital splitting diagrams that can be useful in deciding how the d electrons are configured in transition metal complexes. We can use the relative energy levels of the d orbitals in a given complex to calculate whether the overall energy would be higher or lower in a high-spin vs. a low-spin case, for example. The calculation provides us with a value that is called the ligand field stabilisation energy (LFSE). Although we have been thinking of bonding in transition metal complexes in terms of molecular orbital ideas, ligand field stabilisation energy actually has its roots in a separate approach called crystal field theory.

Origin Story: LFSE originally comes from CFT

Crystal field theory (CFT) was independently developed around 1930 by German physicist Hans Bethe and American physicist John Hasbrouck van Vleck; the two later became professors of physics at Cornell and Harvard, respectively. CFT actually pre-dates the molecular orbital approach that we have been using so far, but it reaches similar conclusions about transition metal electron configurations.

Both scientists were interested in the magnetic properties of metals and metal salts. They knew these properties were related to unpaired electrons. Compounds with unpaired electrons (paramagnetic) are attracted by magnetic fields, whereas compounds having only paired electrons (diamagnetic) are not. They were interested in the factors that influenced the d electron configuration of transition metal salts, because how the d electrons filled could result in different numbers of unpaired electrons. Those differences influenced how strongly the compounds interacted with magnetic fields.

Crystal field theory does not consider any bonding interactions in transition metal compounds. It focuses only on the repulsion between the electrons on an anion and the electrons on a metal cation. Of course, all of these electrons have negative charges. As an anion approaches a metal, the physicists reasoned, both sets of electrons would experience repulsive forces that would increase their energy level.

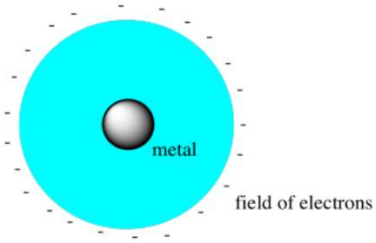


Figure 11.1:

If the metal were surrounded by a spherical field of electrons (physicists like to assume things are spherical because it makes the math easier), then all of the electrons on the metal would be raised equally high in energy by these repulsive forces.



Figure 11.2:

But in a metal salt, electrons are not approaching the metal from all directions. The geometry comes in because of the fact that the cations and anions pack together in specific arrays. For example, if a metal cation is sitting in an octahedral hole, electrons would only approach from six directions: at each end of the x, y, and z axes.

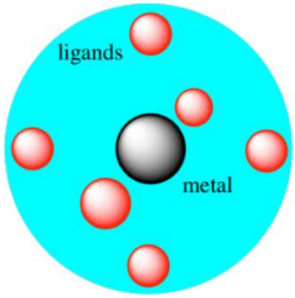


Figure 11.3:

In that case, only the electrons in d orbitals that were aligned along the x, y and z axes would be raised significantly by repulsion with the approaching electrons on the anions. The electrons in the off-axis orbitals would be lower in energy than they would have been in a perfectly spherical field.

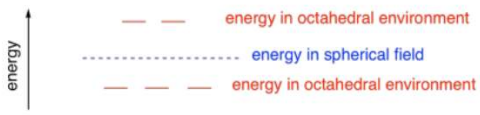


Figure 11.4:

Scientists later adapted this idea to octahedral coordination complexes, in which the metal sits amidst six ligands rather than getting packed among six anions.

That result leads to a picture that is pretty similar to what we get from molecular orbital theory, at least as far as the d orbitals are concerned. In fact, the true mathematical approach to molecular orbital theory does take these electron-electron repulsions into account, but it also factors in attractions between the electrons of the ligands and the nucleus of the metal

(and vice versa). The biggest difference is that molecular orbital theory includes what happens to the kinetic energy of the ligand lone pairs as they become shared with the metal (it goes down; that's a big part of why the bonds form).

The calculation of LFSE

You don't really have to appreciate where this approach came from to be able to see how it is commonly used. If we take the five d orbitals after they have been placed in an octahedral environment, we see that they are at two different energy levels. The average energy level is not, as it might first appear, halfway between these levels. That's because there are three lower energy level orbitals and two higher energy level orbitals. The average is two-fifths of the way up from the bottom three, or three-fifths of the way down from the top two.

That average energy level of the five d orbitals is called the "**barycenter**"; it is assigned a relative energy of zero. The difference between the top level and the bottom level is the field splitting; for an octahedral complex, this field splitting is given the symbol Δ_o; here, Δ stands for the energy difference and *o* stands for octahedral.

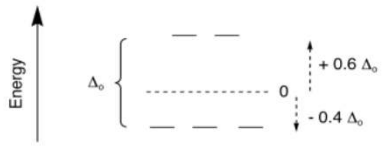


Figure 11.5:

If the barycenter is at an energy level of zero, then the lower orbitals are below zero. How far? They are two-fifths of the total Δ_o below the barycenter. Any electrons in those orbitals are **$-0.4\Delta_o$** below 0 in energy. Electrons in the upper orbitals are **$+0.6\Delta_o$** above zero in energy.

Example d^4:

Suppose there are four electrons. The first three electrons sit in each of the three lower orbitals, the ones we sometimes label the t_{2g} orbitals. The fourth will either go into the upper level, which we sometimes call the e_g level, or else pair up with another electron at the lower level.



Figure 11.6:

We can now calculate the energy difference between these two possible cases. We can calculate what is called the ligand field stabilisation energy, LFSE (sometimes called crystal field stabilisation energy, or CFSE). It's just the sum of the energies of each of the electrons.

$$\boldsymbol{LFSE = [(0.6 \times number\ of\ e_g\ electrons) - (0.4 \times number\ of\ t_{2g}\ electrons)]\Delta_o} \quad (11.1)$$

or if that's too much jargon, $LFSE = [(0.6 \times \#upper\ e^-) - (0.4 \times \#lower\ e^-)]\Delta_o$

For the d^4 high-spin case:

$$LFSE = [(0.6 \times 1) - (0.4 \times 3)]\Delta_o = [0.6 - 1.2]\Delta_o = -0.6\Delta_o \quad (11.2)$$

For the \(d^4 low-spin case:

$$LFSE = [(0.6 \times 0) - (0.4 \times 4)]\Delta_o = -1.6\Delta_o \quad (11.3)$$

So far, it certainly seems like the low-spin case is at lower energy and thus more stable. Remember, though, that low-spin configuration requires that we place two electrons together into the same orbital.



Figure 11.7:

Pairing electrons in the same orbital is going to cost some energy. But how much?

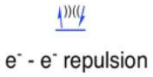


Figure 11.8:

This repulsion between a pair of electrons in one orbital is called the pairing energy (PE). For each pair of electrons that occupy the same orbital, that energy must be added to take that repulsion into account. As a result, a calculation of the overall stabilization energy (SE) includes both the LFSE and the PE.

$$SE = LFSE + PE \quad (11.4)$$

If there were two sets of paired electrons, we would add 2PE; if there were three sets of paired electrons, we would add 3PE, and so on.

Overall, deciding quantitatively whether a complex will be high spin or low spin is the most useful application of an LFSE calculation. However, you do have to know the values of the parameters (the field splitting and the pairing energy) for a definitive decision.

? Exercise 11.1

Use SE calculations to determine stabilisation in both high spin and low spin cases. Just leave your answer expressed in terms of Δ_o and PE.

a. Fe^{+2}

b. Co^{+2}

c. Co^{+3}

d. Mn^{+2}

e. Ti^{+3}

Answer a)

Fe^{+2}

d^6 low spin
SE = [-0.4(6)+ 0.6(0)] Δo + 3PE
= [-2.4] Δo + 3PE

d^6 high spin
SE = [-0.4(4)+ 0.6(2)] Δo + 1PE
= [-.4] Δo + 1PE

Answer b)

Co^{+2}

d^7 low spin
SE = [-0.4(6)+ 0.6(1)] Δo + 3PE
= [-1.8] Δo + 3PE

d^7 high spin
SE = [-0.4(5)+ 0.6(2)] Δo + 2PE
= [-.8] Δo + 2PE

Answer c)

Co^{+3}
d^6 so this looks the same as Fe^{+2}

Answer d)

Mn^{+2}

d^5 low spin
SE = [-0.4(5)+ 0.6(0)] Δo + 2PE
= [-2.0] Δo + 2PE

d^5 high spin
SE = [-0.4(3)+ 0.6(2)] Δo + 0PE
= [0] Δo

Answer e)

Ti^{+3}
d^1 so there is no possibility of low spin or high spin

SE depends on the Magnitude of Δ_o and total PE

Right now, let's think about Δ_o. How much energy is it? How big is the gap between the d orbitals? And how do we know? Well, we can easily measure this gap using a simple spectrophotometer. A spectrophotometer measures how much light is absorbed by a sample. Furthermore, it measures what specific colors of light are absorbed by the sample. As it happens, the absorption of ultraviolet and visible light by a material is associated with electrons in that material becoming promoted to a higher energy level. Shine a light on a transition metal complex, and an electron may jump the gap.

So all we have to do is shine different colors of monochromatic light on the complex and see whether it absorbs one of the colors.

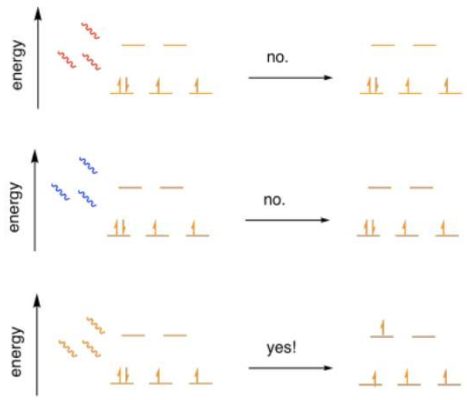


Figure 11.9:

This experiment is quite reproducible. A specific compound will always absorb the same colors of light. That's why specific materials have specific colors; the color we see represents the light that is *not* absorbed by the material.

Different colors of light have different amounts of energy. Blue light has higher energy than orange light, which has higher energy than red light. Max Planck and Albert Einstein worked out that the energy of a photon (a "particle" or "packet" of light) is directly proportional to the frequency at which the photon oscillates or vibrates. Blue light has a higher frequency than red light, so it has higher energy.

Planck and Einstein expressed this idea with an equation,

$$E = h\nu$$

in which the Greek letter ν, pronounced "noo," stands for the frequency (some people just use *f* for frequency) and *h* stands for a sort of conversion factor called Planck's constant.

Blue light has too much energy to promote an electron to the next energy level in this case. It would send the electron way past the next level, and quantum mechanics does not allow that sort of thing. Red light does not have enough energy for the electron to get there. Orange light, in this case, is just right. It has exactly the right amount of energy to jump the gap.

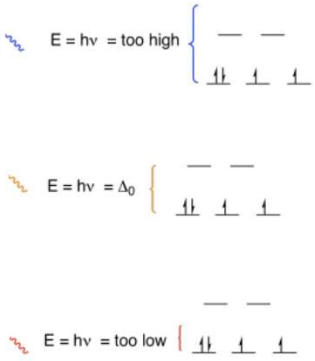


Figure 11.10:

So, if we know the frequency of orange light, we know how much energy there is in an orange photon, and we know how big the field splitting is between the d orbitals.

Historically, it turns out that people have most often described visible light in terms of wavelength rather than frequencies. The wavelength is just the distance from one "peak" to the next as the wave of the photon rolls along. The higher the frequency, the closer these peaks are together, and the shorter the wavelength. Blue light has a shorter wavelength, around 400 nm, than red light, around 700 nm. A nanometer (nm) is 10^{-9} meters (m); a meter is around a yard.

Orange light has a wavelength of around 600 nm, or 600 x 10^{-9} m, or 6 x 10^{-7} m. For reasons we won't get into, spectroscopists in the past (people who measure the interaction of light and matter) sometimes preferred to work in centimeters, cm; there are 100 cm in 1 m, so orange light has a wavelength of 6 x 10^{-5} cm. Now, because they knew there was an inverse relationship between wavelength and energy (the longer the wavelength, the lower the energy; the shorter the wavelength, the higher the energy), they simply took the reciprocal of the wavelength in centimeters to get a number in cm^{-1}, which they called wavenumbers. They used this as a unit of energy. An orange photon has an energy of 1/0.00006 cm = 16,000 cm^{-1}.

So the gap, the field splitting, Δ_o in this complex is 16,000 cm^{-1}.

Let's go back to our comparison between the high-spin and low-spin case. For high spin:

$$LFSE = [(0.6 \times 1) - (0.4 \times 3)]\Delta_o = [0.6 - 1.2]\Delta_o = -0.6\Delta_o = -0.6 \times 16000cm^{-1} = -9600cm^{-1} \quad (11.5)$$

For the low-spin case:

$$LFSE = [(0.6 \times 0) - (0.4 \times 4)]\Delta_o = -1.6\Delta_o = -1.6 \times 16000cm^{-1} = -25600cm^{-1} \quad (11.6)$$

These LFSE calculations show that the low-spin case is lower in energy, by 14,000 cm^{-1}. However, we still need to include the pairing energy. Like the field splitting, the pairing energy varies from one complex to another. 20,000 cm^{-1} is a ballpark estimate of a typical pairing energy.

If we use this average value for PE in the example we were discussing above for the high-spin case:

$$SE = LFSE + PE = -9600 + 0cm^{-1} = -9600cm^{-1} \quad (11.7)$$

For the low-spin case:

$$SE = LFSE + PE = -25600 + 20000cm^{-1} = -5600cm^{-1} \quad (11.8)$$

Taking the pairing energy into account in this case suggests that the high-spin case is favored. It cost less energy to jump the gap and put an electron in a high-lying e_g orbital than it did to pair electrons in a low-lying t_{2g} orbital.

Reminder: Factors that influence Δ_o

Let's take a look at some real examples of field splitting values to get an idea of how large they are, and what factors they depend on.

The metal influences Δ_o

For example, we can look at the charge on the metal ion:

Table of Field Splitting Values, Δ_o, in Hexaquo Complexes of Differing Charges[a]

Metal Complex	$[Mn(OH_2)_6]^{2+}$	$[Mn(OH_2)_6]^{3+}$	$[Fe(OH_2)_6]^{2+}$	$[Fe(OH_2)_6]^{3+}$	$[Co(OH_2)_6]^{2+}$	$[Co(OH_2)_6]^{3+}$
Δ_o (cm^{-1})	7,800	21,100	10,400	13,800	9,300	18,300

a) Holleman, A. F.; Wiberg, E.; Wiberg, N. Inorganic Chemistry, 34th Ed. Academic Press: Berlin, 2001.

In this case, it looks like increased charge on the metal ion results in an increased field splitting. The same thing happens in all three examples: manganese, iron, and cobalt. As the metal ion becomes more charged, attraction of the d electrons toward the nucleus increases. The lower-lying t_{2g} level is more strongly attracted to the nucleus because it is a little closer; consequently, it drops a little further than the e_g level, and the gap gets bigger.

Charge on the metal ion is one of two key factors that influences the size of the field splitting. The other factor is the period or row in the periodic table.

Table of Field Splitting Values, Δ_o, in Hexammine Complexes of Group 9[a,b]			
Metal Complex	$[Co(NH_3)_6]^{3+}$	$[Rh(NH_3)_6]^{3+}$	$[Ir(NH_3)_6]^{3+}$
Δ_o (cm^{-1})	21,500	33,100	41,100
a) Holleman, A. F.; Wiberg, E.; Wiberg, N. Inorganic Chemistry, 34th Ed. Academic Press: Berlin, 2001. b) Miessler, G. L.; Tarr, D. A. Inorganic Chemistry, 4th Ed. Pearson, 2010.			

Moving from one row to the next in group 9 of the periodic table, we see that the field splitting increases by about 10,000 cm^{-1} each row.

In general:

- Δ_o increases with charge on the metal
- Δ_o increases with the period in the periodic table

The ligand identity influences Δ_o

The metal ion is not the only factor that affects the field splitting. The ligands also play an important role, as seen in the table below.

Table of Field Splitting Values, Δ_o, in Assorted Complexes[a]							
Metal Complex	$[CrCl_6]^{3-}$	$[CrF_6]^{3-}$	$[Fe(OH_2)_6]^{2+}$	$[Fe(CN)_6]^{4-}$	$[Co(OH_2)_6]^{3+}$	$[Co(NH_3)_6]^{3+}$	$[Co(CN)_6]^{3-}$
Δ_o (cm^{-1})	13,300	15,300	10,400	33,200	18,300	23,000	33,700
a) Holleman, A. F.; Wiberg, E.; Wiberg, N. Inorganic Chemistry, 34th Ed. Academic Press: Berlin, 2001.							

If we sort these ligands into three broad categories, we can form a trend for these effects. It may be easiest to start with the three entries on the right, involving cobalt. The oxygen donor in water has two lone pairs, whereas the nitrogen donor in ammonia has only one. The extra lone pair allows water to act as a π (pi) donor; the lone pair can donate to an orbital on the metal to form a pi bond. In this case, it looks like the π donor (water) results in a smaller Δ_o than the normal σ (sigma) donor (ammonia).

The cyanide ligand has a donor atom that is also participating in a π bond within the ligand; there is a triple bond between the C and N of the cyanide. That means there is also an associated antibonding orbital, π*. That antibonding orbital raises the possibility of back-bonding from the metal. The metal can donate into the π* orbital to make a pi bond. Cyanide is a π-acceptor. Its field splitting is much larger than the sigma donor.

Those conclusions can be confirmed by looking at the entries for iron in the middle of the table. Cyanide is a π-acceptor whereas water is a π-donor. The field splitting in the aquo complex should be much smaller than the field splitting in the cyano complex, and it is.

The two entries for chromium on the left both show halides, which are π-donors. They illustrate a factor that can be used to predict field strength between two ligands from the same group, such as two π-donors or two π-acceptors. In general, the more basic the ligand, the greater the field splitting. Fluoride ion is more basic than chloride ion (because chloride is a more stable anion than fluoride) so it results in a slightly greater value of Δ_o.

The Pairing Energy

In order to thoroughly estimate the stabilisation energy, we also need reliable values for the pairing energy. Pairing energies can be calculated for free metal ions; correction factors can be applied to arrive at a corresponding value in a complex. In general, the values in coordination complexes are somewhat lower than the values in free metal ions. In the table below, we have made a general estimate that the value in the complex is about 20% lower than in the free metal ion.

Table of Pairing Energies, PE, in Free Ions, with Estimated PE in Complexes						
Metal Ion	Mn^{2+}	Mn^{3+}	Fe^{2+}	Fe^{3+}	Co^{3+}	Ru^{3+}
PE, free ion (cm^{-1})	28,000	25,500	17,700	30,100	21,100	~15,000[b]
PE, complex (est., cm^{-1})	20,400	22,900	14,200	24,100	16,900	~12,000[b]
a) Holleman, A. F.; Wiberg, E.; Wiberg, N. Inorganic Chemistry, 34th Ed. Academic Press: Berlin, 2001. b) Estimate.						

If we compare the pairing energies (PE) of the 2+ ions to those of the 3+ ions, we see that PE is always lower in the more highly charged ion. That's the opposite of the trend in Δ_o. Pairing energy is largely dependent on the size of the ion. The smaller the ion, the smaller the orbital, and the more repulsion between two electrons in the same orbital. Because a Mn^{3+} ion is smaller than a Mn^{2+} ion (Coulomb's Law says there is greater attraction for the electrons in the former case, so the ion shrinks), a pair of electrons on Mn^{3+} is closer together than a pair of electrons on Mn^{2+}.

In general, pairing energies also get smaller upon moving down a column in the periodic table. Second row transition metals are larger than first-row transition metals, so the pairing energy is smaller in the second row than in the first. Third row transition metals are about the same size as first row metals, so their pairing energies are similar to those of the second row. That's because of a phenomenon called "the lanthanide contraction": third row transition metals contain an extra set of protons in their nuclei because of the f block elements before them; consequently they are a little smaller than might be expected.

? Exercise 11.2

Compare pairing energies to field splitting values to determine whether the following complexes would be high-spin or low spin.

a) $Mn(OH_2)_6^{2+}$ b) $Fe(CN)_6^{4-}$ c) $Co(NH_3)_6^{3+}$

Answer a)

Δ_o < PE, so high-spin.

Answer b)

Δ_o > PE, so low-spin.

Answer c)

Δ_o > PE, so low-spin.

Attribution

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11.1: The Effect of the Metal Ion on d-Orbital Splitting

The Magnitude of Δ_o

For octahedral complexes, the magnitude of Δ_o dictates whether a complex with four, five, six, or seven d electrons is high spin or low spin, which affects its magnetic properties, structure, and reactivity. Large values of Δ_o (i.e., $\Delta_o > P$) yield a low-spin complex, whereas small values of Δ_o (i.e., $\Delta_o < P$) produce a high-spin complex. As we noted, the magnitude of Δ_o depends on three factors: the charge on the metal ion, the principal quantum number of the metal (and thus its location in the periodic table), and the nature of the ligand. Values of Δ_o for some representative transition-metal complexes are given in Table 11.1.1.

***Table* 11.1.1:** *Crystal Field Splitting Energies for Some Octahedral (Δ_o)* and Tetrahedral (Δ_t) Transition-Metal Complexes*

Octahedral Complexes	Δ_o (cm^{-1})	Octahedral Complexes	Δ_o (cm^{-1})	Tetrahedral Complexes	Δ_t (cm^{-1})
$[Ti(H_2O)_6]^{3+}$	20,300	$[Fe(CN)_6]^{4-}$	32,800	VCl_4	9010
$[V(H_2O)_6]^{2+}$	12,600	$[Fe(CN)_6]^{3-}$	35,000	$[CoCl_4]^{2-}$	3300
$[V(H_2O)_6]^{3+}$	18,900	$[CoF_6]^{3-}$	13,000	$[CoBr_4]^{2-}$	2900
$[CrCl_6]^{3-}$	13,000	$[Co(H_2O)_6]^{2+}$	9300	$[CoI_4]^{2-}$	2700
$[Cr(H_2O)_6]^{2+}$	13,900	$[Co(H_2O)_6]^{3+}$	27,000		
$[Cr(H_2O)_6]^{3+}$	17,400	$[Co(NH_3)_6]^{3+}$	22,900		
$[Cr(NH_3)_6]^{3+}$	21,500	$[Co(CN)_6]^{3-}$	34,800		
$[Cr(CN)_6]^{3-}$	26,600	$[Ni(H_2O)_6]^{2+}$	8500		
$Cr(CO)_6$	34,150	$[Ni(NH_3)_6]^{2+}$	10,800		
$[MnCl_6]^{4-}$	7500	$[RhCl_6]^{3-}$	20,400		
$[Mn(H_2O)_6]^{2+}$	8500	$[Rh(H_2O)_6]^{3+}$	27,000		
$[MnCl_6]^{3-}$	20,000	$[Rh(NH_3)_6]^{3+}$	34,000		
$[Mn(H_2O)_6]^{3+}$	21,000	$[Rh(CN)_6]^{3-}$	45,500		
$[Fe(H_2O)_6]^{2+}$	10,400	$[IrCl_6]^{3-}$	25,000		
$[Fe(H_2O)_6]^{3+}$	14,300	$[Ir(NH_3)_6]^{3+}$	41,000		

*Energies obtained by spectroscopic measurements are often given in units of wave numbers (cm^{-1}); the wave number is the reciprocal of the wavelength of the corresponding electromagnetic radiation expressed in centimeters: 1 cm^{-1} = 11.96 J/mol.

Source of data: Duward F. Shriver, Peter W. Atkins, and Cooper H. Langford, Inorganic Chemistry, 2nd ed. (New York: W. H. Freeman and Company, 1994).

Charge on the Metal Ion

Increasing the charge on a metal ion has two effects: the radius of the metal ion decreases, and negatively charged ligands are more strongly attracted to the metal. Both factors decrease the metal–ligand distance, which in turn causes the negatively charged ligands to interact more strongly with the d orbitals. Consequently, the magnitude of Δ_o increases as the charge on the metal ion increases.

Typically, Δ_o for a tripositive ion is about 50% greater than for the dipositive ion of the same metal; for example, for $[V(H_2O)_6]^{2+}$, Δ_o = 11,800 cm^{-1}; for $[V(H_2O)_6]^{3+}$, Δ_o = 17,850 cm^{-1}.

Principal Quantum Number of the Metal

For a series of complexes of metals from the same group in the periodic table with the same charge and the same ligands, the magnitude of Δ_o increases with increasing principal quantum number: Δ_o (3d) < Δ_o (4d) < Δ_o (5d). The data for hexaammine complexes of the trivalent Group 9 metals illustrate this point:

$$[Co(NH_3)_6]^{3+}\ \Delta_o = 22{,}900\ cm^{-1}$$
$$[Rh(NH_3)_6]^{3+}\ \Delta_o = 34{,}100\ cm^{-1}$$
$$[Ir(NH_3)_6]^{3+}\ \Delta_o = 40{,}000\ cm^{-1}$$

The increase in Δ_o with increasing principal quantum number is due to the larger radius of valence orbitals down a column. In addition, repulsive ligand–ligand interactions are most important for smaller metal ions. Relatively speaking, this results in shorter M–L distances and stronger d orbital–ligand interactions.

Reasons for Low-spin vs. High-spin: The Effect of the Metal Ion

There are a few factors that determine the magnitude of the d orbital splitting and dictate whether or not an electron can occupy the higher energy set of orbitals instead of pairing up. These factors are based partly on ligand field strength, which is explored on the next page. They also depend on the charge on the metal ion and whether the metal is in the first, second, or third row of the transition metals.

The higher the charge on the metal, the greater the splitting between the d orbital energy levels. For example, Fe(II) is usually high spin. It has a smaller splitting between the lower and higher d orbital levels, so electrons can more easily go to the higher level rather than pair up un the lower level.

On the other hand, Fe(III) is usually low spin. It has a larger splitting between the d levels. In that case, it costs less energy for electrons to pair up in the lower level than to go up to the higher level.

- High-spin versus low-spin cases involve a trade-off between the d orbital splitting energy and the pairing energy.
- 2nd and 3rd row transition metals are usually low spin
- 1st row transition metals are often high spin
- However, 1st row transition metals and be low spin if they are very positive (usually 3+ or greater)

There is a lot going on in metal ions, but we'll take a simplified view of things. Thinking only about electrostatics, we can try to imagine what happens to those electrons when the charge on the metal ion changes.

First we need to know about Coulomb's law. Coulomb's law states that the force of attraction between the electron and the nucleus depends on only two factors: the amount of positive charge in the nucleus, and the distance between the nucleus and the electron.

The greater the charge on the nucleus, the greater the attraction between the electron and the nucleus.

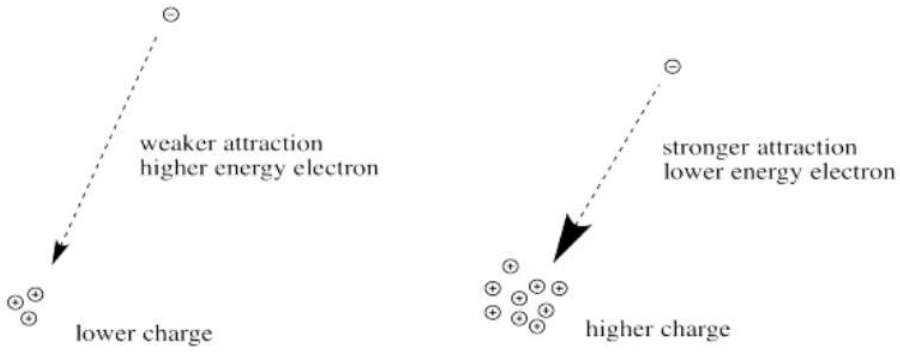


Figure 11.1.10:

The farther an electron is from the nucleus, the weaker the attraction between the electron and the nucleus.

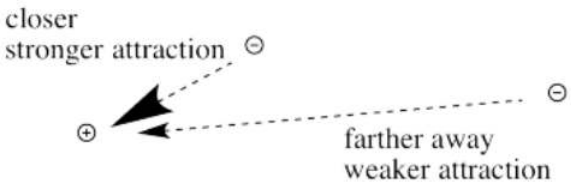


Figure 11.1.11:

Coulomb's law can be used to evaluate the potential energy of the electron. It is one of the factors that determines how high or low those electronic energy levels are that we see in energy level diagrams for atoms, ions and molecules. The energy of the electron varies in a roughly similar way: the greater the charge on the nucleus, the lower the energy of the electron. Also, the closer the electron is to the nucleus, the lower its energy.

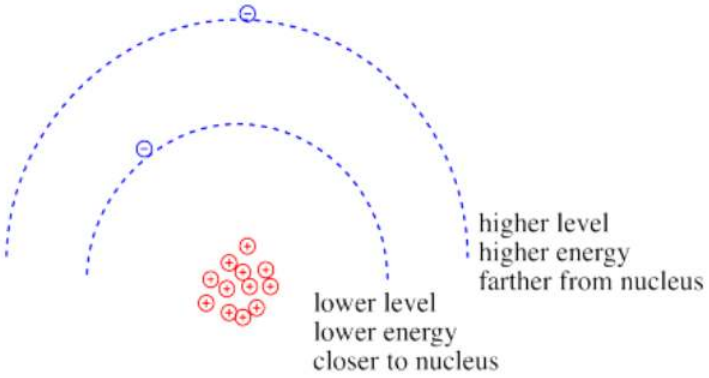


Figure 11.1.12:

Roughly speaking, electrons at higher energy are farther from the nucleus. Electrons at lower energy are closer to the nucleus.

What happens if the charge increases? Maybe a lot more protons are added to the nucleus. Maybe some electrons are lost, so that to the remaining electrons it just *feels like* the charge of the nucleus has increased. Then the electrons should be more attracted to the nucleus. They get a little closer. Their potential energy drops.

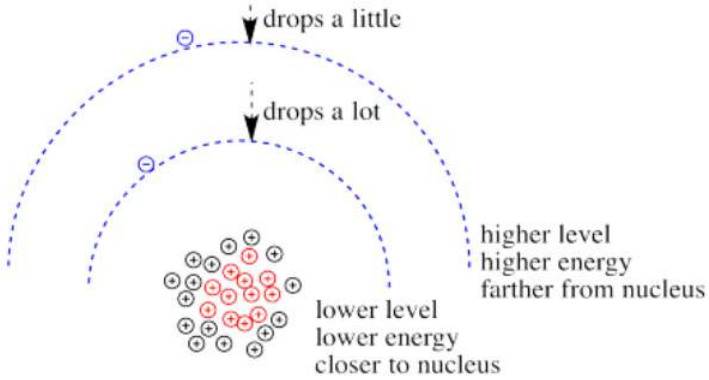


Figure 11.1.13:

Of course, if one electron is closer to the nucleus already, it feels that increase in positive charge more strongly than an electron that is farther away. Consequently it drops further in energy than an electron that is further away.

If we translate that idea into a picture of the d orbital energy levels in an octahedral geometry, it looks like this:

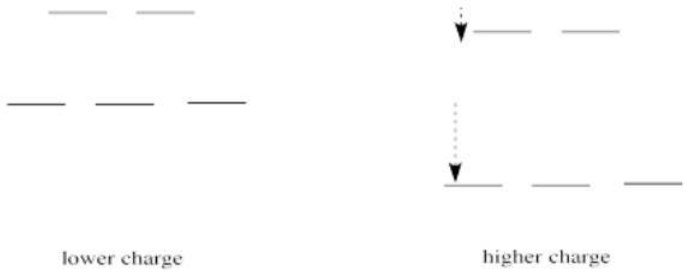


Figure 11.1.14:

When the charge on the metal ion is increased, both the higher and the lower levels drop in energy. However, the lower level drops more. Thus, the gap between the levels gets wider.

Metals in the second and third row of the periodic table almost never form high-spin complexes. The d orbital energy splitting in these cases is larger than for first row metals. From a very simple point of view, these metals have many more protons in their nuclei than the first row transition metals, dropping that lower set of d electrons lower with respect to the higher set.

That isn't the whole picture for the second and third row transition metals, however. Remember, we are simplifying, and there are factors we won't go into. However, it is important to know that metal-ligand bond strengths are much greater in the second and third row than in the first. We'll look at the whole interaction diagram for an octahedral complex now, including contributions form metal s and p orbitals.

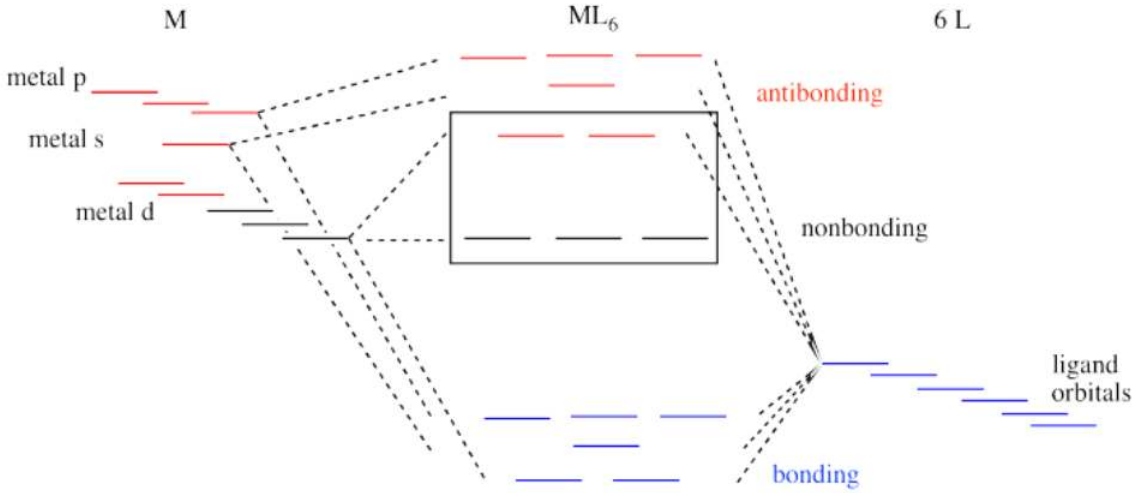


Figure 11.1.15:

Like all ligand-metal interaction diagrams, the energy levels of the ligands by themselves are shown on one side. The metal's electronic energy levels are shown on the other side. The result of their interaction, a metal-ligand complex, is shown in the middle. The d orbital splitting diagram is shown in a box.

Suppose the diagram above is for a first row transition metal. The diagram for a second or third row metal is similar, but with stronger bonds.

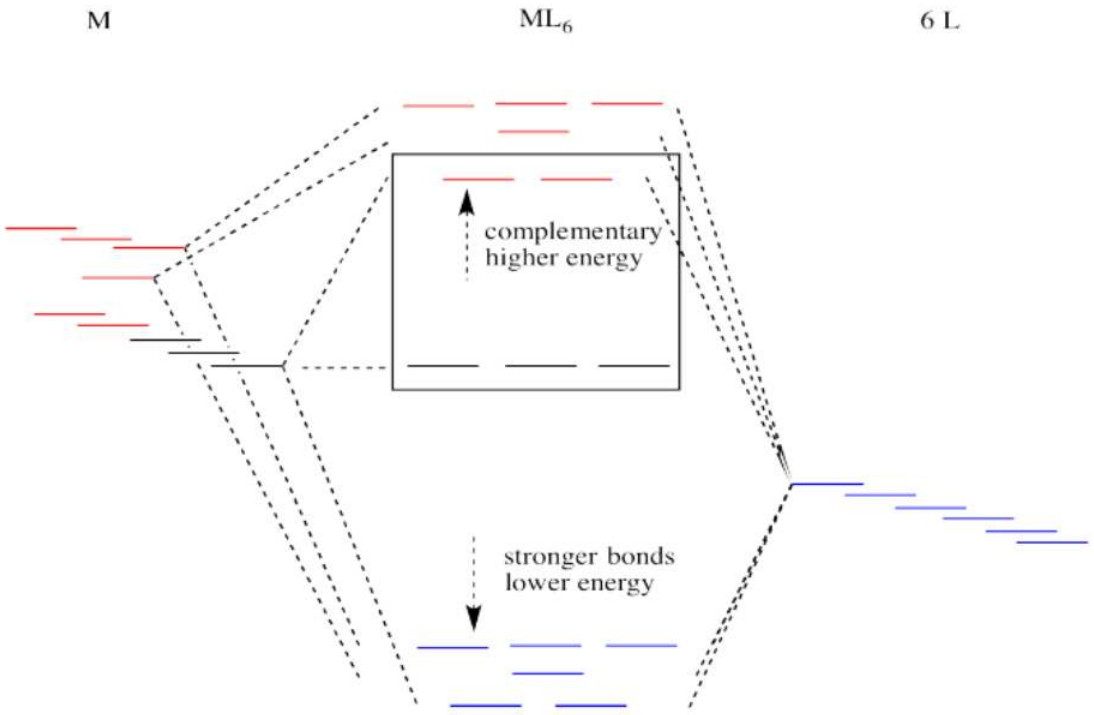


Figure 11.1.16:

If the bonding interaction is stronger between the metal and ligand, then so is the antibonding interaction. The antibonding levels are bumped higher in energy as the bonding levels sink lower. Generally that's OK, because when the electrons are filled in, they will be found preferentially at the lower levels, not the higher ones. There will be a net lowering of electronic energy.

Why do second and third row transition metals form such strong bonds? Bond strengths are very complicated. In general, there is greater covalency between these metals and their ligands because of increased spatial and energetic overlap. Rather than go into those factors, we'll just think about all those extra protons in the nucleus that are attracting the ligand electrons more strongly.

There is one more important distinction that makes second and third row transition metals low spin. In addition, the pairing energy is lower in these metals because the orbitals are larger. There is more room for two electrons in one orbital, with less repulsion. As a result, electrons are much more likely to pair up than to occupy the next energy level.

- 2nd and 3rd row transition metals have stronger bonds, leading to a larger gap between d orbital levels
- 2nd and 3rd row transition metals have more diffuse orbitals, leading to a lower pairing energy

It is significant that most important transition metal ions in biology are from the first row of the transition block and are pretty labile. That fact plays an important role in the ease of formation and deconstruction of transition-metal containing proteins. In terms of formation, if the metal is more easily released by its previous ligands (either water or some compound that delivers the metal to the site of protein construction), it can form the necessary protein more quickly. However, even if a metal-containing enzyme plays a useful role, it should not be too stable, because we need to be able to regulate the level of protein concentration for optimum activity, or disassemble protein if it becomes damaged. Thus, it is important that the metal ion can be removed easily.

Metal ion properties that effect Δ_o

- **Position on the periodic table (period or shell number)**
  The splitting of the d-orbitals in any ligand field *increases as shell number increases going down the periodic table*. In general, with octahedral ligand fields, the $3d$ metal ions can be either weak-field or strong-field depending on other factors. With octahedral complexes, the $4d$ and larger metal ions are generally strong-field.
- **Oxidation state (charge of the metal ion)**
  As the *metal oxidation state increases, the strength of the field also increases*. The charge on a $3d$ metal ion can contribute to

whether it is weak-field or strong-field (and thus high-spin or low-spin for $d^4 - d^7$ metal ions). In octahedral $3d$ metals, the +3 metal ions favor stronger-field (and sometimes low spin) complexes. The +2 metal ions in this series favor weaker-field (and usually high spin); but we cannot make a good prediction about this without knowing about the identity of the ligands.

Exercise 11.1.1

Predict whether each compound will be high or low spin.

a. $[Fe(py)_6]^{2+}$

b. $[Fe(H_2O)_6]^{2+}$

c. $[FeBr_6]^{3-}$

d. $[Co(NH_3)_6]^{3+}$

e. $[Cu(NH_3)_6]^{2+}$

f. $[Rh(CO)_6]^{3+}$

g. $[Cr(CO)_6]^{3+}$

h. $[PtCl_6]^{2-}$

Answer a)

$[Fe(py)_6]^{2+}$ 3d metal, M^{+2}, pi acceptor ligand → low spin

Answer b)

$[Fe(H_2O)_6]^{2+}$ 3d metal, M^{+2}, pi donor ligand → high spin

Answer c)

$[FeBr_6]^{3-}$ 3d metal, M^{+3}, pi donor ligand → high spin

Answer d)

$[Co(NH_3)_6]^{3+}$ 3d metal, M^{+3}, sigma donor ligand → low spin

Answer e)

$[Cu(NH_3)_6]^{2+}$ 3d metal, M^{+2}, sigma donor ligand → low spin

Answer f)

$[Rh(CO)_6]^{3+}$ 4d metal, M^{+3} → low spin

Answer g)

$[Cr(CO)_6]^{3+}$ 3d metal, M^{+3}, pi acceptor ligand → low spin

Answer h)

$[PtCl_6]^{2-}$ 5d metal, M^{+4} → low spin

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12: The Effect of Ligands and the Spectrochemical Series

The Nature of the Ligands

Experimentally, it is found that the Δ_o observed for a series of complexes of the same metal ion depends strongly on the nature of the ligands. For a series of chemically similar ligands, the magnitude of Δ_o decreases as the size of the donor atom increases. For example, Δ_o values for halide complexes generally decrease in the order $F^- > Cl^- > Br^- > I-$ because smaller, more localized charges, such as we see for F^-, interact more strongly with the d orbitals of the metal ion. In addition, a small neutral ligand with a highly localized lone pair, such as NH_3, results in significantly larger Δ_o values than might be expected. Because the lone pair points directly at the metal ion, the electron density along the M–L axis is greater than for a spherical anion such as F^-. The experimentally observed order of the crystal field splitting energies produced by different ligands is called the spectrochemical series, shown here in order of decreasing Δ_o:

$$\underset{\text{strong-field ligands}}{CO \approx CN^- > NO_2^-} > en > NH_3 > \underset{\text{intermediate-field ligands}}{SCN^- > H_2O > oxalate^{2-}} > OH^- > F > acetate^- > \underset{\text{weak-field ligands}}{Cl^- > Br^- > I^-}$$

The values of Δ_o listed in Table 12.1 illustrate the effects of the charge on the metal ion, the principal quantum number of the metal, and the nature of the ligand.

> *The largest Δ_os are found in complexes of metal ions from the third row of the transition metals with charges of at least +3 and ligands with localized lone pairs of electrons.*

Another factor that plays a key role in whether a transition metal complex is high- or low-spin is the nature of the ligands. The d orbital energy splitting is influenced by how strongly the ligand interacts with the metal. Ligands that interact weakly only produce little change in the d orbital energy levels, whereas ligands that interact strongly produce a larger change in d orbital energy levels. The spectrochemical series is a list of ligands based on the strength of their interaction with metal ions. Ligands are often listed from weaker to stronger ligands, something like this:

$$I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_3^- < N_3^- < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < CH_3CN < py < NH_3$$

$$< en < bipy < phen < NO_2^- < PPh_3 < CN^- < CO$$

in which py = pyridine; en = ethylenediamine; bipy = 2,2'-bipyridine; phen = 1,10-phenanthroline; SCN means the ligand is bound via sulfur and NCS via nitrogen. The list can vary from one metal ion to another, since some ligands bind preferentially to certain metals (as seen in hard and soft acid and base chemistry).

Exercise 12.1

What empirical trends can you see within the spectrochemical series? Are there any factors that make something a stronger field ligand?

Answer

The weaker donors include halides and oxygen donors. Nitrogen atom donors are mostly a little stronger than that. The strongest donors include carbon donors, especially with pi bonds.

The d orbitals that rise in energy in the presence of a ligand can be thought of as forming an antibonding molecular orbital combination with an orbital on the ligand. In addition, there would also be a bonding combination for this interaction. That bonding orbital would be more like the initial ligand orbital. This premise is based on the idea that a ligand orbital is initially lower in energy than the metal orbital, so a bonding combination between these two orbitals is more like the initial ligand orbital, both in energy and location. The d orbital is initially higher in energy than the ligand orbital, so an antibonding combination between these two orbitals is more like the initial d orbital, both in energy and location.

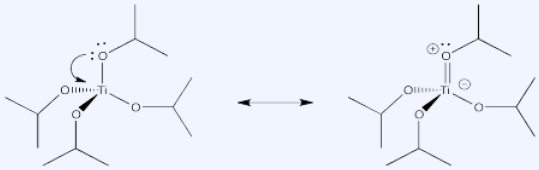
- When orbitals on two different kinds of atoms combine, the antibonding orbital is considered to be more like the orbital that was initially at higher energy.
- In this case, it is still close to a d orbital in energy, location, and shape.

- When orbitals on two different kinds of atoms combine, the bonding orbital is considered to be more like the orbital that was initially at lower energy.

Exercise 12.2

Suppose a ligand has more than one lone pair on the donor atom. The donor atom could share an extra pair of electrons with the metal, to form a double bond. This type of interaction is called pi-donation, because a π bond is formed (not to be confused with sigma donation from a π bond, as in alkene binding). Show an example using titanium isopropoxide $Ti(OiPr)_4$.

Answer

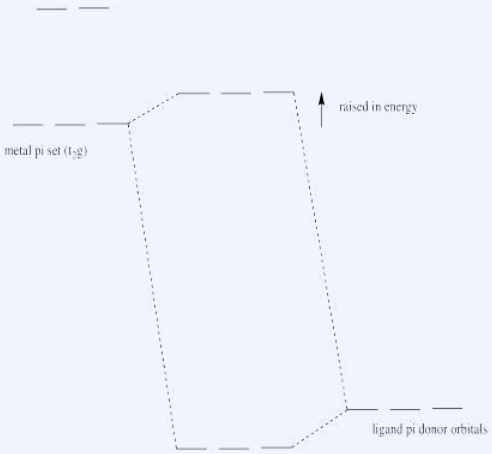


Exercise 12.3

In an octahedral environment, three of the d orbitals were not affected by sigma donation from the ligands. Show what happens to the energy level of these d orbitals in the presence of a π donor.

Answer

Pi donation raises the t_{2g} electrons (the d electrons of proper symmetry for pi overlap with the ligands in an octahedral geometry).



Exercise 12.4

Some ligands can accept a pair of electrons from the metal. An example is a carbonyl complex, which has a C=O π antibonding orbital that can interact with a d orbital.

a. Show the antibonding orbital on the carbonyl (CO) ligand.
b. Show how a metal d orbital can interact with this orbital.

Exercise 12.5

In the previous problem, a lower-energy atomic orbital on the metal interacts with a higher-energy antibonding orbital on the ligand. Show what happens to the energies of these two orbitals when they interact with each other.

Some of the trends we see in the spectrochemical series arise from pi-donating and pi-accepting effects in the ligand. Ligands that have additional lone pairs (other than the one that sigma donates) are π donors. π donors raise the otherwise non-bonding t_{2g} orbitals, because the lone pair on the ligand forms a π bond with the metal. The t_{2g} orbitals and the ligand lone pair orbitals form two new orbitals. The antibonding orbital is closer in energy to the high-energy d orbitals. The bonding orbital is closer in energy to the low-energy ligand orbital.

- π donation raises the t_{2g} set of d orbitals in energy.
- As a result, the d orbital splitting gets smaller.
- Also as a result, a complex with π donation is a little less stable than a complex without π donation.

This type of interaction can be seen in the following pictures (a tetrahedral case).

On the other hand, ligands in which the donor atom is already π bonding to another atom can accept π donation from the metal. This happens by donating an electron pair from a metal t_{2g} orbital into a $\pi*$ orbital on the ligand. In this case, because the $\pi*$ is an antibonding orbital, it is higher in energy than the metal d orbital (or the t_{2g} orbital). The resulting bonding orbital is more like the lower energy metal orbital, whereas the resulting antibonding orbital is more like the higher energy $\pi*$ orbital on the ligand.

- π accepting ligands lower the t_{2g} set of d orbitals in energy.
- As a result, the d orbital splitting gets larger.
- Also as a result, a complex with a π accepting ligand is a little more stable than a complex without a π accepting ligand.

This type of interaction can be seen in the following case (a tetrahedral complex).

The spectrochemical series gets its name because of a shift in a band of the UV-Vis spectrum when two similar complexes are compared that have two different ligands. The effect of the ligand on the d orbital splitting has an effect on the wavelength of light associated with a d orbital (filled) to d orbital (empty) electronic transition. This transition is actually not associated with a major absorption. However, because it often occurs in the region of visible light, it is associated with colored transition metal complexes.

Exercise 12.6

Explain what happens to the wavelength of light absorbed for the d-d transition when a chloride ligand on a metal complex is replaced with a hydroxide ligand.

Answer

Because chloride is a weaker ligand than hydroxide, the d orbital splitting gets smaller. A d-d transition would involve less energy, so it would move to longer wavelength (red shift).

Exercise 12.7

Predict whether each compound will be square planar or tetrahedral.

a. $[Zn(NH_3)_4]^{2+}$

b. $[NiCl_4]^{2+}$

c. $[Ni(CN)_4]^{2-}$

d. $[Ir(CO)(OH)(PCy_3)_2]^{2+}$; Cy = cyclohexyl

e. $[Ag(dppb)_2]^{+}$; dppb = 1,4-bis(diphenylphosphino)butane

f. $PtCl_2(NH_3)_2$

g. $PdCl_2(NH_3)_2$

h. $[CoCl_4]^{2-}$

i. $Rh(PPh_3)_3Cl$

Answer a)

$[Zn(NH_3)4]^{2+}$ 3d metal, d^{10}, sigma donor ligand → tetrahedral

Answer b)

$[NiCl_4]^{2+}$ 3d metal, d^8, pi donor ligand → tetrahedral

Answer c)

$[Ni(CN)_4]^{2-}$ 3d metal, d^8, pi acceptor ligand → square planar

Answer d)

$[Ir(CO)(OH)(PCy_3)_2]^{2+}$ 5d metal, d^8 → square planar

Answer e)

$[Ag(dppb)_2]^{1+}$ 4d metal, d^{10}, sigma donor ligand → tetrahedral

Answer f)

$[PtCl_2(NH_3)_2]$ 5d metal, d^8 → square planar

Answer g)

$[PdCl_2(NH_3)_2]$ 4d metal, d^8, M^{+2}, sigma donor ligand → square planar

Answer h)

$[CoCl_4]^{2-}$ 3d metal, d^7, sigma donor ligand → tetrahedral

Answer i)

$[Rh(PPh_3)_3Cl]$ 5d metal, d^8 → square planar

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SECTION OVERVIEW

13: Absorption Spectra and Magnetic Properties

13.1: Colors of Coordination Compounds (Electronic Absorption Spectra)

13.2: Predicting UV-visible Absorption

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13.1: Colors of Coordination Compounds (Electronic Absorption Spectra)

The d-orbital splitting in coordination complexes results in a gap (Δ) that happens to be just the right magnitude to absorb visible light. Because metal complexes can absorb visible light, the display an array of colors. Not only is the color attractive to the eye, it is an indication of the chemical and physical properties of the metal complex. The color (like the magnitude of Δ) depends on the identity of the metal ion, the coordination geometry, and the ligand identity. Chemists don't just "look" at color, though - we measure it using a UV-visible spectrometer.

An example of such a measurement is shown below in Figure 13.1.1 for a Cu(II) complex. The sample appears a pinky-purple color to the eye, and when it is measured using a UV-visible spectrometer, it is shown to absorb visible light at 525 nm. The absorption spectrum can tell us a lot about which ligands are bound to the Cu(II) ion and what the coordination geometry is. This example might be familiar to you if you've had Advanced Lab with Dr. Haas!

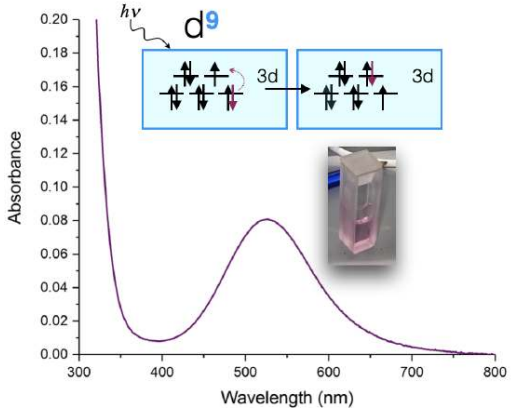


Figure 13.1.1: A UV-visible spectrum of a Cu(II)-peptide complex. A photo of the sample shows its pinky-purple color. The splitting diagram for its approximation as an octahdral complex is shown, where an electronic transition from t_{2g} to e_g is shown. (CC-BY-NC-SA; Kathryn Haas)

In some ways this is a "simple" spectrum because it has only one visible-light d-d transition at 525 nm. Let's assume that the coordination geometry is *approximately* octahedral (although it is actually a Jhan-Teller distorted octahedron, and more like a square plane). If we assume it's octahedral, then the d-orbital splitting diagram might lead us to expect one transition: an electron from the t_{2g} is excited to e_g. We might expect then, that the energy absorbed is equal to the energy of the Δ_o. However, the actual energy of the transition is also effected by electron-electron repulsion energies, and so it is not quite so simple.

If we would want to determine Δ_o from the spectrum shown in Figure 13.1.1, we need to use Tanabe-Sugano diagrams, which account for electronelectron repulsions, to extract the value of Δ_o. An objective in the next Unit is to learn use Tanabe-Sugano diagrams to extract Δ values and assign the specific electronic transitions that result in UV-vis spectra. But first, let's remind ourselves of where color comes from and learn the basics of how this applies to transition metal complexes.

The Electromagnetic Spectrum

The electromagnetic spectrum (EM) spectrum is made up of photons of different wavelengths. Photons, unique in displaying the properties of both waves and particles, create visible light and colors in a small portion of the EM spectrum. This visible light portion has wavelengths in approximately the 400-700 nanometer range (a nanometer, “nm,” is 10^{-9} meters). Each specific wavelength corresponds to a different color (Figure 13.1.2), and when all the wavelengths are present, it appears as white light.



Figure 13.1.2: A linear representation of the visible light spectrum. (Public Domain; Gringer via Wikipedia)

The wavelength (λ) and frequency (ν) of a wave are inversely proportional: as one increases, the other decreases; this is a consequence of all light traveling at the same speed.

$$\lambda = \nu^{-1} \tag{13.1.1}$$

Because of this relationship, blue light has a shorter wavelength, higher frequency, more energy than red light. In general, photons to the right of the EM spectrum have increasingly higher energy than photons to the left.

Perceiving Color

Color is perceived in two ways, through additive mixing, where different colors are made by combining different colors of light, and through subtractive mixing, where different wavelengths of light are taken out so that the light is no longer pure white. For colors of coordination complexes, subtractive mixing is considered. As shown in Figure 13.1.3, the idea behind subtractive mixing is that white light (which is made from all the colors mixed together) interacts with an object. The object absorbs some of the light, and then reflects or transmits (or both, depending on the object) the rest of the light, which contacts the eye. The object is perceived as whichever color is not absorbed. In Figure 13.1.2, white light (simplified as blue, green, yellow, orange, and red squiggly arrows) is shone through a solution. The solution absorbs the yellow wavelengths; other wavelengths are transmitted and the appears a pinky-purple color.



Figure 13.1.3: Subtractive mixing. (CC-BY-NC-SA; Kathryn Haas)

This phenomenon takes place whenever an object displays visible color. If none of the light is absorbed, and all is reflected back off, the object appears white; if all of the light is absorbed, and there is none left to reflect or transmit through, the object appears black.

Colors of metal complexes (d-d transitions)

In the case of an octahedral metal complex, as certain wavelengths of visible light are absorbed, subtractive color mixing occurs and the coordination complex solution appears colored. If there is no electronic transition (eg a d^{10} complex), the solutions appear colorless; in reality, they still have a measured energy and absorb certain wavelengths of light, but these wavelengths are not in the visible portion of the EM spectrum and no color is perceived by the eye.

In general, a larger Δ_o indicates that higher energy photons are absorbed, and the solution appears further to the left on the EM spectrum shown in Figure 13.1.1. This relationship is described in the equation

$$\Delta_o \approx hc/\lambda \tag{13.1.2}$$

where h and c are constants, and λ is the wavelength of light absorbed. The "≈ symbol is used to indicate that this relationship is only approximate. As mentioned earlier, changes in electron-electron repulsion energies must also be accounted for.

Determining color

Using a color wheel can be useful for determining what color a solution will appear based on what wavelengths it absorbs (Figure 13.1.4). If a complex absorbs a particular color, it will have the appearance of whatever color is directly opposite it on the wheel. For example, if a complex is known to absorb photons in the orange range, it can be concluded that the solution will look blue. This concept can be used in reverse to determine Δ for a complex from the color of its solution.

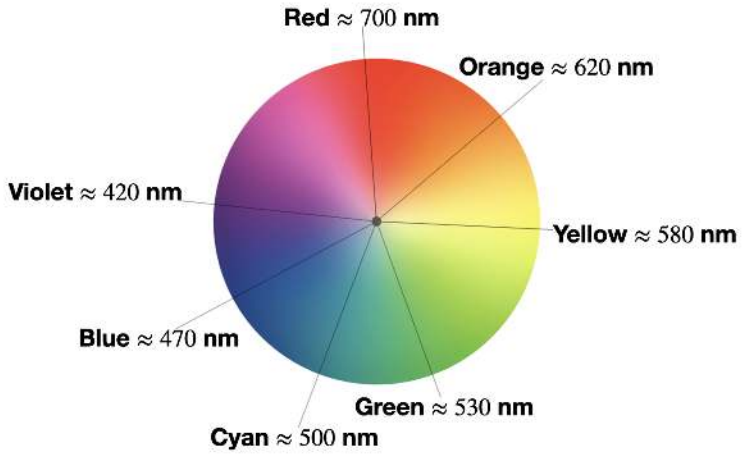


Figure 13.1.4: Color wheel with approximate wavelengths of colors. (CC-BY-NC-SA; Kathryn Haas)

Relating the Colors of Coordination Complexes to the Spectrochemical Series

A description of the spectrochemical series is available in a previous section. Weaker-field ligands contribute to smaller Δ values, and thus *absorbance* of lower-energy light with longer λ (ie a "red shift"). Stronger-field ligands do the opposite; they contribute to a larger magnitude of Δ and *absorbance* of higher-energy light with shorter λ (ie a "blue shift").

Example 13.1.1

If a solution with a dissolved octahedral complex appears yellow to the eye, approximately what wavelength/color of light does it absorb? If the "borderline" between high and low spin complexes is roughly around 588 nm, is this complex expected to be low spin or high spin?

Solution

A solution that looks yellow absorbs light that is violet, which is roughly 410 nm from the color wheel. This is higher-energy than 588 nm, and so this complex must have a rather large Δ; at least large enough to expect low spin.

Example 13.1.2

An octahedral metal complex absorbs light with wavelength 535 nm. What is the crystal field splitting Δ_o for the complex? Approximately what color is it to the eye?

Solution

To solve this question, we need to use the equation $\Delta_o \approx \frac{hc}{\lambda}$

with

- h is Planck's constant and is $6.625 \times 10^{-34} J \cdot s$ and
- c is the speed of light and is $2.998 \times 10^8\ m/s$.

It is also important to remember that 1 nm is equal to 1×10^{-9} meters. With all this information, the final equation looks like this:

$$\Delta_o \approx \frac{(6.625 \times 10^{-34}\ J \cdot s)(2.998 \times 10^8\ m/s)}{(535nm)\left(\frac{1\ m}{1 \times 10^9\ nm}\right)} = 3.712\ J/molecule$$

It is not necessary to use any equations to solve the second part of the problem. Light that is 535 nm is green, and because green light is absorbed, the complex appears redish (light red is pink) (refer to Figures 13.1.2 and 13.1.4 for this information).

Note: the fact that the complex is octahedral makes no impact when solving this problem. Although the splitting is different for complexes of different structures, the mechanics of solving the problem are identical.

Example 13.1.3

There are two solutions, one orange and one blue. Both solutions are known to be made up of a cobalt complex; however, one has chloride ligands, while the other has ammonia ligands. Which solution is expected to be orange?

Solution

In order to solve this problem, it is necessary to know the relative field-strengths of the ligands involved. NH_3 is a stronger-field ligand than Cl^-, which means that the complex involving NH_3 has a greater Δ_o. Because of the larger Δ, the electrons absorb higher-energy light, and the solution will have the appearance of a lower energy (more red) color. Since orange light is less energetic than blue light, the orange solution is the cobalt complex with NH_3 ligands.

References

1. Cox, P. A. Instant Notes Inorganic Chemistry. Second ed. Grand Rapids: Garland, Incorporated, 2004.
2. Nassau, Kurt. The Physics and Chemistry of Color : The Fifteen Causes of Color. Second ed. New York: Wiley-Interscience, 2001.
3. Petrucci, Ralph H., William S. Harwood, and Geoff E. Herring. General Chemistry : Principles and Modern Applications. Ninth ed. Upper Saddle River: Prentice Hall PTR, 2006.
4. Petrucci, Ralph H., Carey Bissonnette, F. Geoffrey Herring, Jeffrey D. Madura. General Chemistry: Principles and Modern Applications. Tenth Ed. Upper Saddle River: Pearson Education, Inc. 2011.

Problems

1. What color will a complex be that absorbs light that is 600 nm be?
2. What color will a complex an octahedral complex appear if it has a Δ_o of $3.75 \times 10^{-19}\ J$?
3. Would you expect a green coordination complex to be high spin or low spin? What about a yellow complex?
4. There are two solutions, one which is yellow and another which is violet. The solutions are $[Co(H_2O)_6]^{3+}$and $[Co(CN^-)_6]^{3-}$. What are the colors of each solution?

Answers

1. Blue. The color absorbed is orange.
2. It is red. Using Δ=hc/λ, h=6.626*10^{-34}J*s, c=2.998*10^8m/s, wavelength would equal 530 nm. So green is absorbed, and the complementary color of green is red, so red is the color of the complex.
3. We were told in a previous exercise that the "line" between high and low spin is approximately 580 nm.
   Green Complex: The complementary color of green is red, which has $\lambda \approx 420$ nm. The green solution has a rather small Δ and we could expect it to be high-spin.
   Yellow complex: The complementary color of yellow is violet, absorbed is green, which has $\lambda \approx 700$ nm. The yellow complex has a rather large Δ_o and thus we could expect a low-spin complex.
4. $[Co(H_2O)_6]^{3+}$ is violet and $[Co(CN^-)_6]^{3-}$ is yellow. Looking at the spectrochemical series, H_2O is a weak-field ligand, so it absorbs colors of long wavelengths—in this case, the longer wavelength is yellow, so the color reflected is violet. CN^- is a strong-field ligand, so it absorbs colors of shorter wavelengths-in this case, the shorter wavelength is violet, so the color reflected is yellow.

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13.2: Predicting UV-visible Absorption

A note from Dr. Haas: The Inorganic Spectroscopy Tutorial from the University of Alberta is an excellent resource for brushing up on Inorganic Spectroscopies. Conveniently, it has a tutorial on UV-visible spectroscopy for Inorganic complexes. Please review this tutorial before reading the page below.

Types of transitions related to the metal ion:

1. **d-d transitions**: d-d transitions are electronic transitions that occur between the molecular orbitals (MOs) that are mostly metal in character; specifically the orbitals that we think of as the d-orbitals of a transition metal complex. These transitions are useful in determining the energy of splitting and can be used to indicate coordination chemistry (geometry and ligand sets). In octahedral complexes, d-d transitions occur between the t_{2g} and e_g orbitals (across Δ). These transitions cannot occur in metal complexes where the d-orbital is completely empty (d^0) or completely full (d^{10}). In other words, a d-d transition is only possible in $d^1 - d^9$ metal ions. In a UV-visible absorption spectrum, d-d transitions appear as relatively weak absorption with extinction coefficients (ε) less than 1,000.
2. **Charge transfer (CT) transitions**: Charge transfer transitions occur between MOs that are mostly metal in character and those that are mostly ligand in character. These transitions depend on the type of ligand: they occur only when the metal is bound to ligands that are π-donors or π-acceptors. And there are two types of CT transitions. If the metal is bound to a π-donor ligand, electrons from lower-energy MO's that are mostly ligand in character can become excited to MO's that are mostly metal in character. These are **ligand to metal charge transfers (LMCT) transitions** (Figure 13.2.1, left diagram). If the the metal is bound to ligands that are π-acceptors, electrons from the MO's that are mostly metal in character can become excited to higher-energy orbitals that are mostly ligand in character. These are **metal to ligand charge transfer (MLCT)** transitions (Figure 13.2.1, right diagram). In a UV-visible absorption spectrum, CT transitions appear as relatively intense absorptions with extinction coefficients (ε) much greater than 1,000.

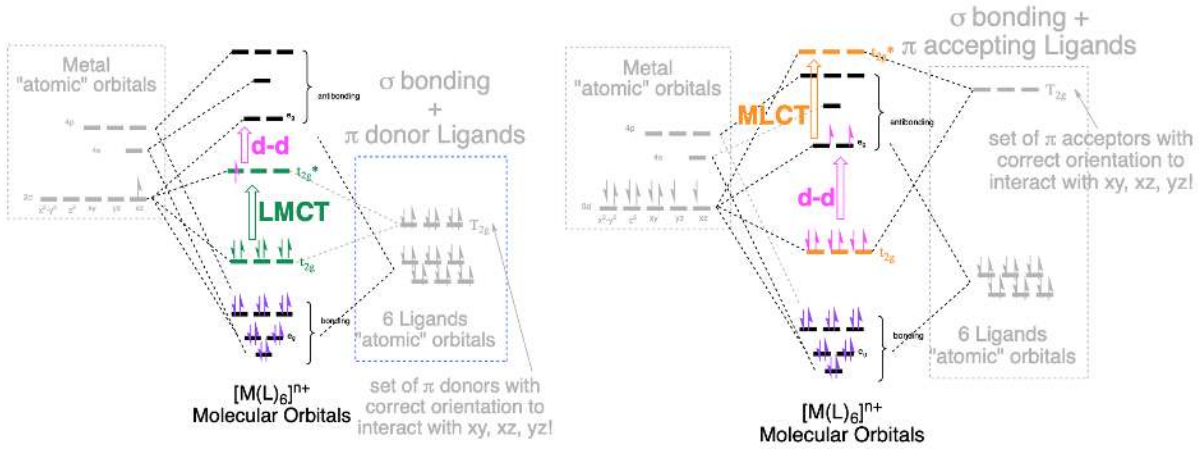


Figure 13.2.1: Abbreviated and annotated MO diagrams for example cases of metal ions in octahdral geometry with sets of π-donor and π-acceptor lignads. In both example MO diagrams, d-d transitions are shown (pink, open arrow from t_{2g} to e_g). **Left:** LMCT transitions are possible with π-donor ligands when electrons are excited from MOs that are mostly ligand in character to MOs that are mostly metal in character. An example of LMCT is shown (green, open arrow from t_{2g} to $t*_{2g}$). **Right:** MLCT transitions are possible with π-acceptor ligands when electrons from MOs that are mostly metal in character are excited to orbitals that are mostly ligand in character (the π^* orbitals from ligands). An example MLCT is shown ((orange, open arrow from e_g to $t*_{2g}$).

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CHAPTER OVERVIEW

9: Gases

A general chemistry Libretexts Textmap organized around the textbook

Chemistry: The Central Science

by Brown, LeMay, Bursten, Murphy, and Woodward

Template:HideTOC

Previously, we focused on the *microscopic* properties of matter—the properties of individual atoms, ions, and molecules—and how the electronic structures of atoms and ions determine the stoichiometry and three-dimensional geometry of the compounds they form. We will now focus on *macroscopic* properties—the behavior of aggregates with large numbers of atoms, ions, or molecules. An understanding of macroscopic properties is central to an understanding of chemistry. Why, for example, are many substances gases under normal pressures and temperatures (1.0 atm, 25°C), whereas others are liquids or solids? We will examine each form of matter—gases, liquids, and solids—as well as the nature of the forces, such as hydrogen bonding and electrostatic interactions, that hold molecular and ionic compounds together in these three states.

In this chapter, we explore the relationships among pressure, temperature, volume, and the amount of gases. You will learn how to use these relationships to describe the physical behavior of a sample of both a pure gaseous substance and mixtures of gases. By the end of this chapter, your understanding of the gas laws and the model used to explain the behavior of gases will allow you to explain how straws and hot-air balloons work, why hand pumps cannot be used in wells beyond a certain depth, why helium-filled balloons deflate so rapidly, and how a gas can be liquefied for use in preserving biological tissue.

9.1: Review of Gases
- 9.1.1: Characteristics of Gases
- 9.1.2: Pressure
- 9.1.3: The Gas Laws

9.2: The Ideal Gas Equation
9.3: Further Applications of the Ideal-Gas Equations
9.4: Gas Mixtures and Partial Pressures
9.5: Kinetic-Molecular Theory
9.6: Equipartition of Energy (Needs addition)
9.7: Molecular Effusion and Diffusion
9.8: Real Gases - Deviations from Ideal Behavior
9.E: Exercises
9.S: Gases (Summary)

Thumbnail: Motion of gas molecules. The randomized thermal vibrations of fundamental particles such as atoms and molecules—gives a substance its “kinetic temperature.” Here, the size of helium atoms relative to their spacing is shown to scale under 1950 atmospheres of pressure. (CC BY-SA 3.0; Greg L).

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9.1: Review of Gases

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9.1.1: Characteristics of Gases

Learning Objectives

- To describe the characteristics of a gas.

The three common phases (or states) of matter are gases, liquids, and solids. Gases have the lowest density of the three, are highly compressible, and completely fill any container in which they are placed. Gases behave this way because their intermolecular forces are relatively weak, so their molecules are constantly moving independently of the other molecules present. Solids, in contrast, are relatively dense, rigid, and incompressible because their intermolecular forces are so strong that the molecules are essentially locked in place. Liquids are relatively dense and incompressible, like solids, but they flow readily to adapt to the shape of their containers, like gases. We can therefore conclude that the sum of the intermolecular forces in liquids are between those of gases and solids. Figure 9.1.1.1compares the three states of matter and illustrates the differences at the molecular level.

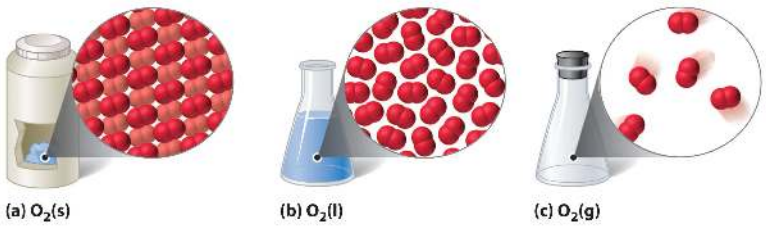


Figure 9.1.1.1: A Diatomic Substance (O_2) in the Solid, Liquid, and Gaseous States: (a) Solid O_2 has a fixed volume and shape, and the molecules are packed tightly together. (b) Liquid O_2 conforms to the shape of its container but has a fixed volume; it contains relatively densely packed molecules. (c) Gaseous O_2 fills its container completely—regardless of the container's size or shape—and consists of widely separated molecules.

The state of a given substance depends strongly on conditions. For example, H_2O is commonly found in all three states: solid ice, liquid water, and water vapor (its gaseous form). Under most conditions, we encounter water as the liquid that is essential for life; we drink it, cook with it, and bathe in it. When the temperature is cold enough to transform the liquid to ice, we can ski or skate on it, pack it into a snowball or snow cone, and even build dwellings with it. Water vapor (the term *vapor* refers to the gaseous form of a substance that is a liquid or a solid under normal conditions so nitrogen (N_2) and oxygen (O_2) are referred to as gases, but gaseous water in the atmosphere is called water vapor) is a component of the air we breathe, and it is produced whenever we heat water for cooking food or making coffee or tea. Water vapor at temperatures greater than 100°C is called steam. Steam is used to drive large machinery, including turbines that generate electricity. The properties of the three states of water are summarized in Table 10.1.

Table 9.1.1.1: Properties of Water at 1.0 atm

Temperature	State	Density (g/cm3)
≤0°C	solid (ice)	0.9167 (at 0.0°C)
0°C–100°C	liquid (water)	0.9997 (at 4.0°C)
≥100°C	vapor (steam)	0.005476 (at 127°C)

The geometric structure and the physical and chemical properties of atoms, ions, and molecules usually do *not* depend on their physical state; the individual water molecules in ice, liquid water, and steam, for example, are all identical. In contrast, the macroscopic properties of a substance depend strongly on its physical state, which is determined by intermolecular forces and conditions such as temperature and pressure.

Figure 9.1.1.2shows the locations in the periodic table of those elements that are commonly found in the gaseous, liquid, and solid states. Except for hydrogen, the elements that occur naturally as gases are on the right side of the periodic table. Of these, all the noble gases (group 18) are monatomic gases, whereas the other gaseous elements are diatomic molecules (**H_2, N_2, O_2, F_2, and Cl_2**). Oxygen can also form a second allotrope, the highly reactive triatomic molecule ozone (**O_3**), which is also a gas. In contrast, bromine (as Br_2) and mercury (Hg) are liquids under normal conditions (25°C and 1.0 atm, commonly referred to as "room temperature and pressure"). Gallium (Ga), which melts at only 29.76°C, can be converted to a liquid simply by holding a container

of it in your hand or keeping it in a non-air-conditioned room on a hot summer day. The rest of the elements are all solids under normal conditions.

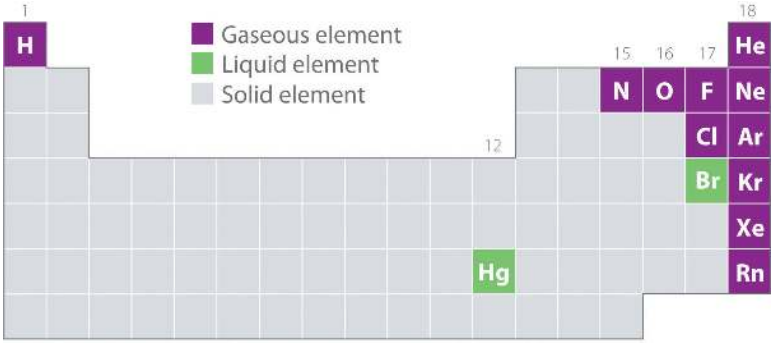


Figure 9.1.1.2: Elements That Occur Naturally as Gases, Liquids, and Solids at 25°C and 1 atm. The noble gases and mercury occur as monatomic species, whereas all other gases and bromine are diatomic molecules.

Purple elements are gaseous elements, green are liquid, and gray and solid. H, N, O, F, Cl, He, Ne, Ar, Kr, Xe, and Rn are all purple. Br and Hg are green. The rest are gray.

All of the gaseous elements (other than the monatomic noble gases) are molecules. Within the same group (1, 15, 16 and 17), the lightest elements are gases. All gaseous substances are characterized by weak interactions between the constituent molecules or atoms.

Summary

Bulk matter can exist in three states: gas, liquid, and solid. Gases have the lowest density of the three, are highly compressible, and fill their containers completely. Elements that exist as gases at room temperature and pressure are clustered on the right side of the periodic table; they occur as either monatomic gases (the noble gases) or diatomic molecules (some halogens, N_2, O_2).



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9.1.2: Pressure

Learning Objectives

- to describe and measure the pressure of a gas.

At the macroscopic level, a complete physical description of a sample of a gas requires four quantities:

- ***temperature*** (expressed in kelvins),
- ***volume*** (expressed in liters),
- ***amount*** (expressed in moles), and
- ***pressure*** (in atmospheres).

As we demonstrated below, these variables are *not* independent (i.e., they cannot be arbitrarily be varied). If we know the values of any *three* of these quantities, we can calculate the fourth and thereby obtain a full physical description of the gas. Temperature, volume, and amount have been discussed in previous chapters. We now discuss pressure and its units of measurement.

Units of Pressure

Any object, whether it is your computer, a person, or a sample of gas, exerts a force on any surface with which it comes in contact. The air in a balloon, for example, exerts a force against the interior surface of the balloon, and a liquid injected into a mold exerts a force against the interior surface of the mold, just as a chair exerts a force against the floor because of its mass and the effects of gravity. If the air in a balloon is heated, the increased kinetic energy of the gas eventually causes the balloon to burst because of the increased pressure (P) of the gas, the force (F) per unit area (A) of surface:

$$P = \frac{\text{Force}}{\text{Area}} = \frac{F}{A} \tag{9.1.2.1}$$

Pressure is dependent on *both* the force exerted *and* the size of the area to which the force is applied. We know from Equation 9.1.2.1 that applying the same force to a smaller area produces a higher pressure. When we use a hose to wash a car, for example, we can increase the pressure of the water by reducing the size of the opening of the hose with a thumb.

The units of pressure are derived from the units used to measure force and area. The SI unit for pressure, derived from the SI units for force (newtons) and area (square meters), is the newton per square meter (N/m^2), which is called the **Pascal (Pa)**, after the French mathematician Blaise Pascal (1623–1662):

$$1\ \text{Pa} = 1\ \text{N/m}^2 \tag{9.1.2.2}$$

Example 9.1.2.1

Assuming a paperback book has a mass of 2.00 kg, a length of 27.0 cm, a width of 21.0 cm, and a thickness of 4.5 cm, what pressure does it exert on a surface if it is

a. lying flat?
b. standing on edge in a bookcase?

Given: mass and dimensions of object

Asked for: pressure

Strategy:

A. Calculate the force exerted by the book and then compute the area that is in contact with a surface.
B. Substitute these two values into Equation 9.1.2.1 to find the pressure exerted on the surface in each orientation.

Solution:

The force exerted by the book does *not* depend on its orientation. Recall that the force exerted by an object is $F = ma$, where m is its mass and a is its acceleration. In Earth's gravitational field, the acceleration is due to gravity (9.8067 m/s^2 at Earth's surface). In SI units, the force exerted by the book is therefore

$$F = ma = 2.00 \text{ kg} \times 9.8067 \frac{\text{m}}{\text{s}^2} = 19.6 \frac{\text{kg} \cdot \text{m}}{\text{s}^2} = 19.6 \text{ N}$$

A We calculated the force as 19.6 N. When the book is lying flat, the area is

$$A = 0.270 \text{ m} \times 0.210 \text{ m} = 0.0567 \text{ m}^2.$$

B The pressure exerted by the text lying flat is thus

$$P = \frac{F}{A} = \frac{19.6 \text{ N}}{0.0567 \text{ m}^2} = 3.46 \times 10^2 \text{Pa}$$

A If the book is standing on its end, the force remains the same, but the area decreases:

$$\text{A} = 21.0 \text{ cm} \times 4.5 \text{ cm} = 0.210 \text{ m} \times 0.045 \text{ m} = 9.5 \times 10^{-3} \text{ m}^2$$

B The pressure exerted by the text lying flat is thus

$$P = \frac{19.6 \text{ N}}{9.5 \times 10^{-3} \text{ m}^2} = 2.06 \times 10^3 \text{ Pa}$$

? Exercise 9.1.2.1

What pressure does a 60.0 kg student exert on the floor

a. when standing flat-footed in the laboratory in a pair of tennis shoes (the surface area of the soles is approximately 180 cm^2)?
b. as she steps heel-first onto a dance floor wearing high-heeled shoes (the area of the heel = 1.0 cm^2)?

Answer a

3.27×10^4 Pa

Answer b

5.9×10^6 Pa

Barometric Pressure

Just as we exert pressure on a surface because of gravity, so does our atmosphere. We live at the bottom of an ocean of gases that becomes progressively less dense with increasing altitude. Approximately 99% of the mass of the atmosphere lies within 30 km of Earth's surface (Figure 9.1.2.1). Every point on Earth's surface experiences a net pressure called ***barometric pressure***. The pressure exerted by the atmosphere is considerable: a 1 m^2 column, measured from sea level to the top of the atmosphere, has a mass of about 10,000 kg, which gives a pressure of about 101 kPa:

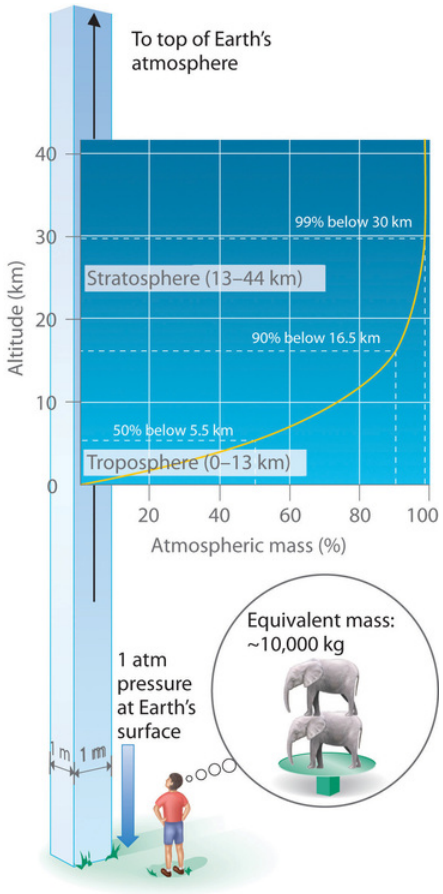


Figure 9.1.2.1: Barometric Pressure. Each square meter of Earth's surface supports a column of air that is more than 200 km high and weighs about 10,000 kg at Earth's surface.

Barometric pressure can be measured using a barometer, a device invented in 1643 by one of Galileo's students, Evangelista Torricelli (1608–1647). A barometer may be constructed from a long glass tube that is closed at one end. It is filled with mercury and placed upside down in a dish of mercury without allowing any air to enter the tube. Some of the mercury will run out of the tube, but a relatively tall column remains inside (Figure 9.1.2.2). Why doesn't all the mercury run out? Gravity is certainly exerting a downward force on the mercury in the tube, but it is opposed by the pressure of the atmosphere pushing down on the surface of the mercury in the dish, which has the net effect of pushing the mercury up into the tube. Because there is no air above the mercury inside the tube in a properly filled barometer (it contains a vacuum), there is no pressure pushing down on the column. Thus the mercury runs out of the tube until the pressure exerted by the mercury column itself exactly balances the pressure of the atmosphere. The pressure exerted by the mercury column can be expressed as:

$$P = \frac{F}{A} \tag{9.1.2.3}$$

$$= \frac{mg}{A} \tag{9.1.2.4}$$

$$= \frac{\rho V \cdot g}{A} \tag{9.1.2.5}$$

$$= \frac{\rho \cdot Ah \cdot g}{A} \tag{9.1.2.6}$$

$$= \rho g h \tag{9.1.2.7}$$

with

- g is the gravitational acceleration,
- m is the mass,
- ρ is the density,

- V is the volume,
- A is the bottom area, and
- h is height of the mercury column.

Under normal weather conditions at sea level, the two forces are balanced when the top of the mercury column is approximately 760 mm above the level of the mercury in the dish, as shown in Figure 9.1.2.2 This value varies with meteorological conditions and altitude. In Denver, Colorado, for example, at an elevation of about 1 mile, or 1609 m (5280 ft), the height of the mercury column is 630 mm rather than 760 mm.

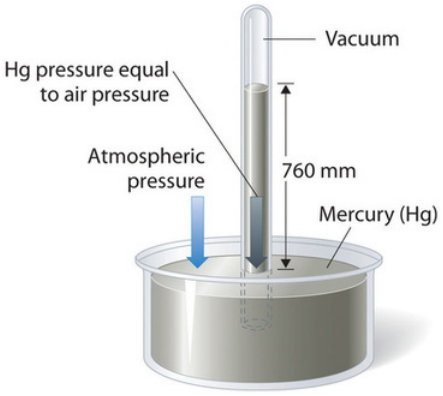


Figure 9.1.2.2: A Mercury Barometer. The pressure exerted by the atmosphere on the surface of the pool of mercury supports a column of mercury in the tube that is about 760 mm tall. Because the boiling point of mercury is quite high (356.73°C), there is very little mercury vapor in the space above the mercury column.

Mercury barometers have been used to measure barometric pressure for so long that they have their own unit for pressure: the millimeter of mercury (mmHg), often called the torr, after Torricelli. Standard barometric pressure is the barometric pressure required to support a column of mercury exactly 760 mm tall; this pressure is also referred to as 1 atmosphere (atm). These units are also related to the pascal:

$$1 \text{ atm} = 760 \ mmHg \tag{9.1.2.8}$$

$$= 760 \ torr \tag{9.1.2.9}$$

$$= 1.01325 \times 10^5 \ Pa \tag{9.1.2.10}$$

$$= 101.325 \ kPa \tag{9.1.2.11}$$

Thus a pressure of 1 atm equals 760 mmHg exactly.

We are so accustomed to living under this pressure that we never notice it. Instead, what we notice are *changes* in the pressure, such as when our ears pop in fast elevators in skyscrapers or in airplanes during rapid changes in altitude. We make use of barometric pressure in many ways. We can use a drinking straw because sucking on it removes air and thereby reduces the pressure inside the straw. The barometric pressure pushing down on the liquid in the glass then forces the liquid up the straw.

✔ Example 9.1.2.2: Barometric Pressure

One of the authors visited Rocky Mountain National Park several years ago. After departing from an airport at sea level in the eastern United States, he arrived in Denver (altitude 5280 ft), rented a car, and drove to the top of the highway outside Estes Park (elevation 14,000 ft). He noticed that even slight exertion was very difficult at this altitude, where the barometric pressure is only 454 mmHg. Convert this pressure to

a. atmospheres (atm).
b. bar.

Given: pressure in millimeters of mercury

Asked for: pressure in atmospheres and bar

Strategy:

Use the conversion factors in Equation 9.1.2.11to convert from millimeters of mercury to atmospheres and kilopascals.

Solution:

From Equation 9.1.2.11, we have 1 atm = 760 mmHg = 101.325 kPa. The pressure at 14,000 ft in atm is thus

$$P = 454 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} \tag{9.1.2.12}$$

$$= 0.597 \ atm$$

The pressure in bar is given by

$$P = 0.597 \text{ atm} \times \frac{1.01325 \text{ bar}}{1 \text{ atm}} \tag{9.1.2.13}$$

$$= 0.605 \ bar$$

? Exercise 9.1.2.2: Barometric Pressure

Mt. Everest, at 29,028 ft above sea level, is the world's tallest mountain. The normal barometric pressure at this altitude is about 0.308 atm. Convert this pressure to

a. millimeters of mercury.
b. bar.

Answer a

234 mmHg;

Answer b

0.312 bar

Manometers

Barometers measure barometric pressure, but manometers measure the pressures of samples of gases contained in an apparatus. The key feature of a manometer is a U-shaped tube containing mercury (or occasionally another nonvolatile liquid). A closed-end manometer is shown schematically in part (a) in Figure 9.1.2.3 When the bulb contains no gas (i.e., when its interior is a near vacuum), the heights of the two columns of mercury are the same because the space above the mercury on the left is a near vacuum (it contains only traces of mercury vapor). If a gas is released into the bulb on the right, it will exert a pressure on the mercury in the right column, and the two columns of mercury will no longer be the same height. The *difference* between the heights of the two columns is equal to the pressure of the gas.

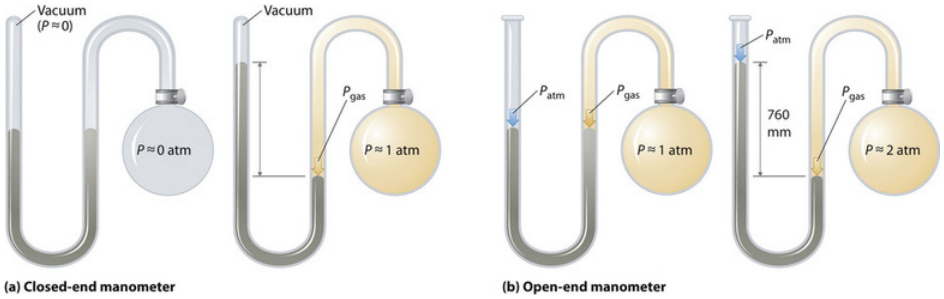


Figure 9.1.2.3: The Two Types of Manometer. (a) In a closed-end manometer, the space above the mercury column on the left (the reference arm) is essentially a vacuum ($P \approx 0$), and the difference in the heights of the two columns gives the pressure of the gas contained in the bulb directly. (b) In an open-end manometer, the left (reference) arm is open to the atmosphere ($P \approx 1$ atm), and the difference in the heights of the two columns gives the *difference* between barometric pressure and the pressure of the gas in the bulb.

If the tube is open to the atmosphere instead of closed, as in the open-end manometer shown in part (b) in Figure 9.1.2.3 then the two columns of mercury have the same height only if the gas in the bulb has a pressure equal to the barometric pressure. If the gas in the bulb has a *higher* pressure, the mercury in the open tube will be forced up by the gas pushing down on the mercury in the other arm of the U-shaped tube. The pressure of the gas in the bulb is therefore the sum of the barometric pressure (measured with a barometer) and the difference in the heights of the two columns. If the gas in the bulb has a pressure *less* than that of the

atmosphere, then the height of the mercury will be greater in the arm attached to the bulb. In this case, the pressure of the gas in the bulb is the barometric pressure minus the difference in the heights of the two columns.

Example 9.1.2.3

Suppose you want to construct a closed-end manometer to measure gas pressures in the range 0.000–0.200 atm. Because of the toxicity of mercury, you decide to use water rather than mercury. How tall a column of water do you need? (The density of water is 1.00 g/cm^3; the density of mercury is 13.53 g/cm^3.)

Given: pressure range and densities of water and mercury

Asked for: column height

Strategy:

A. Calculate the height of a column of mercury corresponding to 0.200 atm in millimeters of mercury. This is the height needed for a mercury-filled column.

B. From the given densities, use a proportion to compute the height needed for a water-filled column.

Solution:

A In millimeters of mercury, a gas pressure of 0.200 atm is

$$P = 0.200 \text{ atm} \times \frac{760 \text{ mmHg}}{1 \text{ atm}} = 152 \text{ mmHg}$$

Using a mercury manometer, you would need a mercury column at least 152 mm high.

B Because water is less dense than mercury, you need a *taller* column of water to achieve the same pressure as a given column of mercury. The height needed for a water-filled column corresponding to a pressure of 0.200 atm is proportional to the ratio of the density of mercury to the density of water

$$P = d_{\text{wat}} g h_{\text{wat}} = d_{\text{Hg}} g h_{\text{Hg}}$$

$$h_{\text{wat}} = h_{\text{Hg}} \times \frac{d_{\text{Hg}}}{g_{\text{wat}}} = 152 \text{ mm} \times \frac{13.53 \text{ g/cm}^3}{1.00 \text{ g/cm}^3} = 2070 \text{ mm}$$

The answer makes sense: it takes a taller column of a less dense liquid to achieve the same pressure.

Exercise 9.1.2.3

Suppose you want to design a barometer to measure barometric pressure in an environment that is always hotter than 30°C. To avoid using mercury, you decide to use gallium, which melts at 29.76°C; the density of liquid gallium at 25°C is 6.114 g/cm^3. How tall a column of gallium do you need if P = 1.00 atm?

Answer

1.68 m

The answer to Example 9.1.2.3 also tells us the maximum depth of a farmer's well if a simple suction pump will be used to get the water out. The 1.00 atm corresponds to a column height of

$$\begin{aligned} h_{\text{wat}} &= h_{\text{Hg}} \times \frac{d_{\text{Hg}}}{g_{\text{wat}}} \\ &= 760 \text{ mm} \times \frac{13.53 \text{ g/cm}^3}{1.00 \text{ g/cm}^3} \\ &= 1.03 \times 10^4 \ mm \\ &= 10.3 \ m \end{aligned}$$

A suction pump is just a more sophisticated version of a straw: it creates a vacuum above a liquid and relies on barometric pressure to force the liquid up a tube. If 1 atm pressure corresponds to a 10.3 m (33.8 ft) column of water, then it is physically impossible for barometric pressure to raise the water in a well higher than this. Until electric pumps were invented to push water mechanically from greater depths, this factor greatly limited where people could live because obtaining water from wells deeper than about 33 ft was difficult.

Summary

Pressure is defined as the force exerted per unit area; it can be measured using a barometer or manometer. Four quantities must be known for a complete physical description of a sample of a gas: *temperature*, *volume*, *amount*, and *pressure*. **Pressure** is force per unit area of surface; the SI unit for pressure is the **pascal (Pa)**, defined as 1 newton per square meter (N/m^2). The pressure exerted by an object is proportional to the force it exerts and inversely proportional to the area on which the force is exerted. The pressure exerted by Earth's atmosphere, called *barometric pressure*, is about 101 kPa or 14.7 $lb/in.^2$ at sea level. barometric pressure can be measured with a **barometer**, a closed, inverted tube filled with mercury. The height of the mercury column is proportional to barometric pressure, which is often reported in units of **millimeters of mercury (mmHg)**, also called **torr**. **Standard barometric pressure**, the pressure required to support a column of mercury 760 mm tall, is yet another unit of pressure: 1 **atmosphere (atm)**. A **manometer** is an apparatus used to measure the pressure of a sample of a gas.



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9.1.3: The Gas Laws

Learning Objectives

- To understand the relationships among pressure, temperature, volume, and the amount of a gas.

Early scientists explored the relationships among the pressure of a gas (P) and its temperature (T), volume (V), and amount (n) by holding two of the four variables constant (amount and temperature, for example), varying a third (such as pressure), and measuring the effect of the change on the fourth (in this case, volume). The history of their discoveries provides several excellent examples of the scientific method.

The Relationship between Pressure and Volume: Boyle's Law

As the pressure on a gas increases, the volume of the gas decreases because the gas particles are forced closer together. Conversely, as the pressure on a gas decreases, the gas volume increases because the gas particles can now move farther apart. Weather balloons get larger as they rise through the atmosphere to regions of lower pressure because the volume of the gas has increased; that is, the atmospheric gas exerts less pressure on the surface of the balloon, so the interior gas expands until the internal and external pressures are equal.

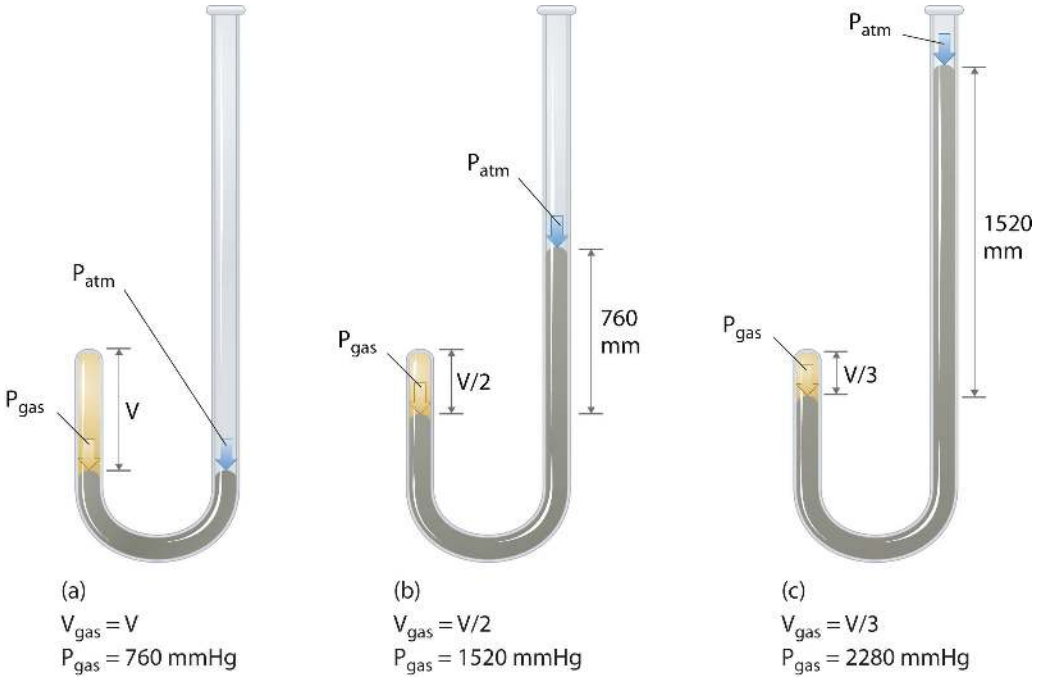


Figure 9.1.3.1: Boyle's Experiment Using a J-Shaped Tube to Determine the Relationship between Gas Pressure and Volume. (a) Initially the gas is at a pressure of 1 atm = 760 mmHg (the mercury is at the same height in both the arm containing the sample and the arm open to the atmosphere); its volume is V. (b) If enough mercury is added to the right side to give a difference in height of 760 mmHg between the two arms, the pressure of the gas is 760 mmHg (atmospheric pressure) + 760 mmHg = 1520 mmHg and the volume is $V/2$. (c) If an additional 760 mmHg is added to the column on the right, the total pressure on the gas increases to 2280 mmHg, and the volume of the gas decreases to $V/3$ (CC BY-SA-NC; anonymous).

The Irish chemist Robert Boyle (1627–1691) carried out some of the earliest experiments that determined the quantitative relationship between the pressure and the volume of a gas. Boyle used a J-shaped tube partially filled with mercury, as shown in Figure 9.1.3.1. In these experiments, a small amount of a gas or air is trapped above the mercury column, and its volume is measured at atmospheric pressure and constant temperature. More mercury is then poured into the open arm to increase the pressure on the gas sample. The pressure on the gas is atmospheric pressure plus the difference in the heights of the mercury columns, and the resulting volume is measured. This process is repeated until either there is no more room in the open arm or the volume of the gas is too small to be measured accurately. Data such as those from one of Boyle's own experiments may be plotted in several ways (Figure 9.1.3.2). A simple plot of V versus P gives a curve called a hyperbola and reveals an inverse relationship between pressure and volume: as the pressure is doubled, the volume decreases by a factor of two. This relationship between the two quantities is described as follows:

$$PV = \text{constant} \tag{9.1.3.1}$$

Dividing both sides by P gives an equation illustrating the inverse relationship between P and V:

$$V = \frac{\text{const.}}{P} = \text{const.} \left(\frac{1}{P}\right) \tag{9.1.3.2}$$

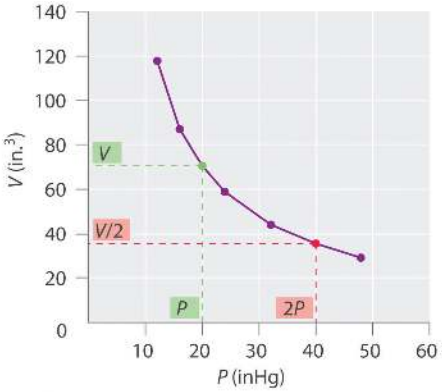
or

$$V \propto \frac{1}{P} \tag{9.1.3.3}$$

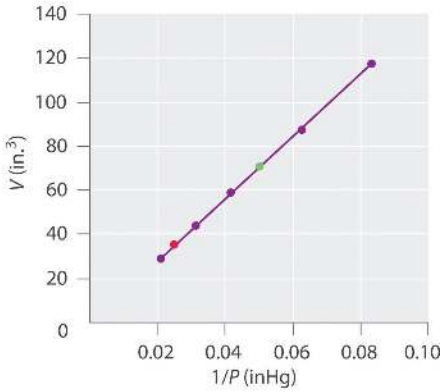
where the $\propto$ symbol is read "is proportional to." A plot of V versus $1/P$ is thus a straight line whose slope is equal to the constant in Equations 9.1.3.1 and 9.1.3.3. Dividing both sides of Equation 9.1.3.1 by V instead of P gives a similar relationship between P and $1/V$. The numerical value of the constant depends on the amount of gas used in the experiment and on the temperature at which the experiments are carried out. This relationship between pressure and volume is known as Boyle's law, after its discoverer, and can be stated as follows: *At constant temperature, the volume of a fixed amount of a gas is inversely proportional to its pressure.* This law in practice is shown in Figure 9.1.3.2

P (inHg)	*V* (in.^{3})	*PV*
12.0	117.5	1410
16.0	87.2	1400
20.0	70.7	1410
24.0	58.8	1410
32.0	44.2	1410
40.0	35.3	1410
48.0	29.1	1400

(a) Data from Boyle's experiment



(b) Volume vs. pressure



(c) Volume vs. 1/pressure

Figure 9.1.3.2: Plots of Boyle's Data. (a) Here are actual data from a typical experiment conducted by Boyle. Boyle used non-SI units to measure the volume (in.^{3} rather than cm^3) and the pressure (in. Hg rather than mmHg). (b) This plot of pressure versus volume is a hyperbola. Because PV is a constant, decreasing the pressure by a factor of two results in a twofold increase in volume and vice versa. (c) A plot of volume versus 1/pressure for the same data shows the inverse linear relationship between the two quantities, as expressed by the equation V = constant/P (CC BY-SA-NC; anonymous).

> *At constant temperature, the volume of a fixed amount of a gas is inversely proportional to its pressure*



The Relationship between Temperature and Volume: Charles's Law

Hot air rises, which is why hot-air balloons ascend through the atmosphere and why warm air collects near the ceiling and cooler air collects at ground level. Because of this behavior, heating registers are placed on or near the floor, and vents for air-conditioning

are placed on or near the ceiling. The fundamental reason for this behavior is that gases expand when they are heated. Because the same amount of substance now occupies a greater volume, hot air is less dense than cold air. The substance with the lower density—in this case hot air—rises through the substance with the higher density, the cooler air.

The first experiments to quantify the relationship between the temperature and the volume of a gas were carried out in 1783 by an avid balloonist, the French chemist Jacques Alexandre César Charles (1746–1823). Charles's initial experiments showed that a plot of the volume of a given sample of gas versus temperature (in degrees Celsius) at constant pressure is a straight line. Similar but more precise studies were carried out by another balloon enthusiast, the Frenchman Joseph-Louis Gay-Lussac (1778–1850), who showed that a plot of V versus T was a straight line that could be extrapolated to a point at zero volume, a theoretical condition now known to correspond to −273.15°C (Figure 9.1.3.3). A sample of gas cannot really have a volume of zero because any sample of matter must have some volume. Furthermore, at 1 atm pressure all gases liquefy at temperatures well above −273.15°C. Note from part (a) in Figure 9.1.3.3 that the slope of the plot of V versus T varies for the same gas at different pressures but that the intercept remains constant at −273.15°C. Similarly, as shown in part (b) in Figure 9.1.3.3, plots of V versus T for different amounts of varied gases are straight lines with different slopes but the same intercept on the T axis.

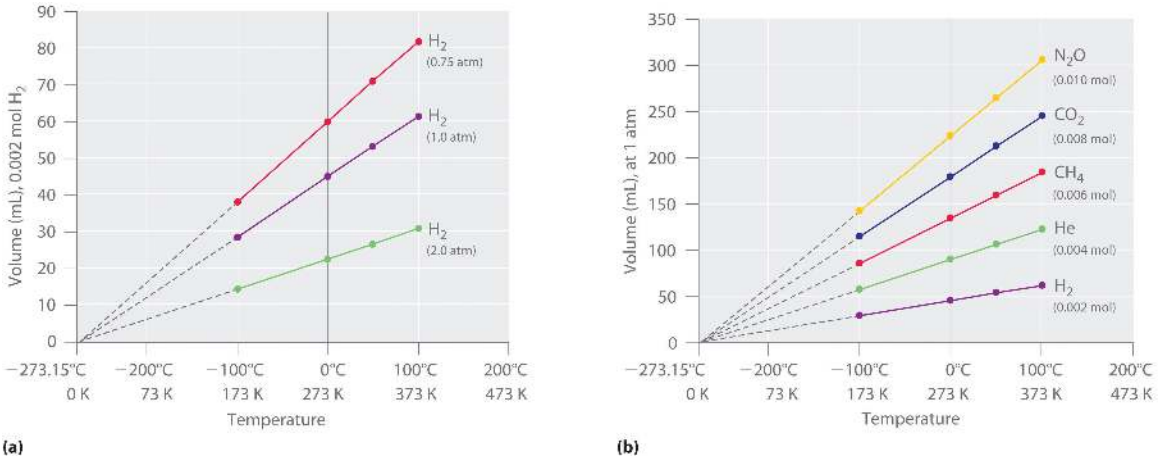


Figure 9.1.3.3: The Relationship between Volume and Temperature. (a) In these plots of volume versus temperature for equal-sized samples of H_2 at three different pressures, the solid lines show the experimentally measured data down to −100°C, and the broken lines show the extrapolation of the data to $V = 0$. The temperature scale is given in both degrees Celsius and kelvins. Although the slopes of the lines decrease with increasing pressure, all of the lines extrapolate to the same temperature at $V = 0$ (−273.15°C = 0 K). (b) In these plots of volume versus temperature for different amounts of selected gases at 1 atm pressure, all the plots extrapolate to a value of $V = 0$ at −273.15°C, regardless of the identity or the amount of the gas (CC BY-SA-NC; anonymous).

The significance of the invariant T intercept in plots of V versus T was recognized in 1848 by the British physicist William Thomson (1824–1907), later named Lord Kelvin. He postulated that −273.15°C was the lowest possible temperature that could theoretically be achieved, for which he coined the term absolute zero (0 K).

We can state Charles's and Gay-Lussac's findings in simple terms: At constant pressure, the volume of a fixed amount of gas is directly proportional to its absolute temperature (in kelvins). This relationship, illustrated in part (b) in Figure 9.1.3.3 is often referred to as Charles's law and is stated mathematically as

$$V = \text{const.}\ T \tag{9.1.3.4}$$

or

$$V \propto T \tag{9.1.3.5}$$

with *temperature expressed in kelvins*, not *in degrees Celsius.* Charles's law is valid for virtually all gases at temperatures well above their boiling points.



The Relationship between Amount and Volume: Avogadro's Law

We can demonstrate the relationship between the volume and the amount of a gas by filling a balloon; as we add more gas, the balloon gets larger. The specific quantitative relationship was discovered by the Italian chemist Amedeo Avogadro, who recognized the importance of Gay-Lussac's work on combining volumes of gases. In 1811, Avogadro postulated that, at the same temperature and pressure, equal volumes of gases contain the same number of gaseous particles (Figure 9.1.3.4). This is the historic "Avogadro's hypothesis."

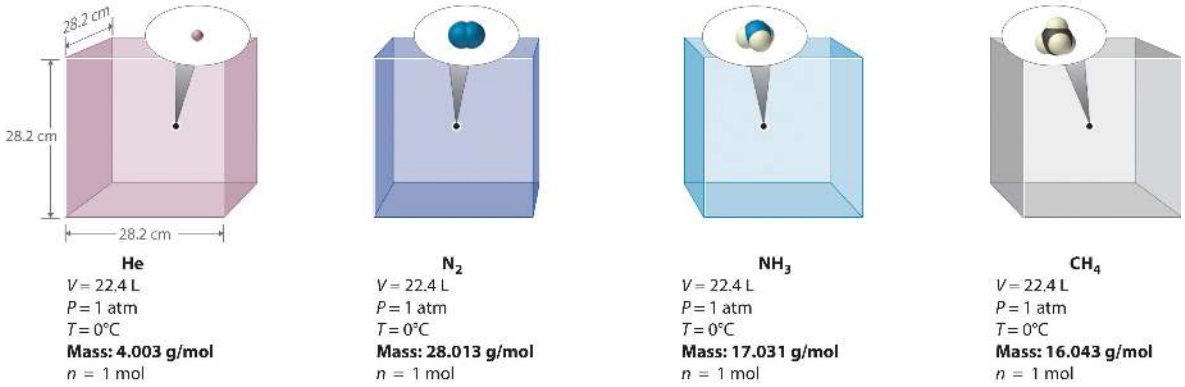


Figure 9.1.3.4: Avogadro's Hypothesis. Equal volumes of four different gases at the same temperature and pressure contain the same number of gaseous particles. Because the molar mass of each gas is different, the *mass* of each gas sample is different even though all contain 1 mol of gas (CC BY-SA-NC; anonymous).

A logical corollary to Avogadro's hypothesis (sometimes called Avogadro's law) describes the relationship between the volume and the amount of a gas: *At constant temperature and pressure, the volume of a sample of gas is directly proportional to the number of moles of gas in the sample.* Stated mathematically,

$$V = \text{const.}\ (n) \tag{9.1.3.6}$$

or

$$V \propto .\, n @ \text{ constant T and P} \tag{9.1.3.7}$$

This relationship is valid for most gases at relatively low pressures, but deviations from strict linearity are observed at elevated pressures.



For a sample of gas,

- V increases as P decreases (and vice versa)
- V increases as T increases (and vice versa)
- V increases as n increases (and vice versa)

The relationships among the volume of a gas and its pressure, temperature, and amount are summarized in Figure 9.1.3.5 Volume *increases* with increasing temperature or amount, but *decreases* with increasing pressure.

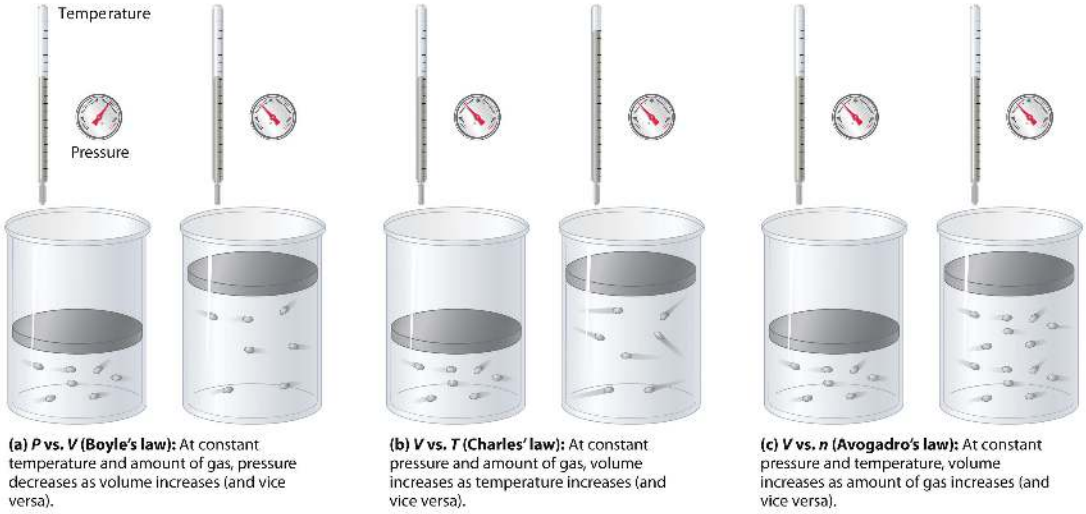


Figure 9.1.3.5: The Empirically Determined Relationships among Pressure, Volume, Temperature, and Amount of a Gas. The thermometer and pressure gauge indicate the temperature and the pressure qualitatively, the level in the flask indicates the volume, and the number of particles in each flask indicates relative amounts (CC BY-SA-NC; anonymous).

Summary

The volume of a gas is inversely proportional to its pressure and directly proportional to its temperature and the amount of gas. Boyle showed that the volume of a sample of a gas is inversely proportional to its pressure (**Boyle's law**), Charles and Gay-Lussac demonstrated that the volume of a gas is directly proportional to its temperature (in kelvins) at constant pressure (**Charles's law**), and Avogadro postulated that the volume of a gas is directly proportional to the number of moles of gas present (**Avogadro's law**). Plots of the volume of gases versus temperature extrapolate to zero volume at −273.15°C, which is **absolute zero (0 K)**, the lowest temperature possible. Charles's law implies that the volume of a gas is directly proportional to its absolute temperature.

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9.2: The Ideal Gas Equation

Learning Objectives

- Derive the ideal gas law from the constituent gas laws
- To use the ideal gas law to describe the behavior of a gas.

In this module, the relationship between pressure, temperature, volume, and amount of a gas are described and how these relationships can be combined to give a general expression that describes the behavior of a gas.

Deriving the Ideal Gas Law

Any set of relationships between a single quantity (such as V) and several other variables (P, T, and n) can be combined into a single expression that describes all the relationships simultaneously. The three individual expressions were derived previously:

- **Boyle's law**

$$V \propto \frac{1}{P} \quad @ \text{ constant n and T}$$

- **Charles's law**

$$V \propto T \quad @ \text{ constant n and P}$$

- **Avogadro's law**

$$V \propto n \quad @ \text{ constant T and P}$$

Combining these three expressions gives

$$V \propto \frac{nT}{P} \tag{9.2.1}$$

which shows that the volume of a gas is proportional to the number of moles and the temperature and inversely proportional to the pressure. This expression can also be written as

$$V = \text{Cons.} \left(\frac{nT}{P} \right) \tag{9.2.2}$$

By convention, the proportionality constant in Equation 9.2.1 is called the gas constant, which is represented by the letter R. Inserting R into Equation 9.2.2 gives

$$V = \frac{RnT}{P} = \frac{nRT}{P} \tag{9.2.3}$$

Clearing the fractions by multiplying both sides of Equation 9.2.4 by P gives

$$PV = nRT \tag{9.2.4}$$

This equation is known as the **ideal gas law**.

An ideal gas is defined as a hypothetical gaseous substance whose behavior is independent of attractive and repulsive forces and can be completely described by the ideal gas law. In reality, there is no such thing as an ideal gas, but an ideal gas is a useful conceptual model that allows us to understand how gases respond to changing conditions. As we shall see, under many conditions, most real gases exhibit behavior that closely approximates that of an ideal gas. The ideal gas law can therefore be used to predict the behavior of real gases under most conditions. The ideal gas law does not work well at very low temperatures or very high pressures, where deviations from ideal behavior are most commonly observed.

> *Significant deviations from ideal gas behavior commonly occur at low temperatures and very high pressures.*

Before we can use the ideal gas law, however, we need to know the value of the gas constant R. Its form depends on the units used for the other quantities in the expression. If V is expressed in liters (L), P in atmospheres (atm), T in kelvins (K), and n in moles

(mol), then

$$R = 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \tag{9.2.5}$$

Because the product PV has the units of energy, R can also have units of J/(K•mol):

$$R = 8.3145 \frac{\text{J}}{\text{K} \cdot \text{mol}} \tag{9.2.6}$$

Standard Conditions of Temperature and Pressure

Scientists have chosen a particular set of conditions to use as a reference: 0°C (273.15 K) and 1 bar = 100 kPa = 10^5 Pa pressure, referred to as standard temperature and pressure (**STP**).

$$\text{STP:} \qquad T = 273.15 \text{ K and } P = 1 \text{ bar} = 10^5 \text{ Pa}$$

Please note that STP was defined differently in the past. The old definition was based on a standard pressure of 1 atm.

We can calculate the volume of 1.000 mol of an ideal gas under standard conditions using the variant of the ideal gas law given in Equation 9.2.4:

$$V = \frac{nRT}{P} \tag{9.2.7}$$

Thus the volume of 1 mol of an ideal gas is **22.71 L at STP** and **22.41 L at 0°C and 1 atm**, approximately equivalent to the volume of three basketballs. The molar volumes of several real gases at 0°C and 1 atm are given in Table 10.3, which shows that the deviations from ideal gas behavior are quite small. Thus the ideal gas law does a good job of approximating the behavior of real gases at 0°C and 1 atm. The relationships described in Section 10.3 as Boyle's, Charles's, and Avogadro's laws are simply special cases of the ideal gas law in which two of the four parameters (P, V, T, and n) are held fixed.

Table 9.2.1: Molar Volumes of Selected Gases at 0°C and 1 atm

Gas	Molar Volume (L)
He	22.434
Ar	22.397
H_2	22.433
N_2	22.402
O_2	22.397
CO_2	22.260
NH_3	22.079

Applying the Ideal Gas Law

The ideal gas law allows us to calculate the value of the fourth variable for a gaseous sample if we know the values of any three of the four variables (*P*, *V*, *T*, and *n*). It also allows us to predict the *final state* of a sample of a gas (i.e., its final temperature, pressure, volume, and amount) following any changes in conditions if the parameters (*P*, *V*, *T*, and *n*) are specified for an *initial state*. Some applications are illustrated in the following examples. The approach used throughout is always to start with the same equation—the ideal gas law—and then determine which quantities are given and which need to be calculated. Let's begin with simple cases in which we are given three of the four parameters needed for a complete physical description of a gaseous sample.

Example 9.2.1

The balloon that Charles used for his initial flight in 1783 was destroyed, but we can estimate that its volume was 31,150 L (1100 ft^3), given the dimensions recorded at the time. If the temperature at ground level was 86°F (30°C) and the atmospheric pressure was 745 mmHg, how many moles of hydrogen gas were needed to fill the balloon?

Given: volume, temperature, and pressure

Asked for: amount of gas

Strategy:

A. Solve the ideal gas law for the unknown quantity, in this case *n*.

B. Make sure that all quantities are given in units that are compatible with the units of the gas constant. If necessary, convert them to the appropriate units, insert them into the equation you have derived, and then calculate the number of moles of hydrogen gas needed.

Solution:

A We are given values for *P*, *T*, and *V* and asked to calculate *n*. If we solve the ideal gas law (Equation 9.2.4) for n, we obtain

$$745 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 0.980 \text{ atm}$$

B *P* and *T* are given in units that are not compatible with the units of the gas constant [*R* = 0.08206 (L•atm)/(K•mol)]. We must therefore convert the temperature to kelvins and the pressure to atmospheres:

$$T = 273 + 30 = 303\text{K}$$

Substituting these values into the expression we derived for *n*, we obtain

$$\begin{aligned} n &= \frac{PV}{RT} \\ &= \frac{0.980 \text{ atm} \times 31150 \text{ L}}{0.08206 \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 303 \text{ K}} \\ &= 1.23 \times 10^3 \ mol \end{aligned}$$

? Exercise 9.2.1

Suppose that an “empty” aerosol spray-paint can has a volume of 0.406 L and contains 0.025 mol of a propellant gas such as CO_2. What is the pressure of the gas at 25°C?

Answer

1.5 atm

In Example 9.2.1, we were given three of the four parameters needed to describe a gas under a particular set of conditions, and we were asked to calculate the fourth. We can also use the ideal gas law to calculate the effect of *changes* in any of the specified conditions on any of the other parameters, as shown in Example 9.2.5.

General Gas Equation

When a gas is described under two different conditions, the ideal gas equation must be applied twice - to an initial condition and a final condition. This is:

$$\begin{matrix} \text{Initial condition } (i) & \text{Final condition} (f) \\ P_i V_i = n_i R T_i & P_f V_f = n_f R T_f \end{matrix}$$

Both equations can be rearranged to give:

$$R = \frac{P_i V_i}{n_i T_i} \qquad R = \frac{P_f V_f}{n_f T_f}$$

The two equations are equal to each other since each is equal to the same constant R. Therefore, we have:

$$\frac{P_i V_i}{n_i T_i} = \frac{P_f V_f}{n_f T_f} \tag{9.2.8}$$

The equation is called the **general gas equation**. The equation is particularly useful when one or two of the gas properties are held constant between the two conditions. In such cases, the equation can be simplified by eliminating these constant gas properties.



Example 9.2.2

Suppose that Charles had changed his plans and carried out his initial flight not in August but on a cold day in January, when the temperature at ground level was −10°C (14°F). How large a balloon would he have needed to contain the same amount of hydrogen gas at the same pressure as in Example 9.2.1?

Given: temperature, pressure, amount, and volume in August; temperature in January

Asked for: volume in January

Strategy:

A. Use the results from Example 9.2.1 for August as the initial conditions and then calculate the *change in volume* due to the change in temperature from 30°C to −10°C. Begin by constructing a table showing the initial and final conditions.
B. Simplify the general gas equation by eliminating the quantities that are held constant between the initial and final conditions, in this case P and n.
C. Solve for the unknown parameter.

Solution:

A To see exactly which parameters have changed and which are constant, prepare a table of the initial and final conditions:

Solution to Example 10.4.2

Initial (August)	Final (January)
$T_i = 30\ ^\circ C = 303\ K$	$T_f = -10\ ^\circ C = 263\ K$
$P_i = 0.980\ atm$	$P_f = 0.980\ atm$
$n_i = 1.23 \times 10^3\ mol$	$n_f = 1.23 \times 10^3\ mol$
$V_i = 31150\ L$	$V_f = ?$

B Both n and P are the same in both cases ($n_i = n_f$, $P_i = P_f$). Therefore, Equation 9.2.8 can be simplified to:

$$\frac{V_i}{T_i} = \frac{V_f}{T_f}$$

This is the relationship first noted by Charles.

C Solving the equation for V_f, we get:

$$V_f = V_i \times \frac{T_f}{T_i}$$

$$= 31150 \text{ L} \times \frac{263 \text{ K}}{303 \text{ K}}$$

$$= 2.70 \times 10^4 \ L$$

It is important to check your answer to be sure that it makes sense, just in case you have accidentally inverted a quantity or multiplied rather than divided. In this case, the temperature of the gas decreases. Because we know that gas volume decreases with decreasing temperature, the final volume must be less than the initial volume, so the answer makes sense. We could have calculated the new volume by plugging all the given numbers into the ideal gas law, but it is generally much easier and faster to focus on only the quantities that change.

? Exercise 9.2.2

At a laboratory party, a helium-filled balloon with a volume of 2.00 L at 22°C is dropped into a large container of liquid nitrogen (T = −196°C). What is the final volume of the gas in the balloon?

Answer

0.52 L

Example 9.2.1 illustrates the relationship originally observed by Charles. We could work through similar examples illustrating the inverse relationship between pressure and volume noted by Boyle (*PV* = constant) and the relationship between volume and amount observed by Avogadro (*V*/*n* = constant). We will not do so, however, because it is more important to note that the historically important gas laws are only special cases of the ideal gas law in which two quantities are varied while the other two remain fixed. The method used in Example 9.2.1 can be applied in *any* such case, as we demonstrate in Example 9.2.2 (which also shows why heating a closed container of a gas, such as a butane lighter cartridge or an aerosol can, may cause an explosion).

✓ Example 9.2.3

Aerosol cans are prominently labeled with a warning such as “Do not incinerate this container when empty.” Assume that you did not notice this warning and tossed the “empty” aerosol can in Exercise 9.2.1 (0.025 mol in 0.406 L, initially at 25°C and 1.5 atm internal pressure) into a fire at 750°C. What would be the pressure inside the can (if it did not explode)?

Given: initial volume, amount, temperature, and pressure; final temperature

Asked for: final pressure

Strategy:

Follow the strategy outlined in Example 9.2.2.

Solution:

Prepare a table to determine which parameters change and which are held constant:

Solution to Example 10.4.3

Initial	Final
$V_i = 0.406 \text{ L}$	$V_f = 0.406 \text{ L}$
$n_i = 0.025 \text{ mol}$	$n_f = 0.025 \text{ mol}$
$T_i = 25 \text{ °C} = 298 \text{ K}$	$T_i = 750 \text{ °C} = 1023 \text{ K}$
$P_i = 1.5 \text{ atm}$	$P_f = ?$

Both V and n are the same in both cases ($V_i = V_f, n_i = n_f$). Therefore, Equation can be simplified to:

$$\frac{P_i}{T_i} = \frac{P_f}{T_f}$$

By solving the equation for P_f, we get:

$$\begin{aligned} P_f &= P_i \times \frac{T_f}{T_i} \\ &= 1.5 \text{ atm} \times \frac{1023 \text{ K}}{298 \text{ K}} \\ &= 5.1 \ atm \end{aligned}$$

This pressure is more than enough to rupture a thin sheet metal container and cause an explosion!

? Exercise 9.2.3

Suppose that a fire extinguisher, filled with CO_2 to a pressure of 20.0 atm at 21°C at the factory, is accidentally left in the sun in a closed automobile in Tucson, Arizona, in July. The interior temperature of the car rises to 160°F (71.1°C). What is the internal pressure in the fire extinguisher?

Answer

23.4 atm

In Examples 9.2.1 and 9.2.2, two of the four parameters (*P*, *V*, *T*, and *n*) were fixed while one was allowed to vary, and we were interested in the effect on the value of the fourth. In fact, we often encounter cases where two of the variables *P*, *V*, and *T* are allowed to vary for a given sample of gas (hence *n* is constant), and we are interested in the change in the value of the third under the new conditions.



✓ Example 9.2.4

We saw in Example 9.2.1 that Charles used a balloon with a volume of 31,150 L for his initial ascent and that the balloon contained 1.23×10^3 mol of H_2 gas initially at 30°C and 745 mmHg. Suppose that Gay-Lussac had also used this balloon for his record-breaking ascent to 23,000 ft and that the pressure and temperature at that altitude were 312 mmHg and −30°C, respectively. To what volume would the balloon have had to expand to hold the same amount of hydrogen gas at the higher altitude?

Given: initial pressure, temperature, amount, and volume; final pressure and temperature

Asked for: final volume

Strategy:

Follow the strategy outlined in Example 9.2.3.

Solution:

Begin by setting up a table of the two sets of conditions:

Solution to Example 10.4.4

Initial	Final
$P_i = 745\ \text{mmHg} = 0.980\ \text{atm}$	$P_f = 312\ \text{mmHg} = 0.411\ \text{atm}$
$T_i = 30\ ^\circ\text{C} = 303\ \text{K}$	$T_f = 750 - 30\ ^\circ\text{C} = 243\ \text{K}$
$n_i = 1.2 \times 10^3\ \text{mol}$	$n_i = 1.2 \times 10^3\ \text{mol}$
$V_i = 31150\ \text{L}$	$V_f = ?$

By eliminating the constant property (n) of the gas, Equation 9.2.8 is simplified to:

$$\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f}$$

By solving the equation for V_f, we get:

$$\begin{aligned} V_f &= V_i \times \frac{P_i}{P_f}\frac{T_f}{T_i} \\ &= 3.115 \times 10^4\ \text{L} \times \frac{0.980\ \text{atm}}{0.411\ \text{atm}}\frac{243\ \text{K}}{303\ \text{K}} \\ &= 5.96 \times 10^4\ L \end{aligned}$$

Does this answer make sense? Two opposing factors are at work in this problem: decreasing the pressure tends to *increase* the volume of the gas, while decreasing the temperature tends to *decrease* the volume of the gas. Which do we expect to predominate? The pressure drops by more than a factor of two, while the absolute temperature drops by only about 20%. Because the volume of a gas sample is directly proportional to both *T* and 1/*P*, the variable that changes the most will have the greatest effect on *V*. In this case, the effect of decreasing pressure predominates, and we expect the volume of the gas to increase, as we found in our calculation.

We could also have solved this problem by solving the ideal gas law for *V* and then substituting the relevant parameters for an altitude of 23,000 ft:

Except for a difference caused by rounding to the last significant figure, this is the same result we obtained previously. *There is often more than one "right" way to solve chemical problems.*

? Exercise 9.2.4

A steel cylinder of compressed argon with a volume of 0.400 L was filled to a pressure of 145 atm at 10°C. At 1.00 atm pressure and 25°C, how many 15.0 mL incandescent light bulbs could be filled from this cylinder? (Hint: find the number of moles of argon in each container.)

Answer

4.07×10^3

Using the Ideal Gas Law to Calculate Gas Densities and Molar Masses

The ideal gas law can also be used to calculate molar masses of gases from experimentally measured gas densities. To see how this is possible, we first rearrange the ideal gas law to obtain

$$\frac{n}{V} = \frac{P}{RT} \tag{9.2.9}$$

The left side has the units of moles per unit volume (mol/L). The number of moles of a substance equals its mass (m, in grams) divided by its molar mass (M, in grams per mole):

$$n = \frac{m}{M} \tag{9.2.10}$$

Substituting this expression for n into Equation 9.2.9 gives

$$\frac{m}{MV} = \frac{P}{RT} \tag{9.2.11}$$

Because m/V is the density d of a substance, we can replace m/V by d and rearrange to give

$$\rho = \frac{m}{V} = \frac{MP}{RT} \tag{9.2.12}$$

The distance between particles in gases is large compared to the size of the particles, so their densities are much lower than the densities of liquids and solids. Consequently, gas density is usually measured in grams per liter (g/L) rather than grams per milliliter (g/mL).



Example 9.2.5

Calculate the density of butane at 25°C and a pressure of 750 mmHg.

Given: compound, temperature, and pressure

Asked for: density

Strategy:

A. Calculate the molar mass of butane and convert all quantities to appropriate units for the value of the gas constant.

B. Substitute these values into Equation 9.2.12 to obtain the density.

Solution:

A The molar mass of butane (C_4H_{10}) is

$$M = (4)(12.011) + (10)(1.0079) = 58.123 \text{g/mol}$$

Using 0.08206 (L•atm)/(K•mol) for *R* means that we need to convert the temperature from degrees Celsius to kelvins (*T* = 25 + 273 = 298 K) and the pressure from millimeters of mercury to atmospheres:

$$P = 750 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 0.987 \text{ atm}$$

B Substituting these values into Equation 9.2.12 gives

$$\rho = \frac{58.123 \text{ g/mol} \times 0.987 \text{ atm}}{0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \times 298 \text{ K}} = 2.35 \text{ g/L}$$

Exercise 9.2.5: Density of Radon

Radon (Rn) is a radioactive gas formed by the decay of naturally occurring uranium in rocks such as granite. It tends to collect in the basements of houses and poses a significant health risk if present in indoor air. Many states now require that houses be tested for radon before they are sold. Calculate the density of radon at 1.00 atm pressure and 20°C and compare it with the density of nitrogen gas, which constitutes 80% of the atmosphere, under the same conditions to see why radon is found in basements rather than in attics.

Answer

radon, 9.23 g/L; N_2, 1.17 g/L

A common use of Equation 9.2.12 is to determine the molar mass of an unknown gas by measuring its density at a known temperature and pressure. This method is particularly useful in identifying a gas that has been produced in a reaction, and it is not difficult to carry out. A flask or glass bulb of known volume is carefully dried, evacuated, sealed, and weighed empty. It is then filled with a sample of a gas at a known temperature and pressure and reweighed. The difference in mass between the two readings is the mass of the gas. The volume of the flask is usually determined by weighing the flask when empty and when filled with a liquid of known density such as water. The use of density measurements to calculate molar masses is illustrated in Example 9.2.6.

Example 9.2.6

The reaction of a copper penny with nitric acid results in the formation of a red-brown gaseous compound containing nitrogen and oxygen. A sample of the gas at a pressure of 727 mmHg and a temperature of 18°C weighs 0.289 g in a flask with a volume of 157.0 mL. Calculate the molar mass of the gas and suggest a reasonable chemical formula for the compound.

Given: pressure, temperature, mass, and volume

Asked for: molar mass and chemical formula

Strategy:

A. Solve Equation 9.2.12 for the molar mass of the gas and then calculate the density of the gas from the information given.

B. Convert all known quantities to the appropriate units for the gas constant being used. Substitute the known values into your equation and solve for the molar mass.

C. Propose a reasonable empirical formula using the atomic masses of nitrogen and oxygen and the calculated molar mass of the gas.

Solution:

A Solving Equation 9.2.12 for the molar mass gives

$$M = \frac{mRT}{PV} = \frac{dRT}{P}$$

Density is the mass of the gas divided by its volume:

$$\rho = \frac{m}{V} = \frac{0.289\text{g}}{0.157\text{L}} = 1.84\text{g/L}$$

B We must convert the other quantities to the appropriate units before inserting them into the equation:

$$T = 18 + 273 = 291K$$

$$P = 727\,mmHg \times \frac{1\text{atm}}{760\text{mmHg}} = 0.957\text{atm}$$

The molar mass of the unknown gas is thus

$$M = \frac{1.84\text{ g/L} \times 0.08206 \dfrac{\text{L}\cdot\text{atm}}{\text{K}\cdot\text{mol}} \times 291\text{ K}}{0.957\text{ atm}} = 45.9\text{g/mol}$$

C The atomic masses of N and O are approximately 14 and 16, respectively, so we can construct a list showing the masses of possible combinations:

$$M(\text{NO}) = 14 + 16 = 30 \text{ g/mol}$$

$$M(\text{N}_2\text{O}) = (2)(14) + 16 = 44 \text{ g/mol}$$

$$M(\text{NO}_2) = 14 + (2)(16) = 46 \text{ g/mol}$$

The most likely choice is NO_2 which is in agreement with the data. The red-brown color of smog also results from the presence of NO_2 gas.

? Exercise 9.2.6

You are in charge of interpreting the data from an unmanned space probe that has just landed on Venus and sent back a report on its atmosphere. The data are as follows: pressure, 90 atm; temperature, 557°C; density, 58 g/L. The major constituent of the atmosphere (>95%) is carbon. Calculate the molar mass of the major gas present and identify it.

Answer

44 g/mol; CO_2

Summary

The ideal gas law is derived from empirical relationships among the pressure, the volume, the temperature, and the number of moles of a gas; it can be used to calculate any of the four properties if the other three are known.

Ideal gas equation: $PV = nRT$,

where $R = 0.08206 \dfrac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} = 8.3145 \dfrac{\text{J}}{\text{K} \cdot \text{mol}}$

General gas equation: $\dfrac{P_i V_i}{n_i T_i} = \dfrac{P_f V_f}{n_f T_f}$

Density of a gas: $\rho = \dfrac{MP}{RT}$

The empirical relationships among the volume, the temperature, the pressure, and the amount of a gas can be combined into the **ideal gas law**, *PV* = *nRT*. The proportionality constant, *R*, is called the **gas constant** and has the value 0.08206 (L•atm)/(K•mol), 8.3145 J/(K•mol), or 1.9872 cal/(K•mol), depending on the units used. The ideal gas law describes the behavior of an **ideal gas**, a hypothetical substance whose behavior can be explained quantitatively by the ideal gas law and the kinetic molecular theory of gases. **Standard temperature and pressure (STP)** is 0°C and 1 atm. The volume of 1 mol of an ideal gas at STP is 22.41 L, the **standard molar volume**. All of the empirical gas relationships are special cases of the ideal gas law in which two of the four parameters are held constant. The ideal gas law allows us to calculate the value of the fourth quantity (*P*, *V*, *T*, or *n*) needed to describe a gaseous sample when the others are known and also predict the value of these quantities following a change in conditions if the original conditions (values of *P*, *V*, *T*, and *n*) are known. The ideal gas law can also be used to calculate the density of a gas if its molar mass is known or, conversely, the molar mass of an unknown gas sample if its density is measured.

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9.3: Further Applications of the Ideal-Gas Equations

Learning Objectives

- To relate the amount of gas consumed or released in a chemical reaction to the stoichiometry of the reaction.
- To understand how the ideal gas equation and the stoichiometry of a reaction can be used to calculate the volume of gas produced or consumed in a reaction.

With the ideal gas law, we can use the relationship between the amounts of gases (in moles) and their volumes (in liters) to calculate the stoichiometry of reactions involving gases, if the pressure and temperature are known. This is important for several reasons. Many reactions that are carried out in the laboratory involve the formation or reaction of a gas, so chemists must be able to quantitatively treat gaseous products and reactants as readily as they quantitatively treat solids or solutions. Furthermore, many, if not most, industrially important reactions are carried out in the gas phase for practical reasons. Gases mix readily, are easily heated or cooled, and can be transferred from one place to another in a manufacturing facility via simple pumps and plumbing.

Gas Densities and Molar Mass

The ideal-gas equation can be manipulated to solve a variety of different types of problems. For example, the density, ρ, of a gas, depends on the number of gas molecules in a constant volume. To determine this value, we rearrange the ideal gas equation to

$$\frac{n}{V} = \frac{P}{RT} \tag{9.3.1}$$

Density of a gas is generally expressed in g/L (mass over volume). Multiplication of the left and right sides of Equation 9.3.1 by the molar mass in g/mol (M) of the gas gives

$$\rho = \frac{g}{L} = \frac{PM}{RT} \tag{9.3.2}$$

This allows us to determine the density of a gas when we know the molar mass, or vice versa.

> *The density of a gas INCREASES with increasing pressure and DECREASES with increasing temperature*



Example 9.3.1

What is the density of nitrogen gas (N_2) at 248.0 Torr and 18º C?

Solution

Step 1: Write down your given information

- P = 248.0 Torr
- V = ?

- n = ?
- R = 0.0820574 L•atm•mol^{-1} K^{-1}
- T = 18º C

Step 2: Convert as necessary.

$$(248\ \text{Torr}) \times \frac{1\ \text{atm}}{760\ \text{Torr}} = 0.3263\ \text{atm}$$

$$18\,^oC + 273 = 291K$$

Step 3: This one is tricky. We need to manipulate the Ideal Gas Equation to incorporate density into the equation.

Write down all known equations:

$$PV = nRT$$

$$\rho = \frac{m}{V}$$

where ρ is density, m is mass, and V is volume.

$$m = M \times n$$

where M is molar mass and n is the number of moles.

Now take the definition of density (Equation 9.3.1)

$$\rho = \frac{m}{V}$$

Keeping in mind $m = M \times n$ ...replace $(M \times n)$ for $mass$ within the density formula.

$$\rho = \frac{M \times n}{V}$$

$$\frac{\rho}{M} = \frac{n}{V}$$

Now manipulate the Ideal Gas Equation

\[\begin{align*} PV &= nRT \\

4pt] \dfrac{n}{V} &= \dfrac{P}{RT} \end{align*} \nonumber

(n/V) is in both equations.

$$\frac{n}{V} = \frac{\rho}{M}$$

$$= \frac{P}{RT}$$

Now combine them please.

$$\frac{\rho}{M} = \frac{P}{RT}$$

Isolate density.

$$\rho = \frac{PM}{RT}$$

Step 4: Now plug in the information you have.

$$\rho = \frac{PM}{RT}$$
$$= \frac{(0.3263 \text{ atm})(2 * 14.01 \text{ g/mol})}{(0.08206\, L\, atm/Kmol)(291 \text{ K})}$$
$$= 0.3828\ g/L$$

An example of varying density for a useful purpose is the hot air balloon, which consists of a bag (called the envelope) that is capable of containing heated air. As the air in the envelope is heated, it becomes less dense than the surrounding cooler air (Equation 9.3.2), which is has enough lifting power (due to buoyancy) to cause the balloon to float and rise into the air. Constant heating of the air is required to keep the balloon aloft. As the air in the balloon cools, it contracts, allowing outside cool air to enter, and the density increases. When this is carefully controlled by the pilot, the balloon can land as gently as it rose.



Figure 9.3.1: A hot air balloon is inflated partially with cold air from a gas-powered fan, before the propane burners are used for final inflation.

Determining Gas Volumes in Chemical Reactions

The ideal gas law can be used to calculate volume of gases consumed or produced. The ideal-gas equation frequently is used to interconvert between volumes and molar amounts in chemical equations.



Example 9.3.2A

What volume of carbon dioxide gas is produced at STP by the decomposition of 0.150 g $\mathrm{CaCO_3}$ via the equation:

$$\mathrm{CaCO_3(s) \rightarrow CaO(s) + CO_2(g)}$$

Solution

Begin by converting the mass of calcium carbonate to moles.

$$\frac{0.150\ g}{100.1\ g/mol} = 0.00150\ mol$$

The stoichiometry of the reaction dictates that the number of moles $CaCO_3$ decomposed equals the number of moles CO_2 produced. Use the ideal-gas equation to convert moles of CO_2 to a volume.

$$\begin{aligned} V &= \frac{nRT}{PR} \\ &= \frac{(0.00150\ mol)\left(0.08206\ \frac{L \cdot atm}{mol \cdot K}\right)(273.15\ K)}{1\ atm} \\ &= 0.0336\ L\ or\ 33.6\ mL \end{aligned}$$

Example $9.3.2B$

A 3.00 L container is filled with $Ne(g)$ at 770 mmHg at 27°C. A 0.633 gsample of CO_2 vapor is then added.

- What is the partial pressure of CO_2 and Ne in atm?
- What is the total pressure in the container in atm?

Solution

Step 1: Write down all given information, and convert as necessary.

Before:

- \(P = 770\,mmHg \rigtharrow 1.01 \,atm \nonumber \]
- $V = 3.00\ L$
- n_{Ne} =?
- $T = 27^oC \rightarrow 300\ K$

Other Unknowns: n_{CO_2} = ?

$$n_{CO_2} = 0.633\ \text{g CO}_2 \times \frac{1\ \text{mol}}{44\ \text{g}} = 0.0144\ \text{mol CO}_2$$

Step 2: After writing down all your given information, find the unknown moles of Ne***.***

$$\begin{aligned} n_{Ne} &= \frac{PV}{RT} \\ &= \frac{(1.01\ \text{atm})(3.00\ \text{L})}{(0.08206\ atm\ L/mol\ K)(300\ \text{K})} \\ &= 0.123\ \text{mol} \end{aligned}$$

Because the pressure of the container before the CO_2 was added contained only Ne, that is your partial pressure of Ne. After converting it to atm, you have already answered part of the question!

$$P_{Ne} = 1.01\ \text{atm}$$

Step 3: Now that have pressure for Ne, you must find the partial pressure for CO_2. Use the ideal gas equation.

$$\frac{P_{Ne}\ \cancel{V}}{n_{Ne}\ \cancel{RT}} = \frac{P_{CO_2}\ \cancel{V}}{n_{CO_2}\ \cancel{RT}}$$

but because both gases share the same Volume (V) and Temperature (T) and since the Gas Constant (R) is constants, all three terms cancel.

$$\begin{aligned} \frac{P}{n_{Ne}} &= \frac{P}{n_{CO_2}} \\ \frac{1.01\ \text{atm}}{0.123\ \text{mol Ne}} &= \frac{P_{CO_2}}{0.0144\ \text{mol CO}_2} \\ P_{CO_2} &= 0.118\ \text{atm} \end{aligned}$$

This is the partial pressure CO_2.

Step 4: Now find total pressure.

$$\begin{aligned} P_{total} &= P_{Ne} + P_{CO_2} \\ &= 1.01 \text{ atm} + 0.118 \text{ atm} \\ &= 1.128 \text{ atm} \\ &\approx 1.13 \text{ atm (with appropriate significant figures)} \end{aligned}$$

Example 9.3.2C: Sulfuric Acid

Sulfuric acid, the industrial chemical produced in greatest quantity (almost 45 million tons per year in the United States alone), is prepared by the combustion of sulfur in air to give SO_2, followed by the reaction of SO_2 with O_2 in the presence of a catalyst to give SO_3, which reacts with water to give H_2SO_4. The overall chemical equation is as follows:

$$2\,S(s) + 3\,O_2(g) + 2\,H_2O(l) \rightarrow 2\,H_2SO_4(aq)$$

What volume of O_2 (in liters) at 22°C and 745 mmHg pressure is required to produce 1.00 ton (907.18 kg) of H_2SO_4?

Given: reaction, temperature, pressure, and mass of one product

Asked for: volume of gaseous reactant

Strategy:

A Calculate the number of moles of H_2SO_4 in 1.00 ton. From the stoichiometric coefficients in the balanced chemical equation, calculate the number of moles of O_2 required.

B Use the ideal gas law to determine the volume of O_2 required under the given conditions. Be sure that all quantities are expressed in the appropriate units.

Solution:

$$\text{mass of } H_2SO_4 \rightarrow \text{moles } H_2SO_4 \rightarrow \text{moles } O_2 \rightarrow \text{liters } O_2$$

A We begin by calculating the number of moles of H_2SO_4 in 1.00 ton:

$$\frac{907.18 \times 10^3 \text{ g } H_2SO_4}{(2 \times 1.008 + 32.06 + 4 \times 16.00) \text{ g/mol}} = 9250 \text{ mol } H_2SO_4$$

We next calculate the number of moles of O_2 required:

$$9250 \text{ mol } H_2SO_4 \times \frac{3 \text{mol } O_2}{2 \text{mol } H_2SO_4} = 1.389 \times 10^4 \text{ mol } O_2$$

B After converting all quantities to the appropriate units, we can use the ideal gas law to calculate the volume of O_2:

$$\begin{aligned} V &= \frac{nRT}{P} \\ &= \frac{1.389 \times 10^4 \text{ mol} \times 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times (273 + 22) \text{ K}}{745 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}} \\ &= 3.43 \times 10^5 \text{ L} \end{aligned}$$

The answer means that more than 300,000 L of oxygen gas are needed to produce 1 ton of sulfuric acid. These numbers may give you some appreciation for the magnitude of the engineering and plumbing problems faced in industrial chemistry.

Exercise 9.3.2

Charles used a balloon containing approximately 31,150 L of H_2 for his initial flight in 1783. The hydrogen gas was produced by the reaction of metallic iron with dilute hydrochloric acid according to the following balanced chemical equation:

$$Fe(s) + 2\,HCl(aq) \rightarrow H_2(g) + FeCl_2(aq)$$

How much iron (in kilograms) was needed to produce this volume of H_2 if the temperature were 30°C and the atmospheric pressure was 745 mmHg?

Answer

68.6 kg of Fe (approximately 150 lb)

Example 9.3.3: Emergency Air bags

Sodium azide (NaN_3) decomposes to form sodium metal and nitrogen gas according to the following balanced chemical equation:

$$2\,NaN_3 \rightarrow 2\,Na(s) + 3\,N_2(g)$$

This reaction is used to inflate the air bags that cushion passengers during automobile collisions. The reaction is initiated in air bags by an electrical impulse and results in the rapid evolution of gas. If the N_2 gas that results from the decomposition of a 5.00 g sample of NaN_3 could be collected by displacing water from an inverted flask, what volume of gas would be produced at 21°C and 762 mmHg?

Given: reaction, mass of compound, temperature, and pressure

Asked for: volume of nitrogen gas produced

Strategy:

A Calculate the number of moles of N_2 gas produced. From the data in Table S3, determine the partial pressure of N_2 gas in the flask.

B Use the ideal gas law to find the volume of N_2 gas produced.

Solution:

A Because we know the mass of the reactant and the stoichiometry of the reaction, our first step is to calculate the number of moles of N_2 gas produced:

$$\frac{5.00\text{ g } NaN_3}{(22.99 + 3 \times 14.01)\text{ g/mol}} \times \frac{3\text{mol } N_2}{2\text{mol } NaN_3} = 0.115\text{ mol } N_2$$

The pressure given (762 mmHg) is the *total* pressure in the flask, which is the sum of the pressures due to the N_2 gas and the water vapor present. Table S3 tells us that the vapor pressure of water is 18.65 mmHg at 21°C (294 K), so the partial pressure of the N_2 gas in the flask is only

$$(762 - 18.65)\text{ mmHg} \times \frac{1\text{ atm}}{760\text{ mmHg}} = 743.4\ \cancel{mmHg} \times \frac{1\ atm}{760\ \cancel{mmHg}}$$

$$= 0.978\ atm.$$

B Solving the ideal gas law for *V* and substituting the other quantities (in the appropriate units), we get

$$V = \frac{nRT}{P} = \frac{0.115\text{ mol} \times 0.08206\frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 294\text{ K}}{0.978\text{ atm}} = 2.84\text{ L}$$

Exercise 9.3.3

A 1.00 g sample of zinc metal is added to a solution of dilute hydrochloric acid. It dissolves to produce H_2 gas according to the equation

$$Zn(s) + 2\,HCl(aq) \rightarrow H_2(g) + ZnCl_2(aq).$$

The resulting H_2 gas is collected in a water-filled bottle at 30°C and an atmospheric pressure of 760 mmHg. What volume does it occupy?

Answer

0.397 L

Summary

The relationship between the amounts of products and reactants in a chemical reaction can be expressed in units of moles or masses of pure substances, of volumes of solutions, or of volumes of gaseous substances. The ideal gas law can be used to calculate the volume of gaseous products or reactants as needed. In the laboratory, gases produced in a reaction are often collected by the displacement of water from filled vessels; the amount of gas can then be calculated from the volume of water displaced and the atmospheric pressure. A gas collected in such a way is not pure, however, but contains a significant amount of water vapor. The measured pressure must therefore be corrected for the vapor pressure of water, which depends strongly on the temperature.

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9.4: Gas Mixtures and Partial Pressures

Learning Objectives

- To determine the contribution of each component gas to the total pressure of a mixture of gases

In our use of the ideal gas law thus far, we have focused entirely on the properties of pure gases with only a single chemical species. But what happens when two or more gases are mixed? In this section, we describe how to determine the contribution of each gas present to the total pressure of the mixture.

Partial Pressures

The ideal gas law *assumes* that all gases behave identically and that their behavior is independent of attractive and repulsive forces. If volume and temperature are held constant, the ideal gas equation can be rearranged to show that the pressure of a sample of gas is directly proportional to the number of moles of gas present:

$$P = n\left(\frac{RT}{V}\right) = n \times \text{const.} \tag{9.4.1}$$

Nothing in the equation depends on the *nature* of the gas—only the amount.

With this assumption, let's suppose we have a mixture of two ideal gases that are present in equal amounts. What is the total pressure of the mixture? Because the pressure depends on only the total number of particles of gas present, the total pressure of the mixture will simply be twice the pressure of either component. More generally, the total pressure exerted by a mixture of gases at a given temperature and volume is the sum of the pressures exerted by each gas alone. Furthermore, if we know the volume, the temperature, and the number of moles of each gas in a mixture, then we can calculate the pressure exerted by each gas individually, which is its partial pressure, the pressure the gas would exert if it were the only one present (at the same temperature and volume).

To summarize, ***the total pressure exerted by a mixture of gases is the sum of the partial pressures of component gases***. This law was first discovered by John Dalton, the father of the atomic theory of matter. It is now known as *Dalton's law of partial pressures*. We can write it mathematically as

$$P_{tot} = P_1 + P_2 + P_3 + P_4 \ldots \tag{9.4.2}$$

$$= \sum_{i=1}^{n} P_i \tag{9.4.3}$$

where P_{tot} is the total pressure and the other terms are the partial pressures of the individual gases (up to n component gases).

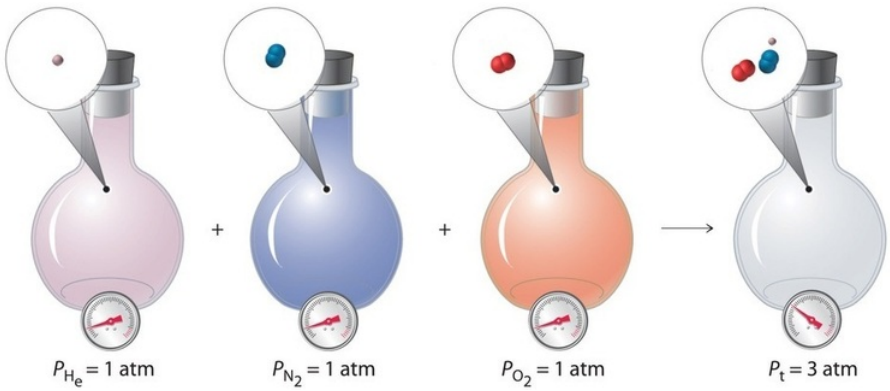


Figure 9.4.1: Dalton's Law. The total pressure of a mixture of gases is the sum of the partial pressures of the individual gases.

For a mixture of two ideal gases, A and B, we can write an expression for the total pressure:

$$P_{tot} = P_A + P_B \tag{9.4.4}$$

$$= n_A \left(\frac{RT}{V}\right) + n_B \left(\frac{RT}{V}\right) \tag{9.4.5}$$

$$= (n_A + n_B) \left(\frac{RT}{V}\right) \tag{9.4.6}$$

More generally, for a mixture of n component gases, the total pressure is given by

$$P_{tot} = (n_1 + n_2 + n_3 + \cdots + n_n) \left(\frac{RT}{V}\right) \tag{9.4.7}$$

$$= \sum_{i=1}^{n} n_i \left(\frac{RT}{V}\right) \tag{9.4.8}$$

Equation 9.4.8 restates Equation 9.4.6 in a more general form and makes it explicitly clear that, at constant temperature and volume, the pressure exerted by a gas depends on only the total number of moles of gas present, whether the gas is a single chemical species or a mixture of dozens or even hundreds of gaseous species. For Equation 9.4.8 to be valid, the identity of the particles present cannot have an effect. Thus an ideal gas must be one whose properties are not affected by either the size of the particles or their intermolecular interactions because both will vary from one gas to another. The calculation of total and partial pressures for mixtures of gases is illustrated in Example 9.4.1.

Example 9.4.1: The Bends

Deep-sea divers must use special gas mixtures in their tanks, rather than compressed air, to avoid serious problems, most notably a condition called "the bends." At depths of about 350 ft, divers are subject to a pressure of approximately 10 atm. A typical gas cylinder used for such depths contains 51.2 g of O_2 and 326.4 g of He and has a volume of 10.0 L. What is the partial pressure of each gas at 20.00°C, and what is the total pressure in the cylinder at this temperature?

Given: masses of components, total volume, and temperature

Asked for: partial pressures and total pressure

Strategy:

A. Calculate the number of moles of He and O_2 present.

B. Use the ideal gas law to calculate the partial pressure of each gas. Then add together the partial pressures to obtain the total pressure of the gaseous mixture.

Solution:

A The number of moles of He is

$$n_{\text{He}} = \frac{326.4\ \text{g}}{4.003\ \text{g/mol}} = 81.54\ \text{mol}$$

The number of moles of O_2 is

$$n_{\text{O}_2} = \frac{51.2\ \text{g}}{32.00\ \text{g/mol}} = 1.60\ \text{mol}$$

B We can now use the ideal gas law to calculate the partial pressure of each:

$$P_{\text{He}} = \frac{n_{\text{He}}\,RT}{V} = \frac{81.54\ \text{mol} \times 0.08206\ \frac{\text{atm}\cdot\text{L}}{\text{mol}\cdot\text{K}} \times 293.15\ \text{K}}{10.0\ \text{L}} = 196.2\ \text{atm}$$

$$P_{\text{O}_2} = \frac{n_{\text{O}_2}\,RT}{V} = \frac{1.60\ \text{mol} \times 0.08206\ \frac{\text{atm}\cdot\text{L}}{\text{mol}\cdot\text{K}} \times 293.15\ \text{K}}{10.0\ \text{L}} = 3.85\ \text{atm}$$

The total pressure is the sum of the two partial pressures:

$$P_{\text{tot}} = P_{\text{He}} + P_{\text{O}_2} = (196.2 + 3.85)\ \text{atm} = 200.1\ \text{atm}$$

? Exercise 9.4.1

A cylinder of compressed natural gas has a volume of 20.0 L and contains 1813 g of methane and 336 g of ethane. Calculate the partial pressure of each gas at 22.0°C and the total pressure in the cylinder.

Answer

$P_{CH_4} = 137\ atm$; $P_{C_2H_6} = 13.4\ atm$; $P_{tot} = 151\ atm$

Mole Fractions of Gas Mixtures

The composition of a gas mixture can be described by the mole fractions of the gases present. The mole fraction (χ) of any component of a mixture is the ratio of the number of moles of that component to the total number of moles of all the species present in the mixture (n_{tot}):

$$\chi_A = \frac{\text{moles of A}}{\text{total moles}} = \frac{n_A}{n_{tot}} = \frac{n_A}{n_A + n_B + \cdots} \tag{9.4.9}$$

The mole fraction is a dimensionless quantity between 0 and 1. If $\chi_A = 1.0$, then the sample is pure A, not a mixture. If $\chi_A = 0$, then no A is present in the mixture. The sum of the mole fractions of all the components present must equal 1.

To see how mole fractions can help us understand the properties of gas mixtures, let's evaluate the ratio of the pressure of a gas A to the total pressure of a gas mixture that contains A. We can use the ideal gas law to describe the pressures of both gas A and the mixture: $P_A = n_A RT/V$ and $P_{tot} = n_t RT/V$. The ratio of the two is thus

$$\frac{P_A}{P_{tot}} = \frac{n_A RT/V}{n_{tot} RT/V} = \frac{n_A}{n_{tot}} = \chi_A \tag{9.4.10}$$

Rearranging this equation gives

$$P_A = \chi_A P_{tot} \tag{9.4.11}$$

That is, the partial pressure of any gas in a mixture is the total pressure multiplied by the mole fraction of that gas. This conclusion is a direct result of the ideal gas law, which assumes that all gas particles behave ideally. Consequently, the pressure of a gas in a mixture depends on only the percentage of particles in the mixture that are of that type, not their specific physical or chemical properties. By volume, Earth's atmosphere is about 78% N_2, 21% O_2, and 0.9% Ar, with trace amounts of gases such as CO_2, H_2O, and others. This means that 78% of the particles present in the atmosphere are N_2; hence the mole fraction of N_2 is 78%/100% = 0.78. Similarly, the mole fractions of O_2 and Ar are 0.21 and 0.009, respectively. Using Equation 9.4.11, we therefore know that the partial pressure of N_2 is 0.78 atm (assuming an atmospheric pressure of exactly 760 mmHg) and, similarly, the partial pressures of O_2 and Ar are 0.21 and 0.009 atm, respectively.



Example 9.4.2: Exhaling Composition

We have just calculated the partial pressures of the major gases in the air we inhale. Experiments that measure the composition of the air we *exhale* yield different results, however. The following table gives the measured pressures of the major gases in both inhaled and exhaled air. Calculate the mole fractions of the gases in exhaled air.

the mole fractions of the gases

	Inhaled Air / mmHg	Exhaled Air / mmHg
P_{N_2}	597	568
P_{O_2}	158	116
P_{H_2O}	0.3	28
P_{CO_2}	5	48
P_{Ar}	8	8
P_{tot}	767	767

Given: pressures of gases in inhaled and exhaled air

Asked for: mole fractions of gases in exhaled air

Strategy:

Calculate the mole fraction of each gas using Equation 9.4.11.

Solution:

The mole fraction of any gas A is given by

$$\chi_A = \frac{P_A}{P_{tot}}$$

where P_A is the partial pressure of A and P_{tot} is the total pressure. For example, the mole fraction of CO_2 is given as:

$$\chi_{CO_2} = \frac{48 \text{ mmHg}}{767 \text{ mmHg}} = 0.063$$

The following table gives the values of χ_A for the gases in the exhaled air.

Solutions to Example 10.6.2

Gas	Mole Fraction
N_2	0.741
O_2	0.151
H_2O	0.037
CO_2	0.063
Ar	0.010

Exercise 9.4.2

Venus is an inhospitable place, with a surface temperature of 560°C and a surface pressure of 90 atm. The atmosphere consists of about 96% CO_2 and 3% N_2, with trace amounts of other gases, including water, sulfur dioxide, and sulfuric acid. Calculate the partial pressures of CO_2 and N_2.

Answer

$$P_{CO_2} = 86 \text{ atm}$$

$$P_{N_2} = 2.7 \text{ atm}$$

Summary

The partial pressure of each gas in a mixture is proportional to its mole fraction. The pressure exerted by each gas in a gas mixture (its **partial pressure**) is independent of the pressure exerted by all other gases present. Consequently, the total pressure exerted by a mixture of gases is the sum of the partial pressures of the components (**Dalton's law of partial pressures**). The amount of gas present in a mixture may be described by its partial pressure or its mole fraction. The **mole fraction** of any component of a mixture is the ratio of the number of moles of that substance to the total number of moles of all substances present. In a mixture of gases, the partial pressure of each gas is the product of the total pressure and the mole fraction of that gas.

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9.5: Kinetic-Molecular Theory

Learning Objectives

- To understand the significance of the kinetic molecular theory of gases.

The laws that describe the behavior of gases were well established long before anyone had developed a coherent model of the properties of gases. In this section, we introduce a theory that describes why gases behave the way they do. The theory we introduce can also be used to derive laws such as the ideal gas law from fundamental principles and the properties of individual particles.

A Molecular Description

The kinetic molecular theory of gases explains the laws that describe the behavior of gases. Developed during the mid-19th century by several physicists, including the Austrian Ludwig Boltzmann (1844–1906), the German Rudolf Clausius (1822–1888), and the Englishman James Clerk Maxwell (1831–1879), who is also known for his contributions to electricity and magnetism, this theory is based on the properties of individual particles as defined for an ideal gas and the fundamental concepts of physics. Thus the kinetic molecular theory of gases provides a molecular explanation for observations that led to the development of the ideal gas law. The kinetic molecular theory of gases is based on the following five postulates:

five postulates of Kinetic Molecular Theory

1. A gas is composed of a large number of particles called molecules (whether monatomic or polyatomic) that are in constant random motion.
2. Because the distance between gas molecules is much greater than the size of the molecules, the volume of the molecules is negligible.
3. Intermolecular interactions, whether repulsive or attractive, are so weak that they are also negligible.
4. Gas molecules collide with one another and with the walls of the container, but these collisions are perfectly elastic; that is, they do not change the average kinetic energy of the molecules.
5. The average kinetic energy of the molecules of any gas depends on only the temperature, and at a given temperature, all gaseous molecules have exactly the same average kinetic energy.

Although the molecules of real gases have nonzero volumes and exert both attractive and repulsive forces on one another, for the moment we will focus on how the kinetic molecular theory of gases relates to the properties of gases we have been discussing. In the following sections, we explain how this theory must be modified to account for the behavior of real gases.

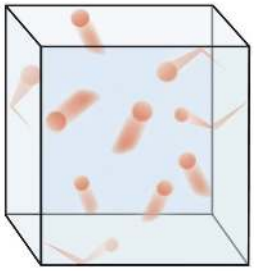


Figure 9.5.1: Visualizing molecular motion. Molecules of a gas are in constant motion and collide with one another and with the container wall.

Postulates 1 and 4 state that gas molecules are in constant motion and collide frequently with the walls of their containers. The collision of molecules with their container walls results in a **momentum transfer** (impulse) from molecules to the walls (Figure 9.5.2).

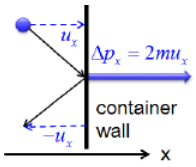


Figure 9.5.2: Momentum transfer (impulse) from a molecule to the container wall as it bounces off the wall. u_x and Δp_x are the x component of the molecular velocity and the momentum transferred to the wall, respectively. The wall is perpendicular to x axis. Since the collisions are elastic, the molecule bounces back with the same velocity in the opposite direction.

The **momentum transfer** to the wall perpendicular to x axis as a molecule with an initial velocity u_x in x direction hits is expressed as:

$$\Delta p_x = 2mu_x \tag{9.5.1}$$

The **collision frequency**, a number of collisions of the molecules to the wall per unit area and per second, increases with the molecular speed and the number of molecules per unit volume.

$$f \propto (u_x) \times \left(\frac{N}{V}\right) \tag{9.5.2}$$

The pressure the gas exerts on the wall is expressed as the product of impulse and the collision frequency.

$$P \propto (2mu_x) \times (u_x) \times \left(\frac{N}{V}\right) \propto \left(\frac{N}{V}\right) mu_x^2 \tag{9.5.3}$$

At any instant, however, the molecules in a gas sample are traveling at different speed. Therefore, we must replace u_x^2 in the expression above with the average value of u_x^2, which is denoted by $\overline{u_x^2}$. The overbar designates the average value over all molecules.

The exact expression for pressure is given as :

$$P = \frac{N}{V} m\overline{u_x^2} \tag{9.5.4}$$

Finally, we must consider that there is nothing special about x direction. We should expect that

$$\overline{u_x^2} = \overline{u_y^2} = \overline{u_z^2} = \frac{1}{3}\overline{u^2}.$$

Here the quantity $\overline{u^2}$ is called the **mean-square speed** defined as the average value of square-speed (u^2) over all molecules. Since

$$u^2 = u_x^2 + u_y^2 + u_z^2$$

for each molecule, then

$$\overline{u^2} = \overline{u_x^2} + \overline{u_y^2} + \overline{u_z^2}.$$

By substituting $\frac{1}{3}\overline{u^2}$ for $\overline{u_x^2}$ in the expression above, we can get the final expression for the pressure:

$$P = \frac{1}{3}\frac{N}{V} m\overline{u^2} \tag{9.5.5}$$

Because volumes and intermolecular interactions are negligible, postulates 2 and 3 state that all gaseous particles behave identically, regardless of the chemical nature of their component molecules. This is the essence of the ideal gas law, which treats all gases as collections of particles that are identical in all respects except mass. Postulate 2 also explains why it is relatively easy to compress a gas; you simply decrease the distance between the gas molecules.

Postulate 5 provides a molecular explanation for the temperature of a gas. Postulate 5 refers to the *average translational* kinetic energy of the molecules of a gas ($\overline{e_K}$), which can be represented as *and states that at a given Kelvin temperature* (T), *all gases have the same value of*

$$\overline{e_K} = \frac{1}{2} m\overline{u^2} = \frac{3}{2}\frac{R}{N_A} T \tag{9.5.6}$$

where N_A is the Avogadro's constant. The total translational kinetic energy of 1 mole of molecules can be obtained by multiplying the equation by N_A:

$$N_A\overline{e_K} = \frac{1}{2}M\overline{u^2} = \frac{3}{2}RT \tag{9.5.7}$$

where M is the molar mass of the gas molecules and is related to the molecular mass by $M = N_A m$. By rearranging the equation, we can get the relationship between the root-mean square speed (u_{rms}) and the temperature. The rms speed (u_{rms}) is the square root of the sum of the squared speeds divided by the number of particles:

$$u_{\text{rms}} = \sqrt{\overline{u^2}} = \sqrt{\frac{u_1^2 + u_2^2 + \cdots u_N^2}{N}} \tag{9.5.8}$$

where N is the number of particles and u_i is the speed of particle i.

The relationship between u_{rms} and the temperature is given by:

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}} \tag{9.5.9}$$

In Equation 9.5.9, u_{rms} has units of meters per second; consequently, the units of molar mass M are kilograms per mole, temperature T is expressed in kelvins, and the ideal gas constant R has the value 8.3145 J/(K•mol). Equation 9.5.9 shows that u_{rms} of a gas is proportional to the square root of its Kelvin temperature and inversely proportional to the square root of its molar mass. The root mean-square speed of a gas increase with increasing temperature. At a given temperature, heavier gas molecules have slower speeds than do lighter ones.

The rms speed and the average speed do not differ greatly (typically by less than 10%). The distinction is important, however, because the rms speed is the speed of a gas particle that has average kinetic energy. Particles of different gases at the same temperature have the same average kinetic energy, not the same average speed. In contrast, the most probable speed (vp) is the speed at which the greatest number of particles is moving. If the average kinetic energy of the particles of a gas increases linearly with increasing temperature, then Equation 9.5.8 tells us that the rms speed must also increase with temperature because the mass of the particles is constant. At higher temperatures, therefore, the molecules of a gas move more rapidly than at lower temperatures, and vp increases.

> *At a given temperature, all gaseous particles have the same average kinetic energy but not the same average speed.*

Example 9.5.1

The speeds of eight particles were found to be 1.0, 4.0, 4.0, 6.0, 6.0, 6.0, 8.0, and 10.0 m/s. Calculate their average speed (v_{av}) root mean square speed (v_{rms}), and most probable speed (v_{m}).

Given: particle speeds

Asked for: average speed (v_{av}), root mean square speed (v_{rms}), and most probable speed (v_{m})

Strategy:

Use Equation 9.5.6 to calculate the average speed and Equation 9.5.8 to calculate the rms speed. Find the most probable speed by determining the speed at which the greatest number of particles is moving.

Solution:

The average speed is the sum of the speeds divided by the number of particles:

$$v_{\text{av}} = \frac{(1.0 + 4.0 + 4.0 + 6.0 + 6.0 + 6.0 + 8.0 + 10.0)\ \text{m/s}}{8} = 5.6\ \text{m/s}$$

The rms speed is the square root of the sum of the squared speeds divided by the number of particles:

$$v_{\text{rms}} = \sqrt{\frac{(1.0^2 + 4.0^2 + 4.0^2 + 6.0^2 + 6.0^2 + 6.0^2 + 8.0^2 + 10.0^2)\ \text{m}^2/\text{s}^2}{8}} = 6.2\ \text{m/s}$$

The most probable speed is the speed at which the greatest number of particles is moving. Of the eight particles, three have speeds of 6.0 m/s, two have speeds of 4.0 m/s, and the other three particles have different speeds. Hence $v_{\mathrm{m}} = 6.0$ m/s. The v_{rms} of the particles, which is related to the average kinetic energy, is greater than their average speed.

Boltzmann Distributions

At any given time, what fraction of the molecules in a particular sample has a given speed? Some of the molecules will be moving more slowly than average, and some will be moving faster than average, but how many in each situation? Answers to questions such as these can have a substantial effect on the amount of product formed during a chemical reaction. This problem was solved mathematically by Maxwell in 1866; he used statistical analysis to obtain an equation that describes the distribution of molecular speeds at a given temperature. Typical curves showing the distributions of speeds of molecules at several temperatures are displayed in Figure 9.5.3. Increasing the temperature has two effects. First, the peak of the curve moves to the right because the most probable speed increases. Second, the curve becomes broader because of the increased spread of the speeds. Thus increased temperature increases the *value* of the most probable speed but decreases the relative number of molecules that have that speed. Although the mathematics behind curves such as those in Figure 9.5.3 were first worked out by Maxwell, the curves are almost universally referred to as Boltzmann distributions, after one of the other major figures responsible for the kinetic molecular theory of gases.

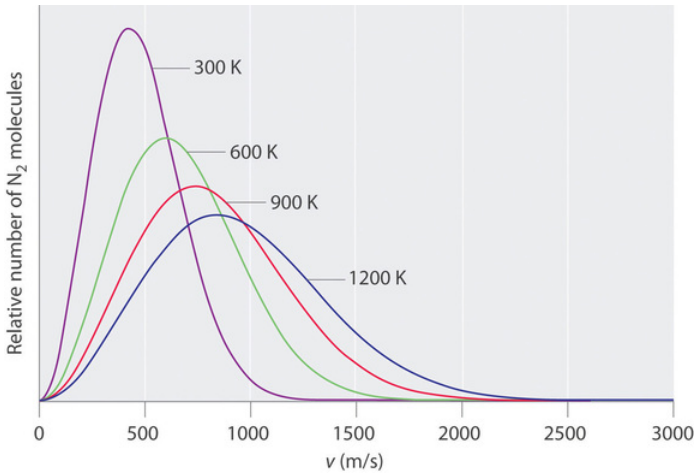


Figure 9.5.3: The Distributions of Molecular Speeds for a Sample of Nitrogen Gas at Various Temperatures. Increasing the temperature increases both the most probable speed (given at the peak of the curve) and the width of the curve.

The Relationships among Pressure, Volume, and Temperature

We now describe how the kinetic molecular theory of gases explains some of the important relationships we have discussed previously.

- **Pressure versus Volume**: At constant temperature, the kinetic energy of the molecules of a gas and hence the rms speed remain unchanged. If a given gas sample is allowed to occupy a larger volume, then the speed of the molecules does not change, but the density of the gas (number of particles per unit volume) decreases, and the average distance between the molecules increases. Hence the molecules must, on average, travel farther between collisions. They therefore collide with one another and with the walls of their containers less often, leading to a decrease in pressure. Conversely, increasing the pressure forces the molecules closer together and increases the density, until the collective impact of the collisions of the molecules with the container walls just balances the applied pressure.
- **Volume versus Temperature**: Raising the temperature of a gas increases the average kinetic energy and therefore the rms speed (and the average speed) of the gas molecules. Hence as the temperature increases, the molecules collide with the walls of their containers more frequently and with greater force. This increases the pressure, *unless* the volume increases to reduce the pressure, as we have just seen. Thus an increase in temperature must be offset by an increase in volume for the net impact (pressure) of the gas molecules on the container walls to remain unchanged.
- **Pressure of Gas Mixtures**: Postulate 3 of the kinetic molecular theory of gases states that gas molecules exert no attractive or repulsive forces on one another. If the gaseous molecules do not interact, then the presence of one gas in a gas mixture will have no effect on the pressure exerted by another, and Dalton's law of partial pressures holds.

Example 9.5.2

The temperature of a 4.75 L container of N_2 gas is increased from 0°C to 117°C. What is the qualitative effect of this change on the

a. average kinetic energy of the N_2 molecules?
b. rms speed of the N_2 molecules?
c. average speed of the N_2 molecules?
d. impact of each N_2 molecule on the wall of the container during a collision with the wall?
e. total number of collisions per second of N_2 molecules with the walls of the entire container?
f. number of collisions per second of N_2 molecules with each square centimeter of the container wall?
g. pressure of the N_2 gas?

Given: temperatures and volume

Asked for: effect of increase in temperature

Strategy:

Use the relationships among pressure, volume, and temperature to predict the qualitative effect of an increase in the temperature of the gas.

Solution:

a. Increasing the temperature increases the average kinetic energy of the N_2 molecules.
b. An increase in average kinetic energy can be due only to an increase in the rms speed of the gas particles.
c. If the rms speed of the N_2 molecules increases, the average speed also increases.
d. If, on average, the particles are moving faster, then they strike the container walls with more energy.
e. Because the particles are moving faster, they collide with the walls of the container more often per unit time.
f. The number of collisions per second of N_2 molecules with each square centimeter of container wall increases because the total number of collisions has increased, but the volume occupied by the gas and hence the total area of the walls are unchanged.
g. The pressure exerted by the N_2 gas increases when the temperature is increased at constant volume, as predicted by the ideal gas law.

Exercise 9.5.2

A sample of helium gas is confined in a cylinder with a gas-tight sliding piston. The initial volume is 1.34 L, and the temperature is 22°C. The piston is moved to allow the gas to expand to 2.12 L at constant temperature. What is the qualitative effect of this change on the

a. average kinetic energy of the He atoms?
b. rms speed of the He atoms?
c. average speed of the He atoms?
d. impact of each He atom on the wall of the container during a collision with the wall?
e. total number of collisions per second of He atoms with the walls of the entire container?
f. number of collisions per second of He atoms with each square centimeter of the container wall?
g. pressure of the He gas?

Answer a

no change

Answer b

no change

Answer c

no change

Answer d

no change

Answer e

decreases

Answer f

decreases

Answer g

decreases



Summary

- The kinetic molecular theory of gases provides a molecular explanation for the observations that led to the development of the ideal gas law.
- **Average kinetic energy:**

$$\overline{e_K} = \frac{1}{2} m {u_{\text{rms}}}^2 = \frac{3}{2} \frac{R}{N_A} T n$$

- **Root mean square speed:**

$$u_{\text{rms}} = \sqrt{\frac{u_1^2 + u_2^2 + \cdots u_N^2}{N}}$$

- **Kinetic molecular theory of gases:**

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

The behavior of ideal gases is explained by the **kinetic molecular theory of gases**. Molecular motion, which leads to collisions between molecules and the container walls, explains pressure, and the large intermolecular distances in gases explain their high compressibility. Although all gases have the same average kinetic energy at a given temperature, they do not all possess the same **root mean square (rms) speed (v_{rms})**. The actual values of speed and kinetic energy are not the same for all particles of a gas but are given by a **Boltzmann distribution**, in which some molecules have higher or lower speeds (and kinetic energies) than average.

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9.6: Equipartition of Energy (Needs addition)

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9.7: Molecular Effusion and Diffusion

Learning Objectives

- To understand the significance of the kinetic molecular theory of gases

We now describe how the kinetic molecular theory of gases explains some of the important relationships we have discussed previously.

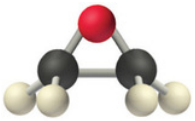
Diffusion and Effusion

As you have learned, the molecules of a gas are *not* stationary but in constant and random motion. If someone opens a bottle of perfume in the next room, for example, you are likely to be aware of it soon. Your sense of smell relies on molecules of the aromatic substance coming into contact with specialized olfactory cells in your nasal passages, which contain specific receptors (protein molecules) that recognize the substance. How do the molecules responsible for the aroma get from the perfume bottle to your nose? You might think that they are blown by drafts, but, in fact, molecules can move from one place to another even in a draft-free environment.

Diffusion is the gradual mixing of gases due to the motion of their component particles even in the absence of mechanical agitation such as stirring. The result is a gas mixture with uniform composition. Diffusion is also a property of the particles in liquids and liquid solutions and, to a lesser extent, of solids and solid solutions. The related process, **effusion**, is the escape of gaseous molecules through a small (usually microscopic) hole, such as a hole in a balloon, into an evacuated space.

The phenomenon of effusion had been known for thousands of years, but it was not until the early 19th century that quantitative experiments related the rate of effusion to molecular properties. The rate of effusion of a gaseous substance is inversely proportional to the square root of its molar mass. This relationship *is referred to as Graham's law*, after the Scottish chemist Thomas Graham (1805–1869). The ratio of the effusion rates of two gases is the square root of the inverse ratio of their molar masses*:*

$$\frac{\text{rate of effusion A}}{\text{rate of effusion B}} = \sqrt{\frac{M_B}{M_A}} \tag{9.7.1}$$



Ethylene oxide

Helium (M = 4.00 g/mol) effuses much more rapidly than ethylene oxide (M = 44.0 g/mol). Because helium is less dense than air, helium-filled balloons "float" at the end of a tethering string. Unfortunately, rubber balloons filled with helium soon lose their buoyancy along with much of their volume. In contrast, rubber balloons filled with air tend to retain their shape and volume for a much longer time. Because helium has a molar mass of 4.00 g/mol, whereas air has an average molar mass of about 29 g/mol, pure helium effuses through the microscopic pores in the rubber balloon $\sqrt{\frac{29}{4.00}} = 2.7$ times faster than air. For this reason, high-quality helium-filled balloons are usually made of Mylar, a dense, strong, opaque material with a high molecular mass that forms films that have many fewer pores than rubber. Hence, mylar balloons can retain their helium for days.

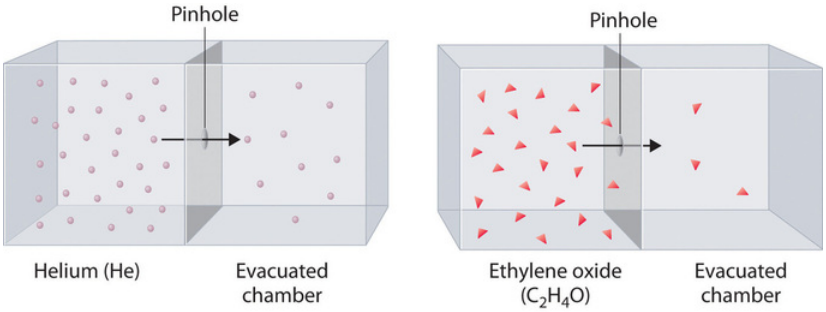


Figure 9.7.1: The Relative Rates of Effusion of Two Gases with Different Masses. The lighter He atoms (M = 4.00 g/mol) effuse through the small hole more rapidly than the heavier ethylene oxide (C_2H_4O) molecules (M = 44.0 g/mol), as predicted by Graham's law (Equation 9.7.1).

> *At a given temperature, heavier molecules move more slowly than lighter molecules.*



Example 9.7.1

During World War II, scientists working on the first atomic bomb were faced with the challenge of finding a way to obtain large amounts of ^{235}U. Naturally occurring uranium is only 0.720% ^{235}U, whereas most of the rest (99.275%) is ^{238}U, which is not fissionable (i.e., it will not break apart to release nuclear energy) and also actually poisons the fission process. Because both isotopes of uranium have the same reactivity, they cannot be separated chemically. Instead, a process of gaseous effusion was developed using the volatile compound UF_6 (boiling point = 56°C).

1. Calculate the ratio of the rates of effusion of $^{235}UF_6$ and $^{238}UF_6$ for a single step in which UF_6 is allowed to pass through a porous barrier. (The atomic mass of ^{235}U is 235.04, and the atomic mass of ^{238}U is 238.05.)
2. If n identical successive separation steps are used, the overall separation is given by the separation in a single step (in this case, the ratio of effusion rates) raised to the nth power. How many effusion steps are needed to obtain 99.0% pure $^{235}UF_6$?

Given: isotopic content of naturally occurring uranium and atomic masses of ^{235}U and ^{238}U

Asked for: ratio of rates of effusion and number of effusion steps needed to obtain 99.0% pure $^{235}UF_6$

Strategy:

A. Calculate the molar masses of $^{235}UF_6$ and $^{238}UF_6$, and then use Graham's law to determine the ratio of the effusion rates. Use this value to determine the isotopic content of $^{235}UF_6$ after a single effusion step.
B. Divide the final purity by the initial purity to obtain a value for the number of separation steps needed to achieve the desired purity. Use a logarithmic expression to compute the number of separation steps required.

Solution:

A The first step is to calculate the molar mass of UF_6 containing ^{235}U and ^{238}U. Luckily for the success of the separation method, fluorine consists of a single isotope of atomic mass 18.998. The molar mass of $^{235}UF_6$ is

$$234.04 + (6)(18.998) = 349.03 \text{ g/mol}$$

The molar mass of $^{238}UF_6$ is

$$238.05 + (6)(18.998) = 352.04 \text{ g/mol}$$

The difference is only 3.01 g/mol (less than 1%). The ratio of the effusion rates can be calculated from Graham's law using Equation 9.7.1:

$$\frac{\text{rate } ^{235}UF_6}{\text{rate } ^{238}UF_6} = \sqrt{\frac{352.04 \text{ g/mol}}{349.03 \text{ g/mol}}} = 1.0043$$

B To obtain 99.0% pure $^{235}UF_6$ requires many steps. We can set up an equation that relates the initial and final purity to the number of times the separation process is repeated:

final purity = (initial purity)(separation)^n

In this case, 0.990 = (0.00720)(1.0043)^n, which can be rearranged to give

$$1.0043^n = \frac{0.990}{0.00720} = 137.50$$

Taking the logarithm of both sides gives

$$n \ln(1.0043) = \ln(137.50) \tag{9.7.2}$$

$$n = \frac{\ln(137.50)}{\ln(1.0043)} \tag{9.7.3}$$

$$= 1148 \tag{9.7.4}$$

Thus at least a thousand effusion steps are necessary to obtain highly enriched ^{235}U. Below is a small part of a system that is used to prepare enriched uranium on a large scale.



A Portion of a Plant for Separating Uranium Isotopes by Effusion of UF_6. The large cylindrical objects (note the human for scale) are so-called diffuser (actually effuser) units, in which gaseous UF_6 is pumped through a porous barrier to partially separate the isotopes. The UF_6 must be passed through multiple units to become substantially enriched in ^{235}U.

? Exercise 9.7.1

Helium consists of two isotopes: ^3He (natural abundance = 0.000134%) and ^4He (natural abundance = 99.999866%). Their atomic masses are 3.01603 and 4.00260, respectively. Helium-3 has unique physical properties and is used in the study of ultralow temperatures. It is separated from the more abundant ^4He by a process of gaseous effusion.

a. Calculate the ratio of the effusion rates of ^3He and ^4He and thus the enrichment possible in a single effusion step.
b. How many effusion steps are necessary to yield 99.0% pure ^3He?

Answer a

ratio of effusion rates = 1.15200; one step gives 0.000154% ^3He

Answer b

96 steps

Rates of Diffusion or Effusion

Graham's law is an empirical relationship that states that the ratio of the rates of diffusion or effusion of two gases is the square root of the inverse ratio of their molar masses. The relationship is based on the postulate that all gases at the same temperature have the same average kinetic energy. We can write the expression for the average kinetic energy of two gases with different molar masses:

$$KE = \frac{1}{2}\frac{M_{\text{A}}}{N_A}v^2_{\text{rms,A}} = \frac{1}{2}\frac{M_{\text{B}}}{N_A}v^2_{\text{rms,B}} \tag{9.7.5}$$

Multiplying both sides by 2 and rearranging give

$$\frac{v^2_{\text{rms,B}}}{v^2_{\text{rms,A}}} = \frac{M_{\text{A}}}{M_{\text{B}}} \tag{9.7.6}$$

Taking the square root of both sides gives

$$\frac{v_{\text{rms,B}}}{v_{\text{rms,A}}} = \sqrt{\frac{M_{\text{A}}}{M_{\text{B}}}} \tag{9.7.7}$$

Thus the rate at which a molecule, or a mole of molecules, diffuses or effuses is directly related to the speed at which it moves. Equation 9.7.7 shows that Graham's law is a direct consequence of the fact that gaseous molecules at the same temperature have the same average kinetic energy.

Typically, gaseous molecules have a speed of hundreds of meters per second (hundreds of miles per hour). The effect of molar mass on these speeds is dramatic, as illustrated in Figure 9.7.3 for some common gases. Because all gases have the same average kinetic energy, according to the Boltzmann distribution, molecules with lower masses, such as hydrogen and helium, have a wider distribution of speeds.

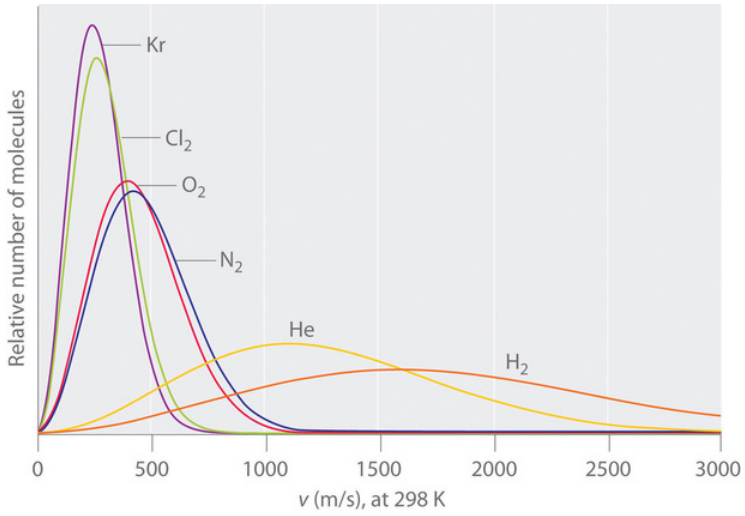


Figure 9.7.3: The Wide Variation in Molecular Speeds Observed at 298 K for Gases with Different Molar Masses

The lightest gases have a wider distribution of speeds and the highest average speeds.

> *Molecules with lower masses have a wider distribution of speeds and a higher average speed.*

Gas molecules do not diffuse nearly as rapidly as their very high speeds might suggest. If molecules actually moved through a room at hundreds of miles per hour, we would detect odors faster than we hear sound. Instead, it can take several minutes for us to detect an aroma because molecules are traveling in a medium with other gas molecules. Because gas molecules collide as often as 10^{10} times per second, changing direction and speed with each collision, they do not diffuse across a room in a straight line, as illustrated schematically in Figure 9.7.4.

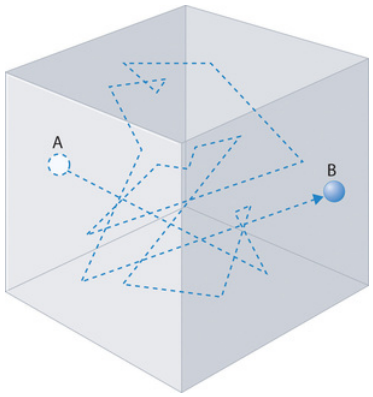


Figure 9.7.4: The Path of a Single Particle in a Gas Sample. The frequent changes in direction are the result of collisions with other gas molecules and with the walls of the container.

The average distance traveled by a molecule between collisions is the mean free path. The denser the gas, the shorter the mean free path; conversely, as density decreases, the mean free path becomes longer because collisions occur less frequently. At 1 atm pressure and 25°C, for example, an oxygen or nitrogen molecule in the atmosphere travels only about 6.0×10^{-8} m (60 nm) between collisions. In the upper atmosphere at about 100 km altitude, where gas density is much lower, the mean free path is about 10 cm; in space between galaxies, it can be as long as 1×10^{10} m (about 6 million miles).

> *The **denser** the gas, the **shorter** the mean free path.*

Example 9.7.2

Calculate the rms speed of a sample -butene (C_4H_8) at 20°C.

Given: compound and temperature

Asked for: rms speed

Strategy:

Calculate the molar mass of cis-2-butene. Be certain that all quantities are expressed in the appropriate units and then use Equation 10.8.5 to calculate the rms speed of the gas.

Solution:

To use Equation 10.8.4, we need to calculate the molar mass of *cis*-2-butene and make sure that each quantity is expressed in the appropriate units. Butene is C_4H_8, so its molar mass is 56.11 g/mol. Thus

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}} \tag{9.7.8}$$

$$= \sqrt{\frac{3 \times 8.3145 \ \frac{\text{J}}{\text{K} \cdot \text{mol}} \times (20 + 273) \ \text{K}}{56.11 \times 10^{-3} \ \text{kg}}} \tag{9.7.9}$$

$$= 361 \ m/s \tag{9.7.10}$$

or approximately 810 mi/h.

Exercise 9.7.1

Calculate the rms speed of a sample of radon gas at 23°C.

Answer

$1.82 \times 10^2 \ m/s$ (about 410 mi/h)

The kinetic molecular theory of gases demonstrates how a successful theory can explain previously observed empirical relationships (laws) in an intuitively satisfying way. Unfortunately, the actual gases that we encounter are not “ideal,” although their behavior usually approximates that of an ideal gas.

Summary

- The kinetic molecular theory of gases provides a molecular explanation for the observations that led to the development of the ideal gas law.
- **Average kinetic energy:**

$$\overline{e_K} = \frac{1}{2} m {u_{\text{rms}}}^2 = \frac{3}{2} \frac{R}{N_A} T,$$

- **Root mean square speed:**

$$u_{\text{rms}} = \sqrt{\frac{u_1^2 + u_2^2 + \cdots u_N^2}{N}},$$

- **Kinetic molecular theory of gases**:

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}.$$

- **Graham’s law for effusion:**

$$\frac{v_{\text{rms,B}}}{v_{\text{rms,A}}} = \sqrt{\frac{M_{\text{A}}}{M_{\text{B}}}}$$

Diffusion is the gradual mixing of gases to form a sample of uniform composition even in the absence of mechanical agitation. In contrast, **effusion** is the escape of a gas from a container through a tiny opening into an evacuated space. The rate of effusion of a gas is inversely proportional to the square root of its molar mass (**Graham’s law**), a relationship that closely approximates the rate of diffusion. As a result, light gases tend to diffuse and effuse much more rapidly than heavier gases. The **mean free path** of a molecule is the average distance it travels between collisions.

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9.8: Real Gases - Deviations from Ideal Behavior

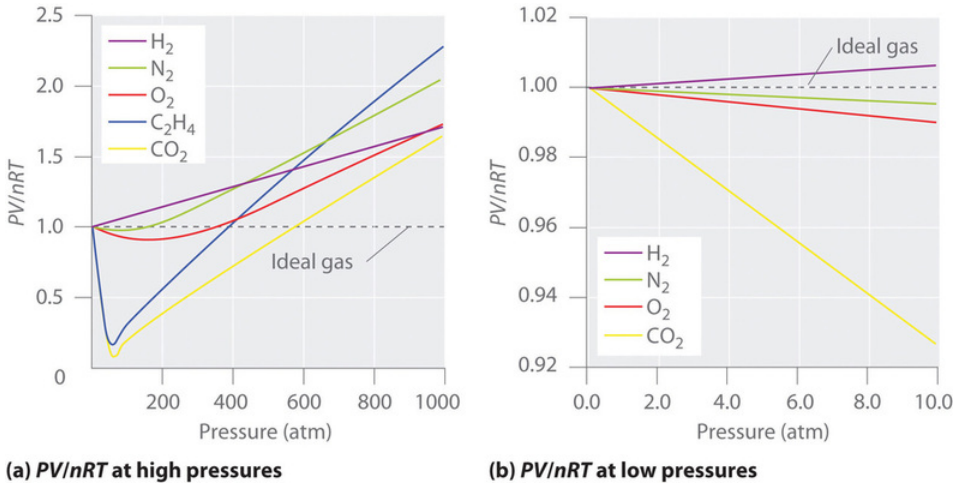
Learning Objectives

- To recognize the differences between the behavior of an ideal gas and a real gas
- To understand how molecular volumes and intermolecular attractions cause the properties of real gases to deviate from those predicted by the ideal gas law.

The postulates of the kinetic molecular theory of gases ignore both the volume occupied by the molecules of a gas and all interactions between molecules, whether attractive or repulsive. In reality, however, all gases have nonzero molecular volumes. Furthermore, the molecules of real gases interact with one another in ways that depend on the structure of the molecules and therefore differ for each gaseous substance. In this section, we consider the properties of real gases and how and why they differ from the predictions of the ideal gas law. We also examine liquefaction, a key property of real gases that is not predicted by the kinetic molecular theory of gases.

Pressure, Volume, and Temperature Relationships in Real Gases

For an ideal gas, a plot of PV/nRT versus P gives a horizontal line with an intercept of 1 on the PV/nRT axis. Real gases, however, show significant deviations from the behavior expected for an ideal gas, particularly at high pressures (Figure $9.8.1a$). Only at relatively low pressures (less than 1 atm) do real gases approximate ideal gas behavior (Figure $9.8.1b$).



(a) *PV/nRT* at high pressures **(b) *PV/nRT* at low pressures**

Figure 9.8.1: Real Gases Do Not Obey the Ideal Gas Law, Especially at High Pressures. (a) In these plots of *PV*/*nRT* versus *P* at 273 K for several common gases, there are large negative deviations observed for C_2H_4 and CO_2 because they liquefy at relatively low pressures. (b) These plots illustrate the relatively good agreement between experimental data for real gases and the ideal gas law at low pressures.

Real gases also approach ideal gas behavior more closely at higher temperatures, as shown in Figure $9.8.2$ for N_2. Why do real gases behave so differently from ideal gases at high pressures and low temperatures? Under these conditions, the two basic assumptions behind the ideal gas law—namely, that gas molecules have negligible volume and that intermolecular interactions are negligible—are no longer valid.

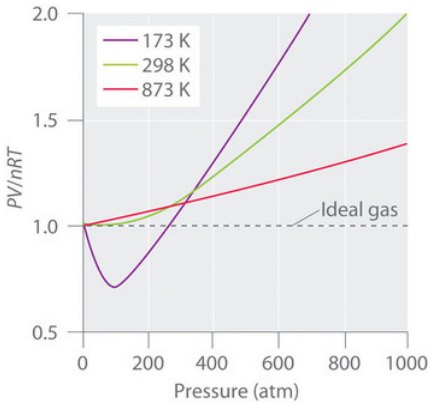


Figure 9.8.2: The Effect of Temperature on the Behavior of Real Gases. A plot of PV/nRT versus P for nitrogen gas at three temperatures shows that the approximation to ideal gas behavior becomes better as the temperature increases.

Because the molecules of an ideal gas are assumed to have zero volume, the volume available to them for motion is always the same as the volume of the container. In contrast, the molecules of a real gas have small but measurable volumes. At low pressures, the gaseous molecules are relatively far apart, but as the pressure of the gas increases, the intermolecular distances become smaller and smaller (Figure 9.8.3). As a result, the volume occupied by the molecules becomes significant compared with the volume of the container. Consequently, the total volume occupied by the gas is greater than the volume predicted by the ideal gas law. Thus at very high pressures, the experimentally measured value of *PV*/*nRT* is greater than the value predicted by the ideal gas law.

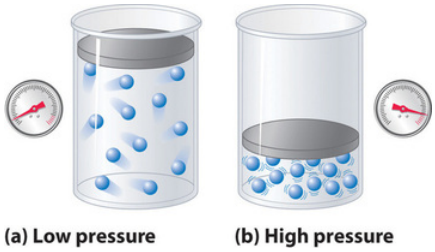


Figure 9.8.3: The Effect of Nonzero Volume of Gas Particles on the Behavior of Gases at Low and High Pressures. (a) At low pressures, the volume occupied by the molecules themselves is small compared with the volume of the container. (b) At high pressures, the molecules occupy a large portion of the volume of the container, resulting in significantly decreased space in which the molecules can move.

Moreover, all molecules are attracted to one another by a combination of forces. These forces become particularly important for gases at low temperatures and high pressures, where intermolecular distances are shorter. Attractions between molecules reduce the number of collisions with the container wall, an effect that becomes more pronounced as the number of attractive interactions increases. Because the average distance between molecules decreases, the pressure exerted by the gas on the container wall decreases, and the observed pressure is *less* than expected (Figure 9.8.4). Thus as shown in Figure 9.8.2, at low temperatures, the ratio of \(PV/nRT\) is lower than predicted for an ideal gas, an effect that becomes particularly evident for complex gases and for simple gases at low temperatures. At very high pressures, the effect of nonzero molecular volume predominates. The competition between these effects is responsible for the minimum observed in the PV/nRT versus P plot for many gases.

> *Nonzero molecular volume makes the actual volume greater than predicted at high pressures; intermolecular attractions make the pressure less than predicted.*

At high temperatures, the molecules have sufficient kinetic energy to overcome intermolecular attractive forces, and the effects of nonzero molecular volume predominate. Conversely, as the temperature is lowered, the kinetic energy of the gas molecules decreases. Eventually, a point is reached where the molecules can no longer overcome the intermolecular attractive forces, and the gas liquefies (condenses to a liquid).

The van der Waals Equation

The Dutch physicist Johannes van der Waals (1837–1923; Nobel Prize in Physics, 1910) modified the ideal gas law to describe the behavior of real gases by explicitly including the effects of molecular size and intermolecular forces. In his description of gas behavior, the so-called *van der Waals* equation,

$$\underbrace{\left(P+\frac{an^2}{V^2}\right)}_{\text{Pressure Term}}\overbrace{(V-nb)}^{\text{Pressure Term}}=nRT \tag{9.8.1}$$

a and b are empirical constants that are different for each gas. The values of a and b are listed in Table 9.8.1 for several common gases.

Table 9.8.1:: van der Waals Constants for Some Common Gases (see Table A8 for more complete list)

Gas	a ($L^2 \cdot atm/mol^2$)	b (L/mol)
He	0.03410	0.0238
Ne	0.205	0.0167
Ar	1.337	0.032
H_2	0.2420	0.0265
N_2	1.352	0.0387
O_2	1.364	0.0319
Cl_2	6.260	0.0542
NH_3	4.170	0.0371
CH_4	2.273	0.0430
CO_2	3.610	0.0429

The pressure term in Equation 9.8.1 corrects for intermolecular attractive forces that tend to reduce the pressure from that predicted by the ideal gas law. Here, n^2/V^2 represents the concentration of the gas (n/V) squared because it takes two particles to engage in the pairwise intermolecular interactions of the type shown in Figure 9.8.4. The volume term corrects for the volume occupied by the gaseous molecules.

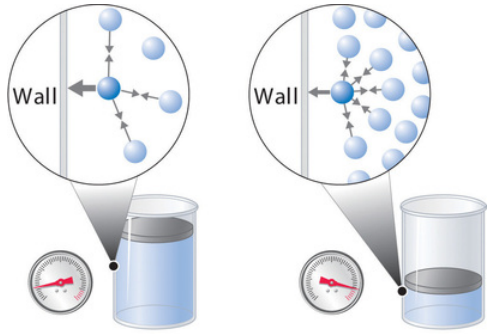


Figure 9.8.4: The Effect of Intermolecular Attractive Forces on the Pressure a Gas Exerts on the Container Walls. (a) At low pressures, there are relatively few attractive intermolecular interactions to lessen the impact of the molecule striking the wall of the container, and the pressure is close to that predicted by the ideal gas law. (b) At high pressures, with the average intermolecular distance relatively small, the effect of intermolecular interactions is to lessen the impact of a given molecule striking the container wall, resulting in a lower pressure than predicted by the ideal gas law.

The correction for volume is negative, but the correction for pressure is positive to reflect the effect of each factor on V and P, respectively. Because nonzero molecular volumes produce a measured volume that is *larger* than that predicted by the ideal gas law, we must subtract the molecular volumes to obtain the actual volume available. Conversely, attractive intermolecular forces produce a pressure that is *less* than that expected based on the ideal gas law, so the an^2/V^2 term must be added to the measured pressure to correct for these effects.

Example 9.8.1

You are in charge of the manufacture of cylinders of compressed gas at a small company. Your company president would like to offer a 4.00 L cylinder containing 500 g of chlorine in the new catalog. The cylinders you have on hand have a rupture pressure of 40 atm. Use both the ideal gas law and the van der Waals equation to calculate the pressure in a cylinder at 25°C. Is this cylinder likely to be safe against sudden rupture (which would be disastrous and certainly result in lawsuits because chlorine gas is highly toxic)?

Given: volume of cylinder, mass of compound, pressure, and temperature

Asked for: safety

Strategy:

A Use the molar mass of chlorine to calculate the amount of chlorine in the cylinder. Then calculate the pressure of the gas using the ideal gas law.

B Obtain *a* and *b* values for Cl_2 from Table 9.8.1. Use the van der Waals equation (9.8.1) to solve for the pressure of the gas. Based on the value obtained, predict whether the cylinder is likely to be safe against sudden rupture.

Solution:

A We begin by calculating the amount of chlorine in the cylinder using the molar mass of chlorine (70.906 g/mol):

$$n = \frac{m}{M} \tag{9.8.2}$$

$$= \frac{500\ \text{g}}{70.906\ \text{g/mol}} \tag{9.8.3}$$

$$= 7.052\ mol$$

Using the ideal gas law and the temperature in kelvin (298 K), we calculate the pressure:

$$P = \frac{nRT}{V} \tag{9.8.4}$$

$$= \frac{7.052\ \text{mol} \times 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 298\ \text{K}}{4.00\ \text{L}} \tag{9.8.5}$$

$$= 43.1\ atm \tag{9.8.6}$$

If chlorine behaves like an ideal gas, you have a real problem!

B Now let's use the van der Waals equation with the *a* and *b* values for Cl_2 from Table 9.8.1. Solving for P gives

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2} \tag{9.8.7}$$

$$= \frac{7.052\ \text{mol} \times 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 298\ \text{K}}{4.00\ \text{L} - 7.052\ \text{mol} \times 0.0542 \frac{\text{L}}{\text{mol}}} - \frac{6.260 \frac{\text{L}^2\text{atm}}{\text{mol}^2} \times (7.052\ \text{mol})^2}{(4.00\ \text{L})^2} \tag{9.8.8}$$

$$= 28.2\ \text{atm} \tag{9.8.9}$$

This pressure is well within the safety limits of the cylinder. The ideal gas law predicts a pressure 15 atm higher than that of the van der Waals equation.

Exercise 9.8.1

A 10.0 L cylinder contains 500 g of methane. Calculate its pressure to two significant figures at 27°C using the

a. ideal gas law.
b. van der Waals equation.

Answer a

77 atm

Answer b

67 atm

Liquefaction of Gases

Liquefaction of gases is the condensation of gases into a liquid form, which is neither anticipated nor explained by the kinetic molecular theory of gases. Both the theory and the ideal gas law predict that gases compressed to very high pressures and cooled to very low temperatures should still behave like gases, albeit cold, dense ones. As gases are compressed and cooled, however, they invariably condense to form liquids, although very low temperatures are needed to liquefy light elements such as helium (for He, 4.2 K at 1 atm pressure).

Liquefaction can be viewed as an extreme deviation from ideal gas behavior. It occurs when the molecules of a gas are cooled to the point where they no longer possess sufficient kinetic energy to overcome intermolecular attractive forces. The precise combination of temperature and pressure needed to liquefy a gas depends strongly on its molar mass and structure, with heavier and more complex molecules usually liquefying at higher temperatures. In general, substances with large van der Waals *a* coefficients are relatively easy to liquefy because large *a* coefficients indicate relatively strong intermolecular attractive interactions. Conversely, small molecules with only light elements have small *a* coefficients, indicating weak intermolecular interactions, and they are relatively difficult to liquefy. Gas liquefaction is used on a massive scale to separate O_2, N_2, Ar, Ne, Kr, and Xe. After a sample of air is liquefied, the mixture is warmed, and the gases are separated according to their boiling points.

> *A large value of a in the van der Waals equation indicates the presence of relatively strong intermolecular attractive interactions.*

The ultracold liquids formed from the liquefaction of gases are called cryogenic liquids, from the Greek *kryo*, meaning “cold,” and *genes*, meaning “producing.” They have applications as refrigerants in both industry and biology. For example, under carefully controlled conditions, the very cold temperatures afforded by liquefied gases such as nitrogen (boiling point = 77 K at 1 atm) can preserve biological materials, such as semen for the artificial insemination of cows and other farm animals. These liquids can also be used in a specialized type of surgery called *cryosurgery*, which selectively destroys tissues with a minimal loss of blood by the use of extreme cold.



Figure 9.8.5: A Liquid Natural Gas Transport Ship.

Moreover, the liquefaction of gases is tremendously important in the storage and shipment of fossil fuels (Figure 9.8.5). Liquefied natural gas (LNG) and liquefied petroleum gas (LPG) are liquefied forms of hydrocarbons produced from natural gas or petroleum reserves. LNG consists mostly of methane, with small amounts of heavier hydrocarbons; it is prepared by cooling natural gas to below about −162°C. It can be stored in double-walled, vacuum-insulated containers at or slightly above atmospheric pressure. Because LNG occupies only about 1/600 the volume of natural gas, it is easier and more economical to transport. LPG is typically a mixture of propane, propene, butane, and butenes and is primarily used as a fuel for home heating. It is also used as a feedstock for chemical plants and as an inexpensive and relatively nonpolluting fuel for some automobiles.

Summary

No real gas exhibits ideal gas behavior, although many real gases approximate it over a range of conditions. Deviations from ideal gas behavior can be seen in plots of *PV*/*nRT* versus *P* at a given temperature; for an ideal gas, *PV*/*nRT* versus *P* = 1 under all

conditions. At high pressures, most real gases exhibit larger *PV*/*nRT* values than predicted by the ideal gas law, whereas at low pressures, most real gases exhibit *PV*/*nRT* values close to those predicted by the ideal gas law. Gases most closely approximate ideal gas behavior at high temperatures and low pressures. Deviations from ideal gas law behavior can be described by the **van der Waals equation**, which includes empirical constants to correct for the actual volume of the gaseous molecules and quantify the reduction in pressure due to intermolecular attractive forces. If the temperature of a gas is decreased sufficiently, **liquefaction** occurs, in which the gas condenses into a liquid form. Liquefied gases have many commercial applications, including the transport of large amounts of gases in small volumes and the uses of ultracold **cryogenic liquids**.

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9.E: Exercises

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10.1: Characteristics of Gases

Conceptual Problems

Q10.1.1

Explain the differences between the microscopic and the macroscopic properties of matter. Is the boiling point of a compound a microscopic or macroscopic property? molecular mass? Why?

Q10.1.2

How do the microscopic properties of matter influence the macroscopic properties? Can you relate molecular mass to boiling point? Why or why not?

Q10.1.3

For a substance that has gas, liquid, and solid phases, arrange these phases in order of increasing density.

a. strength of intermolecular interactions.
b. compressibility.
c. molecular motion.
d. order in the arrangement of the molecules or atoms.

Q10.1.4

Which elements of the periodic table exist as gases at room temperature and pressure? Of these, which are diatomic molecules and which are monatomic? Which elements are liquids at room temperature and pressure? Which portion of the periodic table contains elements whose binary hydrides are most likely gases at room temperature?

10.2: Pressure

Q10.2.1

What four quantities must be known to completely describe a sample of a gas? What units are commonly used for each quantity?

Q10.2.2

If the applied force is constant, how does the pressure exerted by an object change as the area on which the force is exerted decreases? In the real world, how does this relationship apply to the ease of driving a small nail versus a large nail?

Q10.2.3

As the force on a fixed area increases, does the pressure increase or decrease? With this in mind, would you expect a heavy person to need smaller or larger snowshoes than a lighter person? Explain.

Q10.2.4

What do we mean by *barometric pressure*? Is the barometric pressure at the summit of Mt. Rainier greater than or less than the pressure in Miami, Florida? Why?

Q10.2.5

Which has the highest barometric pressure—a cave in the Himalayas, a mine in South Africa, or a beach house in Florida? Which has the lowest?

Q10.2.6

Mars has an average barometric pressure of 0.007 atm. Would it be easier or harder to drink liquid from a straw on Mars than on Earth? Explain your answer.

Q10.2.7

Is the pressure exerted by a 1.0 kg mass on a 2.0 m^2 area greater than or less than the pressure exerted by a 1.0 kg mass on a 1.0 m^2 area? What is the difference, if any, between the pressure of the atmosphere exerted on a 1.0 m^2 piston and a 2.0 m^2 piston?

Q10.2.8

If you used water in a barometer instead of mercury, what would be the major difference in the instrument?

Numerical Problems

Q10.2.9

Calculate the pressure in pascals and in atmospheres exerted by a carton of milk that weighs 1.5 kg and has a base of 7.0 cm × 7.0 cm. If the carton were lying on its side (height = 25 cm), would it exert more or less pressure? Explain your reasoning.

Q10.2.10

If barometric pressure at sea level is 1.0×10^5 Pa, what is the mass of air in kilograms above a 1.0 cm^2 area of your skin as you lie on the beach? If barometric pressure is 8.2×10^4 Pa on a mountaintop, what is the mass of air in kilograms above a 4.0 cm^2 patch of skin?

Q10.2.11

Complete the following table:

atm	kPa	mmHg	torr
1.40			
		723	
	43.2		

Q10.2.12

The SI unit of pressure is the pascal, which is equal to 1 N/m^2. Show how the product of the mass of an object and the acceleration due to gravity result in a force that, when exerted on a given area, leads to a pressure in the correct SI units. What mass in kilograms applied to a 1.0 cm^2 area is required to produce a pressure of

a. 1.0 atm?
b. 1.0 torr?
c. 1 mmHg?
d. 1 kPa?

Q10.2.13

If you constructed a manometer to measure gas pressures over the range 0.60–1.40 atm using the liquids given in the following table, how tall a column would you need for each liquid? The density of mercury is 13.5 g/cm^3. Based on your results, explain why mercury is still used in barometers, despite its toxicity.

	Liquid Density (20°C)	Column Height (m)
isopropanol	0.785	
coconut oil	0.924	
glycerine	1.259	

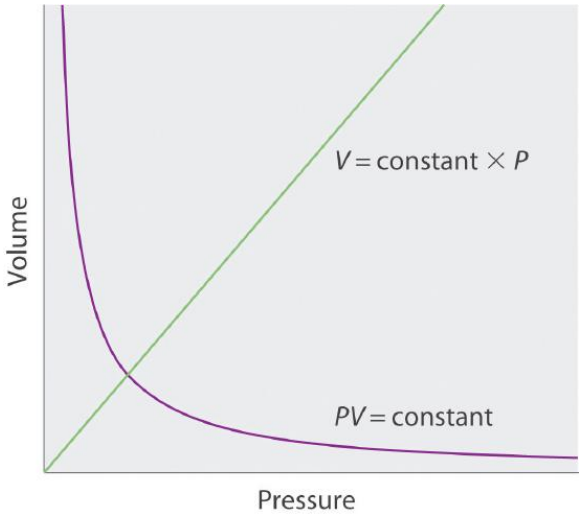
10.3: The Gas Laws

Conceptual Problems

Q10.3.1

Sketch a graph of the volume of a gas versus the pressure on the gas. What would the graph of V versus P look like if volume was directly proportional to pressure?

S10.3.1



Q10.3.2

What properties of a gas are described by Boyle's law, Charles's law, and Avogadro's law? In each law, what quantities are held constant? Why does the constant in Boyle's law depend on the amount of gas used and the temperature at which the experiments are carried out?

Q10.3.3

Use Charles's law to explain why cooler air sinks.

Q10.3.4

Use Boyle's law to explain why it is dangerous to heat even a small quantity of water in a sealed container.

Numerical Problems

Q10.3.5

A 1.00 mol sample of gas at 25°C and 1.0 atm has an initial volume of 22.4 L. Calculate the results of each change, assuming all the other conditions remain constant.

a. The pressure is changed to 85.7 mmHg. How many milliliters does the gas occupy?
b. The volume is reduced to 275 mL. What is the pressure in millimeters of mercury?
c. The pressure is increased to 25.3 atm. What is the temperature in degrees Celsius?
d. The sample is heated to 30°C. What is the volume in liters?
e. The sample is compressed to 1255 mL, and the pressure is increased to 2555 torr. What is the temperature of the gas in kelvins?

S10.3.5

a. 1.99×10^5 mL
b. 6.19×10^4 mmHg
c. 7270°C
d. 22.8 L
e. 51.4 K

Q10.3.6

A 1.00 mol sample of gas is at 300 K and 4.11 atm. What is the volume of the gas under these conditions? The sample is compressed to 6.0 atm at constant temperature, giving a volume of 3.99 L. Is this result consistent with Boyle's law?

10.4: The Ideal Gas Equation

Conceptual Problems

Q10.4.1

For an ideal gas, is volume directly proportional or inversely proportional to temperature? What is the volume of an ideal gas at absolute zero?

Q10.4.2

What is meant by STP? If a gas is at STP, what further information is required to completely describe the state of the gas?

Q10.4.3

For a given amount of a gas, the volume, temperature, and pressure under any one set of conditions are related to the volume, the temperature, and the pressure under any other set of conditions by the equation

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \tag{9.E.1}$$

Q10.4.4

Derive this equation from the ideal gas law. At constant temperature, this equation reduces to one of the gas laws discussed previosuly; which one? At constant pressure, this equation reduces to one of the laws discussed in Section 10.3"; which one?

Q10.4.5

Predict the effect of each change on one variable if the other variables are held constant.

a. If the number of moles of gas increases, what is the effect on the temperature of the gas?
b. If the temperature of a gas decreases, what is the effect on the pressure of the gas?
c. If the volume of a gas increases, what is the effect on the temperature of the gas?
d. If the pressure of a gas increases, what is the effect on the number of moles of the gas?

Q10.4.6

What would the ideal gas law be if the following were true?

a. volume were proportional to pressure
b. temperature were proportional to amount
c. pressure were inversely proportional to temperature
d. volume were inversely proportional to temperature
e. both pressure and volume were inversely proportional to temperature

Given the following initial and final values, what additional information is needed to solve the problem using the ideal gas law?

Given	Solve for
V_1, T_1, T_2, n_1	n_2
P_1, P_2, T_2, n_2	n_1
T_1, T_2	V_2
P_1, n_1	P_2

Q10.4.7

Given the following information and using the ideal gas law, what equation would you use to solve the problem?

Given	Solve for
P_1, P_2, T_1	T_2

Given	Solve for
V_1, n_1, n_2	V_2
T_1, T_2, V_1, V_2, n_2	n_1

Q10.4.8

Using the ideal gas law as a starting point, derive the relationship between the density of a gas and its molar mass. Which would you expect to be denser—nitrogen or oxygen? Why does radon gas accumulate in basements and mine shafts?

Q10.4.9

Use the ideal gas law to derive an equation that relates the remaining variables for a sample of an ideal gas if the following are held constant.

a. amount and volume
b. pressure and amount
c. temperature and volume
d. temperature and amount
e. pressure and temperature

S10.4.9

a. P/T = constant
b. V/T = constant (Charles' law)
c. P/n = constant
d. PV = constant (Boyle's law)
e. V/n = constant (Avogadro's law)

Q10.4.10

Tennis balls that are made for Denver, Colorado, feel soft and do not bounce well at lower altitudes. Use the ideal gas law to explain this observation. Will a tennis ball designed to be used at sea level be harder or softer and bounce better or worse at higher altitudes?

Numerical Problems

Q10.4.11

Calculate the number of moles in each sample at STP.

a. 1580 mL of NO_2
b. 847 cm^3 of HCl
c. 4.792 L of H_2
d. a 15.0 cm × 6.7 cm × 7.5 cm container of ethane

S10.4.11

a. 7.05×10^{-2} mol
b. 3.78×10^{-2} mol
c. 0.2138 mol
d. 3.4×10^{-2} mol

Q10.4.12

Calculate the number of moles in each sample at STP.

a. 2200 cm^3 of CO_2
b. 1200 cm^3 of N_2
c. 3800 mL of SO_2
d. 13.75 L of NH_3

Q10.4.13

Calculate the mass of each sample at STP.

a. 36 mL of HI
b. 550 L of H_2S
c. 1380 cm^3 of CH_4

S10.4.13

a. 0.21 g HI;
b. 840 g H_2S;
c. 0.988 g CH_4

Q10.4.14

Calculate the mass of each sample at STP.

a. 3.2 L of N_2O
b. 65 cm^3 of Cl_2
c. 3600 mL of HBr

Q10.4.15

Calculate the volume in liters of each sample at STP.

a. 1.68 g of Kr
b. 2.97 kg of propane (C_3H_8)
c. 0.643 mg of $(CH_3)_2O$

S10.4.15

a. 0.449 L Kr
b. 1510 L C_3H_8
c. 3.13×10^{-4} L $(CH_3)_2O$

Q10.4.16

Calculate the volume in liters of each sample at STP.

a. 3.2 g of Xe
b. 465 mg of CS_2
c. 5.34 kg of acetylene (C_2H_2)

Q10.4.17

Calculate the volume of each gas at STP.

a. 1.7 L at 28°C and 96.4 kPa
b. 38.0 mL at 17°C and 103.4 torr
c. 650 mL at −15°C and 723 mmHg

Q10.4.18

Calculate the volume of each gas at STP.

a. 2.30 L at 23°C and 740 mmHg
b. 320 mL at 13°C and 97.2 kPa
c. 100.5 mL at 35°C and 1.4 atm

S10.4.18

a. 1.5 L
b. 4.87 mL
c. 650 mL

Q10.4.19

A 8.60 L tank of nitrogen gas at a pressure of 455 mmHg is connected to an empty tank with a volume of 5.35 L. What is the final pressure in the system after the valve connecting the two tanks is opened? Assume that the temperature is constant.

S10.4.19

281 mmHg

Q10.4.20

At constant temperature, what pressure in atmospheres is needed to compress 14.2 L of gas initially at 25.2 atm to a volume of 12.4 L? What pressure is needed to compress 27.8 L of gas to 20.6 L under similar conditions?

Q10.4.21

One method for preparing hydrogen gas is to pass HCl gas over hot aluminum; the other product of the reaction is $AlCl_3$. If you wanted to use this reaction to fill a balloon with a volume of 28,500 L at sea level and a temperature of 78°F, what mass of aluminum would you need? What volume of HCl at STP would you need?

S10.4.21

20.9 kg Al, 5.20×10^4 L HCl

Q10.4.21

An 3.50 g sample of acetylene is burned in excess oxygen according to the following reaction:

$$2\,C_2H_2(g) + 5\,O_2(g) \rightarrow 4\,CO_2(g) + 2\,H_2O(l) \tag{9.E.2}$$

At STP, what volume of CO_2(g) is produced?

Q10.4.22

Calculate the density of ethylene (C_2H_4) under each set of conditions.

a. 7.8 g at 0.89 atm and 26°C
b. 6.3 mol at 102.6 kPa and 38°C
c. 9.8 g at 3.1 atm and −45°C

S10.4.22

a. 1.0 g/L
b. 1.1 g/L
c. 4.6 g/L

Q10.4.23

Determine the density of O_2 under each set of conditions.

a. 42 g at 1.1 atm and 25°C
b. 0.87 mol at 820 mmHg and 45°C
c. 16.7 g at 2.4 atm and 67°C

Q10.4.24

At 140°C, the pressure of a diatomic gas in a 3.0 L flask is 635 kPa. The mass of the gas is 88.7 g. What is the most likely identity of the gas?

Q10.4.25

What volume must a balloon have to hold 6.20 kg of H_2 for an ascent from sea level to an elevation of 20,320 ft, where the temperature is −37°C and the pressure is 369 mmHg?

Q10.4.26

What must be the volume of a balloon that can hold 313.0 g of helium gas and ascend from sea level to an elevation of 1.5 km, where the temperature is 10.0°C and the pressure is 635.4 mmHg?

S10.4.26

2174 L

Q10.4.27

A typical automobile tire is inflated to a pressure of 28.0 lb/in.^{2} Assume that the tire is inflated when the air temperature is 20°C; the car is then driven at high speeds, which increases the temperature of the tire to 43°C. What is the pressure in the tire? If the volume of the tire had increased by 8% at the higher temperature, what would the pressure be?

Q10.4.28

The average respiratory rate for adult humans is 20 breaths per minute. If each breath has a volume of 310 mL of air at 20°C and 0.997 atm, how many moles of air does a person inhale each day? If the density of air is 1.19 kg/m^3, what is the average molecular mass of air?

Q10.4.29

Kerosene has a self-ignition temperature of 255°C. It is a common accelerant used by arsonists, but its presence is easily detected in fire debris by a variety of methods. If a 1.0 L glass bottle containing a mixture of air and kerosene vapor at an initial pressure of 1 atm and an initial temperature of 23°C is pressurized, at what pressure would the kerosene vapor ignite?

10.5: Further Applications of the Ideal-Gas Equations

Conceptual Problems

Q10.5.1

Why are so many industrially important reactions carried out in the gas phase?

Q10.5.2

The volume of gas produced during a chemical reaction can be measured by collecting the gas in an inverted container filled with water. The gas forces water out of the container, and the volume of liquid displaced is a measure of the volume of gas. What additional information must be considered to determine the number of moles of gas produced? The volume of some gases cannot be measured using this method. What property of a gas precludes the use of this method?

Q10.5.3

Equal masses of two solid compounds (A and B) are placed in separate sealed flasks filled with air at 1 atm and heated to 50°C for 10 hours. After cooling to room temperature, the pressure in the flask containing A was 1.5 atm. In contrast, the pressure in the flask containing B was 0.87 atm. Suggest an explanation for these observations. Would the masses of samples A and B still be equal after the experiment? Why or why not?

Numerical Problems

Q10.5.4

Balance each chemical equation and then determine the volume of the indicated reactant at STP that is required for complete reaction. Assuming complete reaction, what is the volume of the products?

a. $SO_2(g) + O_2(g) \rightarrow SO_3(g)$ given 2.4 mol of O_2
b. $H_2(g) + Cl_2(g) \rightarrow HCl(g)$ given 0.78 g of H_2
c. $C_2H_6(g) + O_2(g) \rightarrow CO_2(g) + H_2O(g)$ given 1.91 mol of O_2

Q10.5.5

During the smelting of iron, carbon reacts with oxygen to produce carbon monoxide, which then reacts with iron(III) oxide to produce iron metal and carbon dioxide. If 1.82 L of CO_2 at STP is produced,

a. what mass of CO is consumed?
b. what volume of CO at STP is consumed?
c. how much O_2 (in liters) at STP is used?
d. what mass of carbon is consumed?

e. how much iron metal (in grams) is produced?

Q10.5.6

Complete decomposition of a sample of potassium chlorate produced 1.34 g of potassium chloride and oxygen gas.

a. What is the mass of $KClO_3$ in the original sample?
b. What mass of oxygen is produced?
c. What is the volume of oxygen produced at STP?

S10.5.6

a. 2.20 g $KClO_3$
b. 0.863 g O_2
c. 604 mL O_2

Q10.5.7

The combustion of a 100.0 mg sample of an herbicide in excess oxygen produced 83.16 mL of CO_2 and 72.9 mL of H_2O vapor at STP. A separate analysis showed that the sample contained 16.44 mg of chlorine. If the sample is known to contain only C, H, Cl, and N, determine the percent composition and the empirical formula of the herbicide.

Q10.5.8

The combustion of a 300.0 mg sample of an antidepressant in excess oxygen produced 326 mL of CO_2 and 164 mL of H_2O vapor at STP. A separate analysis showed that the sample contained 23.28% oxygen. If the sample is known to contain only C, H, O, and N, determine the percent composition and the empirical formula of the antidepressant.

S10.5.8

Percent composition: 58.3% C, 4.93% H, 23.28% O, and 13.5% N; empirical formula: $C_{10}H_{10}O_3N_2$

10.6: Gas Mixtures and Partial Pressures

Conceptual Problems

Q10.6.1

Dalton’s law of partial pressures makes one key assumption about the nature of the intermolecular interactions in a mixture of gases. What is it?

Q10.6.2

What is the relationship between the partial pressure of a gas and its mole fraction in a mixture?

Numerical Problems

Q10.6.3

What is the partial pressure of each gas if the following amounts of substances are placed in a 25.0 L container at 25°C? What is the total pressure of each mixture?

a. 1.570 mol of CH_4 and 0.870 mol of CO_2
b. 2.63 g of CO and 1.24 g of NO_2
c. 1.78 kg of CH_3Cl and 0.92 kg of SO_2

Q10.6.4

What is the partial pressure of each gas in the following 3.0 L mixtures at 37°C as well as the total pressure?

a. 0.128 mol of SO_2 and 0.098 mol of methane (CH_4)
b. 3.40 g of acetylene (C_2H_2) and 1.54 g of He
c. 0.267 g of NO, 4.3 g of Ar, and 0.872 g of SO_2

Q10.6.5

In a mixture of helium, oxygen, and methane in a 2.00 L container, the partial pressures of He and O_2 are 13.6 kPa and 29.2 kPa, respectively, and the total pressure inside the container is 95.4 kPa. What is the partial pressure of methane? If the methane is ignited to initiate its combustion with oxygen and the system is then cooled to the original temperature of 30°C, what is the final pressure inside the container (in kilopascals)?

S10.6.5

52.6 kPa, 66.2 kPa

Q10.6.6

A 2.00 L flask originally contains 1.00 g of ethane (C_2H_6) and 32.0 g of oxygen at 21°C. During ignition, the ethane reacts completely with oxygen to produce CO_2 and water vapor, and the temperature of the flask increases to 200°C. Determine the total pressure and the partial pressure of each gas before and after the reaction.

Q10.6.7

If a 20.0 L cylinder at 19°C is charged with 5.0 g each of sulfur dioxide and oxygen, what is the partial pressure of each gas? The sulfur dioxide is ignited in the oxygen to produce sulfur trioxide gas, and the mixture is allowed to cool to 19°C at constant pressure. What is the final volume of the cylinder? What is the partial pressure of each gas in the piston?

Q10.6.8

The highest point on the continent of Europe is Mt. Elbrus in Russia, with an elevation of 18,476 ft. The highest point on the continent of South America is Mt. Aconcagua in Argentina, with an elevation of 22,841 ft.

a. The following table shows the variation of atmospheric pressure with elevation. Use the data in the table to construct a plot of pressure versus elevation.

Elevation (km)	Pressure in Summer (mmHg)	Pressure in Winter (mmHg)
0.0	760.0	760.0
1.0	674.8	670.6
1.5	635.4	629.6
2.0	598.0	590.8
3.0	528.9	519.7
5.0	410.6	398.7
7.0	314.9	301.6
9.0	237.8	224.1

b. Use your graph to estimate the pressures in millimeters of mercury during the summer and the winter at the top of both mountains in both atmospheres and kilopascals.
c. Given that air is 20.95% O_2 by volume, what is the partial pressure of oxygen in atmospheres during the summer at each location?

10.7: Kinetic-Molecular Theory

10.8: Molecular Effusion and Diffusion

Conceptual Problems

Q10.8.1

Which of the following processes represents effusion, and which represents diffusion?

a. helium escaping from a hole in a balloon

b. vapor escaping from the surface of a liquid
c. gas escaping through a membrane

Q10.8.2

Which postulate of the kinetic molecular theory of gases most readily explains the observation that a helium-filled balloon is round?

Q10.8.3

Why is it relatively easy to compress a gas? How does the compressibility of a gas compare with that of a liquid? A solid? Why? Which of the postulates of the kinetic molecular theory of gases most readily explains these observations?

Q10.8.4

What happens to the average kinetic energy of a gas if the rms speed of its particles increases by a factor of 2? How is the rms speed different from the average speed?

Q10.8.5

Which gas—radon or helium—has a higher average kinetic energy at 100°C? Which has a higher average speed? Why? Which postulate of the kinetic molecular theory of gases most readily supports your answer?

Q10.8.6

What is the relationship between the average speed of a gas particle and the temperature of the gas? What happens to the distribution of molecular speeds if the temperature of a gas is increased? Decreased?

Q10.8.7

Qualitatively explain the relationship between the number of collisions of gas particles with the walls of a container and the pressure of a gas. How does increasing the temperature affect the number of collisions?

Q10.8.8

What happens to the average kinetic energy of a gas at constant temperature if the

a. volume of the gas is increased?
b. pressure of the gas is increased?

Q10.8.9

What happens to the density of a gas at constant temperature if the

a. volume of the gas is increased?
b. pressure of the gas is increased?

Q10.8.10

Use the kinetic molecular theory of gases to describe how a decrease in volume produces an increase in pressure at constant temperature. Similarly, explain how a decrease in temperature leads to a decrease in volume at constant pressure.

Q10.8.11

Graham’s law is valid only if the two gases are at the same temperature. Why?

Q10.8.12

If we lived in a helium atmosphere rather than in air, would we detect odors more or less rapidly than we do now? Explain your reasoning. Would we detect odors more or less rapidly at sea level or at high altitude? Why?

Numerical Problems

Q10.8.13

At a given temperature, what is the ratio of the rms speed of the atoms of Ar gas to the rms speed of molecules of H_2 gas?

S10.8.13

At any temperature, the rms speed of hydrogen is 4.45 times that of argon.

Q10.8.14

At a given temperature, what is the ratio of the rms speed of molecules of CO gas to the rms speed of molecules of H_2S gas?

Q10.8.15

What is the ratio of the rms speeds of argon and oxygen at any temperature? Which diffuses more rapidly?

Q10.8.16

What is the ratio of the rms speeds of Kr and NO at any temperature? Which diffuses more rapidly?

Q10.8.17

Deuterium (D) and tritium (T) are heavy isotopes of hydrogen. Tritium has an atomic mass of 3.016 amu and has a natural abundance of 0.000138%. The effusion of hydrogen gas (containing a mixture of H_2, HD, and HT molecules) through a porous membrane can be used to obtain samples of hydrogen that are enriched in tritium. How many membrane passes are necessary to give a sample of hydrogen gas in which 1% of the hydrogen molecules are HT?

Q10.8.18

Samples of HBr gas and NH_3 gas are placed at opposite ends of a 1 m tube. If the two gases are allowed to diffuse through the tube toward one another, at what distance from each end of the tube will the gases meet and form solid NH_4Br?

10.9: Real Gases: Deviations from Ideal Behavior

Conceptual Problems

Q10.9.1

What factors cause deviations from ideal gas behavior? Use a sketch to explain your answer based on interactions at the molecular level.

Q10.9.2

Explain the effect of nonzero atomic volume on the ideal gas law at high pressure. Draw a typical graph of volume versus $1/P$ for an ideal gas and a real gas.

Q10.9.3

For an ideal gas, the product of pressure and volume should be constant, regardless of the pressure. Experimental data for methane, however, show that the value of PV decreases significantly over the pressure range 0 to 120 atm at 0°C. The decrease in PV over the same pressure range is much smaller at 100°C. Explain why PV decreases with increasing temperature. Why is the decrease less significant at higher temperatures.

Q10.9.4

What is the effect of intermolecular forces on the liquefaction of a gas? At constant pressure and volume, does it become easier or harder to liquefy a gas as its temperature increases? Explain your reasoning. What is the effect of increasing the pressure on the liquefaction temperature?

Q10.9.5

Describe qualitatively what a and b, the two empirical constants in the van der Waals equation, represent.

Q10.9.6

In the van der Waals equation, why is the term that corrects for volume negative and the term that corrects for pressure positive? Why is n/V squared?

Q10.9.7

Liquefaction of a gas depends strongly on two factors. What are they? As temperature is decreased, which gas will liquefy first—ammonia, methane, or carbon monoxide? Why?

Q10.9.8

What is a cryogenic liquid? Describe three uses of cryogenic liquids.

Q10.9.9

Air consists primarily of O_2, N_2, Ar, Ne, Kr, and Xe. Use the concepts discussed in this chapter to propose two methods by which air can be separated into its components. Which component of air will be isolated first?

Q10.9.10

How can gas liquefaction facilitate the storage and transport of fossil fuels? What are the potential drawbacks to these methods?

Numerical Problems

Q10.9.11

The van der Waals constants for xenon are a = 4.19 $(L^2 \cdot atm)/mol^2$ and b = 0.0510 L/mol. If a 0.250 mol sample of xenon in a container with a volume of 3.65 L is cooled to −90°C, what is the pressure of the sample assuming ideal gas behavior? What would be the *actual* pressure under these conditions?

Q10.9.12

The van der Waals constants for water vapor are a = 5.46 $(L^2 \cdot atm)/mol^2$ and b = 0.0305 L/mol. If a 20.0 g sample of water in a container with a volume of 5.0 L is heated to 120°C, what is the pressure of the sample assuming ideal gas behavior? What would be the *actual* pressure under these conditions?

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9.S: Gases (Summary)

10.1: Characteristics of Gases

Bulk matter can exist in three states: gas, liquid, and solid. Gases have the lowest density of the three, are highly compressible, and fill their containers completely. Elements that exist as gases at room temperature and pressure are clustered on the right side of the periodic table; they occur as either monatomic gases (the noble gases) or diatomic molecules (some halogens, N_2, O_2).

- Gases expand spontaneously to fill containers in which they are held, equaling their volume. Consequently, they are highly compressible.
- Gases form homogeneous mixtures with each other *regardless* of the identities or relative proportions of the component gases
- The characteristic properties of gases arise because the individual molecules are relatively far apart, hence, acting largely as though they were alone.

10.2: Pressure

Pressure is defined as the force exerted per unit area; it can be measured using a barometer or manometer. Four quantities must be known for a complete physical description of a sample of a gas: temperature, volume, amount, and pressure. Pressure is force per unit area of surface; the SI unit for pressure is the pascal (Pa), defined as 1 newton per square meter (N/m^2). The pressure exerted by an object is proportional to the force it exerts and inversely proportional to the area.

- Pressure, *P*, is the Force, *F*, that acts on a given Area, *A*:

$$P = F/A$$

Atmospheric Pressure and the Barometer

- The force, *F*, exerted by any object is the product of its mass, *m*, times its acceleration, *a*: *F = ma*
- SI unit for force is kg-m/s^2 and is called the *Newton* (N)
- SI unit of pressure is N/m^2, called a Pascal
- **Standard atmospheric pressure**: defined as 760 torr (760 mm Hg), or, in SI units, 101.325 kPa
- **Atmosphere**: unit of pressure equal to 760 torr; 1 atm = 101.325 kPa

10.3: The Gas Laws

The volume of a gas is inversely proportional to its pressure and directly proportional to its temperature and the amount of gas. Boyle showed that the volume of a sample of a gas is inversely proportional to pressure (Boyle's law), Charles and Gay-Lussac demonstrated that the volume of a gas is directly proportional to its temperature at constant pressure (Charles's law), and Avogadro showed that the volume of a gas is directly proportional to the number of moles of gas (Avogadro's law).

The Pressure-Volume Relationship: Boyle's Law

- Boyle's law states that the volume of a fixed quantity of gas maintained at constant temperature is inversely proportional to the pressure. When two measurements are inversely proportional, one gets smaller as the other one gets larger.

$$PV = constant$$

where P = pressure, V = volume

The Temperature-Volume Relationship: Charles's Law

- **Charles's law**: states that the volume of a fixed amount of gas maintained at constant pressure is directly proportional to its absolute temperature. Thus, as the pressure gets higher, so does the temperature.

$$\frac{V}{T} = constant$$

where V = volume, T = Temperature

The Quantity-Volume Relationship: Avogadro's Law

- **Law of combining volumes**: at a given pressure and temperature, the volumes of gases that react with one another are in the ratios of small whole numbers. (ie: $2H_2 + O_2 = 2H_2O$)

- **Avogadro's hypothesis**: equal volumes of gases at the same temperature and pressure contain equal number of molecules
- **Avogadro's law**: The volume of a gas maintained at constant temperature and pressure is directly proportional to the number of moles of the gas

$$V = constant \times n$$

where V = volume, *n* = number of moles

10.4: The Ideal Gas Equation

The empirical relationships among the volume, the temperature, the pressure, and the amount of a gas can be combined into the ideal gas law, PV = nRT. The proportionality constant, R, is called the gas constant. The ideal gas law describes the behavior of an ideal gas, a hypothetical substance whose behavior can be explained quantitatively by the ideal gas law and the kinetic molecular theory of gases. Standard temperature and pressure (STP) is 0°C and 1 atm.

Ideal-gas equation

$$PV = nRT$$

where P = pressure, V = volume, n = number of moles, R = gas constant, T = Temperature (always expressed on absolute-temperature scale, usually Kelvin)

The *Gas constant* (R) is the constant of proportionality in the ideal-gas equation. Some values of R are given below

Some values of R

Units	Numerical value
L-atm/mol-K	0.08206
Cal/mol-K	1.987
J/mol-K	8.314
M^3-Pa/mol-K	8.314
L-torr/mol-K	62.36

Standard temperature and pressure (STP): 0°C and 1 atm. 1 mol of gas at STP has a volume of 22.41 L (*molar volume*)

10.5: Further Applications of the Ideal-Gas Equations

The relationship between the amounts of products and reactants in a chemical reaction can be expressed in units of moles or masses of pure substances, of volumes of solutions, or of volumes of gaseous substances. The ideal gas law can be used to calculate the volume of gaseous products or reactants as needed. In the laboratory, gases produced in a reaction are often collected by the displacement of water from filled vessels; the amount of gas can be calculated from the volume of water displaced.

Density of a gas (*\rho\) = density, M = molar mass):

\[\rho = \dfrac{PM}{ RT} \nonumber \]

Molar mass of a gas:

$$M = \frac{\rho RT}{P}$$

10.6: Gas Mixtures and Partial Pressures

The pressure exerted by each gas in a gas mixture is independent of the pressure exerted by all other gases present. Consequently, the total pressure exerted by a mixture of gases is the sum of the partial pressures of the components (Dalton's law of partial pressures). The amount of gas in a mixture may be described by its partial pressure or its mole fraction. In a mixture, the partial pressure of each gas is the product of the total pressure and the mole fraction.

- **Partial pressure**: the pressure exerted by a particular gas in a mixture

- **Dalton's law of partial pressures**: law stating that the total pressure of a mixture of gases equals the sum of the pressures that each would exert if it were present alone

The total pressure at constant temperature and volume is determined by the total number of moles of gas present, whether that total represents just one substance or a mixture

Partial Pressures and Mole Fractions

- **Mole fraction**: the ratio of the number of one component of a mixture to the total moles of all components; abbreviated χ, with a subscript to identify the components.

The partial pressure of a gas in a mixture is its mole fraction times the total pressure

10.7: Kinetic-Molecular Theory

The behavior of ideal gases is explained by the kinetic molecular theory of gases. Molecular motion, which leads to collisions between molecules and the container walls, explains pressure, and the large intermolecular distances in gases explain their high compressibility. Although all gases have the same average kinetic energy at a given temperature, they do not all possess the same root mean square speed. The actual values of speed and kinetic energy are not the same for all gas particles.

Kinetic-molecular theory: set of assumptions about the nature of gases. These assumptions, when translated into mathematical form, yield the ideal-gas equation

1. Gases consist of large numbers of molecules that are in continuous, random motion
2. The volume of all the molecules of the gas is negligible compared to the total volume in which the gas is contained
3. Attractive and repulsive forces between gas molecules are negligible
4. Energy can be transferred between molecules during collisions, but the *average* kinetic energy of the molecules does *not* change with time, as long as the temperature of the gas remains constant
5. The average kinetic energy of the molecules is proportional to absolute temperature. At any given temperature, the molecules of all gases have the same average kinetic energy

The pressure of a gas is caused by collisions of molecules with the walls of the container. The magnitude of the pressure is determined by how often and how "hard" the molecules strike the walls.

If two different gases are at the same temperature, they have the same average kinetic energy. If the temperature of a gas is doubled, its kinetic energy also doubles. Hence, molecular motion increases with increasing temperature.

- **Root-mean-square (rms) speed**: the square root of the squared speeds of the gas molecules in a gas sample. This quantity is the speed of a molecule possessing average kinetic energy.

The rms speed is important because the average kinetic energy of the gas molecules, ε, is related directly to u^2:

$$\varepsilon = \frac{1}{2}mu^2$$

where m is the mass of the molecule

Because mass doesn't change with temperature, the rms speed (and also the average speed) of molecules must increase as temperature increases

Applications to the Gas Laws

1. *Effect of a volume increase at constant temperature*: If the volume is increased, the molecules must move a longer distance between collisions. Consequently, there are fewer collisions per unit time with the container walls, and pressure decreases.
2. *Effect of a temperature increase at constant volume*: An increases in temperature means an increase in the average kinetic energy of the molecules. If there is no change in volume, there will be more collisions with the walls per unit time. Furthermore, the molecules strike harder, hence explaining how the observed pressure increases.

10.8: Molecular Effusion and Diffusion

Diffusion is the gradual mixing of gases to form a sample of uniform composition even in the absence of mechanical agitation. In contrast, effusion is the escape of a gas from a container through a tiny opening into an evacuated space. The rate of effusion of a

gas is inversely proportional to the square root of its molar mass (Graham's law), a relationship that closely approximates the rate of diffusion. As a result, light gases tend to diffuse and effuse much more rapidly than heavier gases.

A gas composed of light gas particles will have the same average kinetic energy as one composed of much heavier particles, provided that the two gases are at the same temperature. The mass, m, of the particles in the lighter gas is smaller that that in the heavier gas. Consequently, the particles of the lighter gas must have a higher rms speed, u, than the heavier one:

$$u = \sqrt{\frac{3RT}{M}}$$

Since M is in the denominator, the less massive the gas molecules, the higher the rms speed

- **Effusion**: the escape of a gas through an orifice or hole. The rate of effusion depends on the molecular mass of the gas.
- **Diffusion**: the spreading of one substance through a space or through another substance

Graham's Law of Effusion

- **Graham's law**: law stating that the rate of effusion of a gas is inversely proportional to the square root of its molecular weight

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

where r is the rate of effusion

- The rate of effusion is also directly proportional to the rms speed of the molecules. This is because the only way for the molecule to escape is to "collide" with the opening. Hence, the faster the molecules are moving, the greater the likelihood that a molecule will hit the opening and effuse.

Diffusion and Mean Free Path

- Diffusion, like effusion, is faster for light molecules than for heavy ones. The diffusion of gases is much slower than molecular speeds because of molecular collisions. Because of these collisions, the direction of motion of a gas molecule is constantly changing, making this a slow process.
- **Mean free path**: average distance traveled by a molecule between collisions. The higher the density of a gas, the smaller the mean free path

10.9: Real Gases - Deviations from Ideal Behavior

No real gas exhibits ideal gas behavior, although many real gases approximate it over a range of conditions. Gases most closely approximate ideal gas behavior at high temperatures and low pressures. Deviations from ideal gas law behavior can be described by the van der Waals equation, which includes empirical constants to correct for the actual volume of the gaseous molecules and quantify the reduction in pressure due to intermolecular attractive forces.

The ideal gas equation may be rearranged as follows to understand deviations from ideal-gas behavior:

$$\frac{PV}{RT} = n$$

- For a mole of ideal gas (n = 1), the quantity PV / RT = 1 at all pressures. However, real gases do not behave in such a way. At high pressures, the deviation is very high, however it is less with lower pressures. In general, the deviations from idea behavior increase as temperature decreases, becoming significant near the temperature at which the gas is converted into a liquid.
- Basic assumptions in the kinetic molecular theory suggest that molecules of an ideal gas occupy no space and have no attraction for each other. *Real molecules, however, do have finite volumes, and they do attract one another*.
- Also, if the volume of the container in which the gas is contained is large, the molecules have plenty of free space, and do not take much of the container's volume itself. However, as pressure increases, the gas molecules occupy a much larger fraction of the container's volume.
- In addition, the attractive forces between molecules come into play at short distances, as when molecules are crowded together at high pressures. Because of these attractive forces, the impact of a given molecule with the wall of the container is lessened.
- Temperature determines how effective attractive forces between gas molecules are. As the gas is cooled, the average kinetic energy decreases, while intermolecular attractions remain constant.

The Van der Walls Equation

According to the ideal gas equation:

$$\underbrace{P = \frac{nRT}{V}}_{\text{ideal gas}}$$

According to Van der Waals:

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

Correction for volume of molecules – Correction for molecular attractions

- The Van der Waals constant *b* is a measure of the actual volume occupied by a mole of gas molecules; *b* has units of L/mol.
- The Van der Walls constant *a* has units of L^2-atm/mol^2. The magnitude of *a* reflects how strongly the gas molecules attract each other

Van der Waals equation

$$\left[P + \left(\frac{n^2 a}{V^2}\right)\right](V - nb) = nRT$$

The Van der Waals constants *a* and *b* are different for each gas. The values of these constants generally increase with an increase in mass of the molecule and with an increase in the complexity of its structures.

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CHAPTER OVERVIEW

10: Thermochemistry

A general chemistry Libretexts Textmap organized around the textbook

Chemistry: The Central Science

by Brown, LeMay, Bursten, Murphy, and Woodward

Template:HideTOC

This chapter introduces you to **thermochemistry**, a branch of chemistry that describes the energy changes that occur during chemical reactions. In some situations, the energy produced by chemical reactions is actually of greater interest to chemists than the material products of the reaction. For example, the controlled combustion of organic molecules, primarily sugars and fats, within our cells provides the energy for physical activity, thought, and other complex chemical transformations that occur in our bodies. Similarly, our energy-intensive society extracts energy from the combustion of fossil fuels, such as coal, petroleum, and natural gas, to manufacture clothing and furniture, heat your home in winter and cool it in summer, and power the car or bus that gets you to class and to the movies. By the end of this chapter, you will know enough about thermochemistry to explain why ice cubes cool a glass of soda, how instant cold packs and hot packs work, and why swimming pools and waterbeds are heated. You will also understand what factors determine the caloric content of your diet and why even “nonpolluting” uses of fossil fuels may be affecting the environment.

10.1: The Nature of Energy
10.2: The First Law of Thermodynamics
10.3: Enthalpy
10.4: Enthalpy of Reaction
10.5: Heat Capacity, Enthalpy, and Calorimetry
10.6: Calorimetry
10.7: Hess's Law
10.8: Enthalpies of Formation
10.9: Foods and Fuels
10.E: Thermochemistry (Exercises)
10.S: Thermochemistry (Summary)

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10.1: The Nature of Energy

Learning Objectives

- To understand the concept of energy and its various forms.
- To know the relationship between energy, work, and heat.

Because energy takes many forms, only some of which can be seen or felt, it is defined by its effect on matter. For example, microwave ovens produce energy to cook food, but we cannot see that energy. In contrast, we can see the energy produced by a light bulb when we switch on a lamp. In this section, we describe the forms of energy and discuss the relationship between energy, heat, and work.

Forms of Energy

The forms of energy include thermal energy, radiant energy, electrical energy, nuclear energy, and chemical energy (Figure 10.1.1). Thermal energy results from atomic and molecular motion; the faster the motion, the greater the thermal energy. The temperature of an object is a measure of its thermal energy content. Radiant energy is the energy carried by light, microwaves, and radio waves. Objects left in bright sunshine or exposed to microwaves become warm because much of the radiant energy they absorb is converted to thermal energy. Electrical energy results from the flow of electrically charged particles. When the ground and a cloud develop a separation of charge, for example, the resulting flow of electrons from one to the other produces lightning, a natural form of electrical energy. Nuclear energy is stored in the nucleus of an atom, and chemical energy is stored within a chemical compound because of a particular arrangement of atoms.

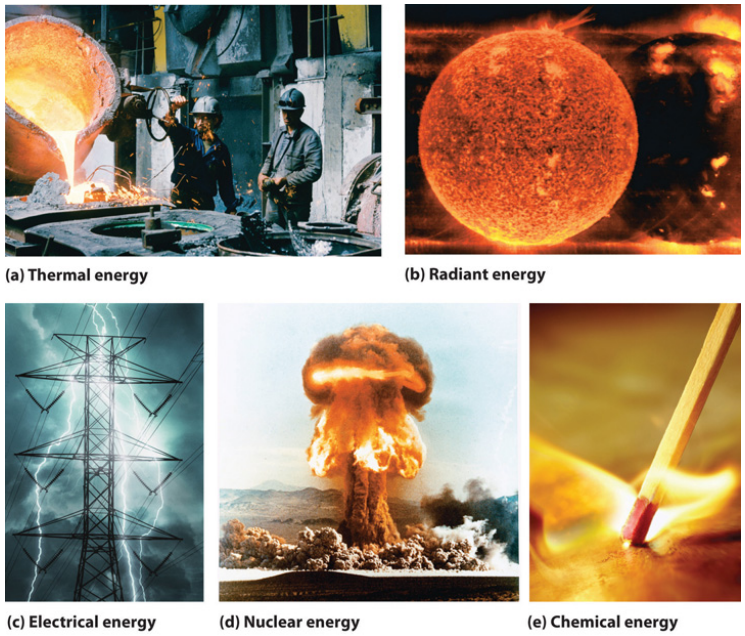


Figure 10.1.1: Forms of Energy. (a) *Thermal energy* results from atomic and molecular motion; molten steel at 2000°C has a very high thermal energy content. (b) *Radiant energy* (e.g., from the sun) is the energy in light, microwaves, and radio waves. (c) Lightning is an example of *electrical energy*, which is due to the flow of electrically charged particles. (d) *Nuclear energy* is released when particles in the nucleus of the atom are rearranged. (e) *Chemical energy* results from the particular arrangement of atoms in a chemical compound; the heat and light produced in this reaction are due to energy released during the breaking and reforming of chemical bonds.

Electrical energy, nuclear energy, and chemical energy are different forms of potential energy (PE), which is energy stored in an object because of the relative positions or orientations of its components. A brick lying on the windowsill of a 10th-floor office has a great deal of potential energy, but until its position changes by falling, the energy is contained. In contrast, kinetic energy (KE) is energy due to the motion of an object. When the brick falls, its potential energy is transformed to kinetic energy, which is then transferred to the object on the ground that it strikes. The electrostatic attraction between oppositely charged particles is a form of potential energy, which is converted to kinetic energy when the charged particles move toward each other.

Energy can be converted from one form to another (Figure 10.1.2) or, as we saw with the brick, transferred from one object to another. For example, when you climb a ladder to a high diving board, your body uses chemical energy produced by the combustion of organic molecules. As you climb, the chemical energy is converted to *mechanical work* to overcome the force of gravity. When you stand on the end of the diving board, your potential energy is greater than it was before you climbed the ladder: the greater the distance from the water, the greater the potential energy. When you then dive into the water, your potential energy is converted to kinetic energy as you fall, and when you hit the surface, some of that energy is transferred to the water, causing it to splash into the air. Chemical energy can also be converted to radiant energy; one common example is the light emitted by fireflies, which is produced from a chemical reaction.

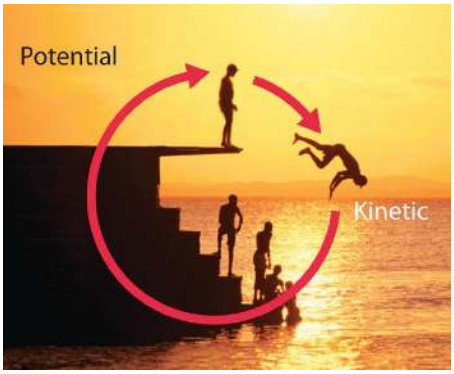


Figure 10.1.2: Interconversion of Forms of Energy. When a swimmer steps off the platform to dive into the water, potential energy is converted to kinetic energy. As the swimmer climbs back up to the top of the diving platform, chemical energy is converted to mechanical work.

Although energy can be converted from one form to another, *the total amount of energy in the universe remains constant*. This is known as the **law of conservation of energy**: *Energy cannot be created or destroyed.*

Energy, Heat, and Work

One definition of energy is the capacity to do work. The easiest form of work to visualize is mechanical work (Figure 10.1.3), which is the energy required to move an object a distance d when opposed by a force F, such as gravity:

work = force x distance

$$w = F\,d \tag{10.1.1}$$

Because the force (F) that opposes the action is equal to the mass (m) of the object times its acceleration (a), we can also write Equation 10.1.1 as follows:

work= mass x acceleration x distance

$$w = m\,a\,d \tag{10.1.2}$$

Recall from that weight is a force caused by the gravitational attraction between two masses, such as you and Earth.

Consider the mechanical work required for you to travel from the first floor of a building to the second. Whether you take an elevator or an escalator, trudge upstairs, or leap up the stairs two at a time, energy is expended to overcome the force of gravity. The amount of work done (*w*) and thus the energy required depends on three things:

1. the height of the second floor (the distance *d*);
2. your mass, which must be raised that distance against the downward acceleration due to gravity; and
3. your path.

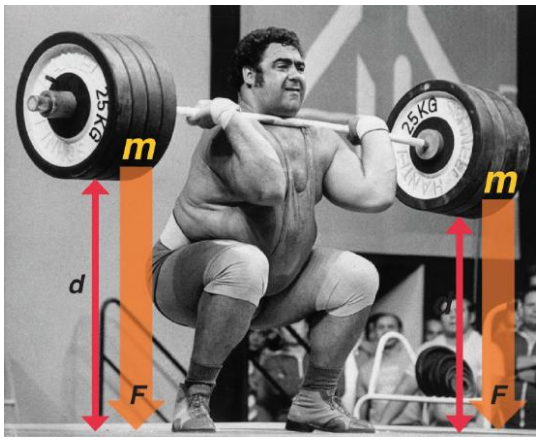


Figure 10.1.2: An Example of Mechanical Work. One form of energy is mechanical work, the energy required to move an object of mass *m* a distance *d* when opposed by a force *F*, such as gravity.

In contrast, heat (*q*) is thermal energy that can be transferred from an object at one temperature to an object at another temperature. The net transfer of thermal energy stops when the two objects reach the same temperature.

Energy is an *extensive* property of matter—for example, the amount of **thermal energy** in an object is proportional to both its mass and its temperature. A water heater that holds 150 L of water at 50°C contains much more thermal energy than does a 1 L pan of water at 50°C. Similarly, a bomb contains much more chemical energy than does a firecracker. We now present a more detailed description of kinetic and potential energy.

Kinetic and Potential Energy

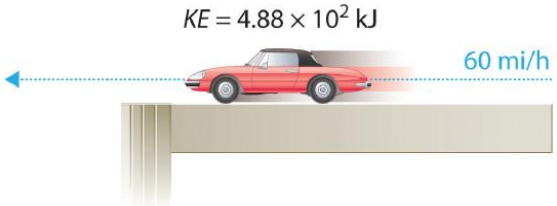
The kinetic energy of an object is related to its mass m and velocity v:

$$KE = \frac{1}{2}mv^2 \tag{10.1.3}$$

For example, the kinetic energy of a 1360 kg (approximately 3000 lb) automobile traveling at a velocity of 26.8 m/s (approximately 60 mi/h) is

$$KE = \frac{1}{2}(1360kg)(26.8ms)^2 = 4.88 \times 10^5 g \cdot m^2 \tag{10.1.4}$$

Because all forms of energy can be interconverted, energy in any form can be expressed using the same units as kinetic energy. The SI unit of energy, the joule (J), is named after the British physicist James Joule (1818–1889), an early worker in the field of energy. is defined as 1 kilogram·meter^2/second^2 (kg·m^2/s^2). Because a joule is such a small quantity of energy, chemists usually express energy in kilojoules (1 kJ = 10^3 J). For example, the kinetic energy of the 1360 kg car traveling at 26.8 m/s is 4.88 × 10^5 J or 4.88 × 10^2 kJ. It is important to remember that *the units of energy are the same regardless of the form of energy*, whether thermal, radiant, chemical, or any other form. Because heat and work result in changes in energy, their units must also be the same.



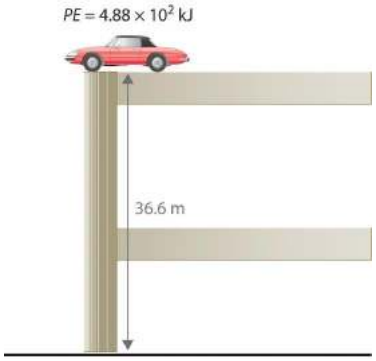
To demonstrate, let's calculate the potential energy of the same 1360 kg automobile if it were parked on the top level of a parking garage 36.6 m (120 ft) high. Its potential energy is equivalent to the amount of work required to raise the vehicle from street level to the top level of the parking garage, which is *w* = *Fd*. According to Equation 10.1.2, the force (*F*) exerted by gravity on any object is equal to its mass (*m*, in this case, 1360 kg) times the acceleration (*a*) due to gravity (*g*, 9.81 m/s^2 at Earth's surface). The distance (*d*) is the height (*h*) above street level (in this case, 36.6 m). Thus the potential energy of the car is as follows:

$$PE = F\ d = m\ a\ d = m\ g\ h \tag{10.1.5}$$

$$PE = (1360, Kg)\left(\frac{9.81\,m}{s^2}\right)(36.6\ m) = 4.88 \times 10^5\ \frac{Kg \cdot m}{s^2} \tag{10.1.6}$$

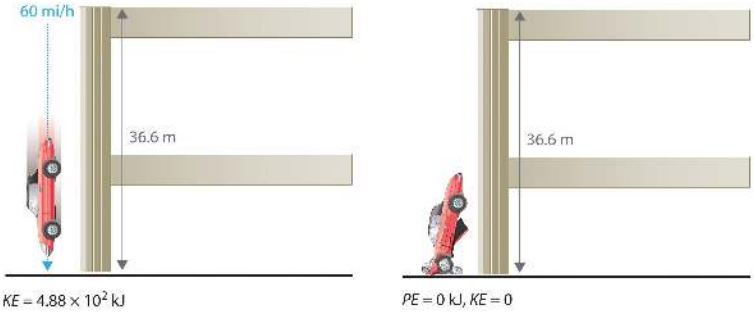
$$= 4.88 \times 10^5 J = 488\ kJ \tag{10.1.7}$$

The units of potential energy are the same as the units of kinetic energy. Notice that in this case the potential energy of the stationary automobile at the top of a 36.6 m high parking garage is the same as its kinetic energy at 60 mi/h.



If the vehicle fell from the roof of the parking garage, its potential energy would be converted to kinetic energy, and it is reasonable to infer that the vehicle would be traveling at 60 mi/h just before it hit the ground, neglecting air resistance. After the car hit the ground, its potential and kinetic energy would both be zero.

Potential energy is usually defined relative to an arbitrary standard position (in this case, the street was assigned an elevation of zero). As a result, we usually calculate only differences in potential energy: in this case, the difference between the potential energy of the car on the top level of the parking garage and the potential energy of the same car on the street at the base of the garage.



When the car is falling from the top of the parking structure it has a kinetic energy of 488 kilojoules. When the car hits the floor is has a potential and kinetic energy of zero.

Units of Energy

The units of energy are the same for all forms of energy. Energy can also be expressed in the non-SI units of calories (cal), where 1 cal was originally defined as the amount of energy needed to raise the temperature of exactly 1 g of water from 14.5°C to 15.5°C.We specify the exact temperatures because the amount of energy needed to raise the temperature of 1 g of water 1°C varies slightly with elevation. To three significant figures, however, this amount is 1.00 cal over the temperature range 0°C–100°C. The name is derived from the Latin *calor*, meaning “heat.” Although energy may be expressed as either calories or joules, calories were defined in terms of heat, whereas joules were defined in terms of motion. Because calories and joules are both units of energy, however, the calorie is now defined in terms of the joule:

$$1\ cal = 4.184\ J \text{ exactly} \tag{10.1.8}$$

$$1\ J = 0.2390\ cal \tag{10.1.9}$$

In this text, we will use the SI units—joules (J) and kilojoules (kJ)—exclusively, except when we deal with nutritional information.

Example 10.1.1

a. If the mass of a baseball is 149 g, what is the kinetic energy of a fastball clocked at 100 mi/h?
b. A batter hits a pop fly, and the baseball (with a mass of 149 g) reaches an altitude of 250 ft. If we assume that the ball was 3 ft above home plate when hit by the batter, what is the increase in its potential energy?

Given: mass and velocity or height

Asked for: kinetic and potential energy

Strategy:

Use Equation 5.1.4 to calculate the kinetic energy and Equation 5.1.6 to calculate the potential energy, as appropriate.

Solution:

a. The kinetic energy of an object is given by $\frac{1}{2}mv^2$ In this case, we know both the mass and the velocity, but we must convert the velocity to SI units:

$$v = \left(\frac{100\ \cancel{mi}}{1\ \cancel{h}}\right)\left(\frac{1\ \cancel{h}}{60\ \cancel{min}}\right)\left(\frac{1\ \cancel{min}}{60\ s}\right)\left(\frac{1.61\ \cancel{km}}{1\ \cancel{mi}}\right)\left(\frac{1000\ m}{1\ \cancel{km}}\right) = 44.7\ m/s$$

The kinetic energy of the baseball is therefore

$$KE = 1492\ \cancel{g}\left(\frac{1\ kg}{1000\ \cancel{g}}\right)\left(\frac{44.7\ m}{s}\right)^2 = 1.49 \times 10^2\ \frac{kg \cdot m^2}{s^2} = 1.49 \times 10^2\ J$$

b. The increase in potential energy is the same as the amount of work required to raise the ball to its new altitude, which is (250 − 3) = 247 feet above its initial position. Thus

$$PE = 149\ \cancel{g}\left(\frac{1\ kg}{1000\ \cancel{g}}\right)\left(\frac{9.81\ m}{s^2}\right)\left(247\ \cancel{ft}\right)\left(\frac{0.3048\ m}{1\ \cancel{ft}}\right) = 1.10 \times 10^2\ \frac{kg \cdot m^2}{s^2} = 1.10 \times 10^2\ J$$

Exercise 10.1.1

a. In a bowling alley, the distance from the foul line to the head pin is 59 ft, 10 13/16 in. (18.26 m). If a 16 lb (7.3 kg) bowling ball takes 2.0 s to reach the head pin, what is its kinetic energy at impact? (Assume its speed is constant.)
b. What is the potential energy of a 16 lb bowling ball held 3.0 ft above your foot?

Answer a

3.10×10^2 J

Answer b

65 J

Summary

All forms of energy can be interconverted. Three things can change the energy of an object: the transfer of heat, work performed on or by an object, or some combination of heat and work. *Thermochemistry* is a branch of chemistry that qualitatively and quantitatively describes the energy changes that occur during chemical reactions. **Energy** is the capacity to do work. **Mechanical work** is the amount of energy required to move an object a given distance when opposed by a force. **Thermal energy** is due to the random motions of atoms, molecules, or ions in a substance. The **temperature** of an object is a measure of the amount of thermal energy it contains. **Heat (*q*)** is the transfer of thermal energy from a hotter object to a cooler one. Energy can take many forms; most are different varieties of **potential energy (*PE*)**, energy caused by the relative position or orientation of an object. **Kinetic energy (*KE*)** is the energy an object possesses due to its motion. The most common units of energy are the **joule (J)**, defined as 1 $(kg \cdot m^2)/s^2$, and the **calorie**, defined as the amount of energy needed to raise the temperature of 1 g of water by 1°C (1 cal = 4.184 J).

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10.2: The First Law of Thermodynamics

Learning Objectives

- To calculate changes in internal energy

To study the flow of energy during a chemical reaction, we need to distinguish between a system, the small, well-defined part of the universe in which we are interested (such as a chemical reaction), and its surroundings, the rest of the universe, including the container in which the reaction is carried out (Figure 10.2.1). In the discussion that follows, the mixture of chemical substances that undergoes a reaction is always the system, and the flow of heat can be from the system to the surroundings or vice versa.

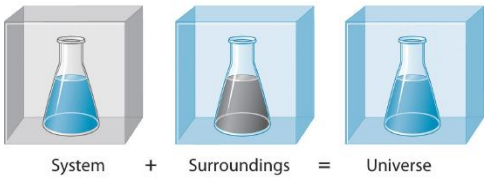


Figure 10.2.1: A System and Its Surroundings. The system is that part of the universe we are interested in studying, such as a chemical reaction inside a flask. The surroundings are the rest of the universe, including the container in which the reaction is carried out.

Three kinds of systems are important in chemistry. An **open system** can exchange both matter and energy with its surroundings. A pot of boiling water is an open system because a burner supplies energy in the form of heat, and matter in the form of water vapor is lost as the water boils. A **closed system** can exchange energy but not matter with its surroundings. The sealed pouch of a ready-made dinner that is dropped into a pot of boiling water is a closed system because thermal energy is transferred to the system from the boiling water but no matter is exchanged (unless the pouch leaks, in which case it is no longer a closed system). An **isolated system** exchanges neither energy nor matter with the surroundings. Energy is always exchanged between a system and its surroundings, although this process may take place very slowly. A truly isolated system does not actually exist. An insulated thermos containing hot coffee approximates an isolated system, but eventually the coffee cools as heat is transferred to the surroundings. In all cases, the amount of heat lost by a system is equal to the amount of heat gained by its surroundings and vice versa. That is, *the total energy of a system plus its surroundings is constant*, which must be true if *energy is conserved*.

The state of a system is a complete description of a system at a given time, including its temperature and pressure, the amount of matter it contains, its chemical composition, and the physical state of the matter. A state function is a property of a system whose magnitude depends on only the present state of the system, not its previous history. Temperature, pressure, volume, and potential energy are all state functions. The temperature of an oven, for example, is independent of however many steps it may have taken for it to reach that temperature. Similarly, the pressure in a tire is independent of how often air is pumped into the tire for it to reach that pressure, as is the final volume of air in the tire. Heat and work, on the other hand, are not state functions because they are *path dependent*. For example, a car sitting on the top level of a parking garage has the same potential energy whether it was lifted by a crane, set there by a helicopter, driven up, or pushed up by a group of students (Figure 10.2.2). The amount of work expended to get it there, however, can differ greatly depending on the path chosen. If the students decided to carry the car to the top of the ramp, they would perform a great deal more work than if they simply pushed the car up the ramp (unless, of course, they neglected to release the parking brake, in which case the work expended would increase substantially!). The potential energy of the car is the same, however, no matter which path they choose.



Figure 10.2.2: Elevation as an Example of a State Function. The change in elevation between state 1 (at the bottom of the parking garage) and state 2 (at the top level of the parking garage) is the same for both paths A and B; it does not depend on which path is taken from the bottom to the top. In contrast, the distance traveled and the work needed to reach the top do depend on which path is taken. Elevation is a state function, but distance and work are *not* state functions.

Direction of Heat Flow

The reaction of powdered aluminum with iron(III) oxide, known as the thermite reaction, generates an enormous amount of heat—enough, in fact, to melt steel (Figure 10.2.3). The balanced chemical equation for the reaction is as follows:

$$2\,\mathrm{Al(s)} + \mathrm{Fe_2O_3(s)} \longrightarrow 2\,\mathrm{Fe(s)} + \mathrm{Al_2O_3(s)} \tag{10.2.1}$$



Figure 10.2.3: The thermite reaction produces so much heat that the iron it produces comes out molten, a property that makes this reaction useful in welding. Image by Kingfisher [CC BY-SA 3.0 (Creative Commons [creativecommons.org])], from Wikimedia Commons.

We can also write this chemical equation as

$$2\,\mathrm{Al(s)} + \mathrm{Fe_2O_3(s)} \rightarrow 2\,\mathrm{Fe(s)} + \mathrm{Al_2O_3(s)} + \mathrm{heat} \tag{10.2.2}$$

to indicate that heat is one of the products. Chemical equations in which heat is shown as either a reactant or a product are called *thermochemical equations*. In this reaction, the system consists of aluminum, iron, and oxygen atoms; everything else, including the container, makes up the surroundings. During the reaction, so much heat is produced that the iron liquefies. Eventually, the system cools; the iron solidifies as heat is transferred to the surroundings. A process in which heat (q) is transferred *from* a system *to* its surroundings is described as exothermic. By convention, $q < 0$ for an exothermic reaction.

When you hold an ice cube in your hand, heat from the surroundings (including your hand) is transferred to the system (the ice), causing the ice to melt and your hand to become cold. We can describe this process by the following thermochemical equation:

$$\mathrm{heat} + \mathrm{H_2O(s)} \rightarrow \mathrm{H_2O(l)} \tag{10.2.3}$$

When heat is transferred *to* a system *from* its surroundings, the process is endothermic. By convention, $q > 0$ for an endothermic reaction.

Heat is technically not a component in Chemical Reactions

Technically, it is poor form to have a $heat$ term in the chemical reaction like in Equations 10.2.2 and 10.2.3 since is it not a true species in the reaction. However, this is a convenient approach to represent exothermic and endothermic behavior and is commonly used by chemists.

The First Law

The relationship between the energy change of a system and that of its surroundings is given by the **first law of thermodynamics**, which states that the energy of the universe is constant. We can express this law mathematically as follows:

$$U_{univ} = \Delta U_{sys} + \Delta U_{surr} = 0 \tag{10.2.4}$$

$$\Delta U_{sys} = -\Delta U_{surr} \tag{10.2.5}$$

where the subscripts univ, sys, and surr refer to the universe, the system, and the surroundings, respectively. Thus the change in energy of a system is identical in magnitude but opposite in sign to the change in energy of its surroundings.

> The tendency of all systems, chemical or otherwise, is to move toward the state with the lowest possible energy.

An important factor that determines the outcome of a chemical reaction is the tendency of all systems, chemical or otherwise, to move toward the lowest possible overall energy state. As a brick dropped from a rooftop falls, its potential energy is converted to kinetic energy; when it reaches ground level, it has achieved a state of lower potential energy. Anyone nearby will notice that energy is transferred to the surroundings as the noise of the impact reverberates and the dust rises when the brick hits the ground. Similarly, if a spark ignites a mixture of isooctane and oxygen in an internal combustion engine, carbon dioxide and water form spontaneously, while potential energy (in the form of the relative positions of atoms in the molecules) is released to the surroundings as heat and work. The internal energy content of the CO_2/H_2O product mixture is less than that of the isooctane/ O_2 reactant mixture. The two cases differ, however, in the form in which the energy is released to the surroundings. In the case of the falling brick, the energy is transferred as work done on whatever happens to be in the path of the brick; in the case of burning isooctane, the energy can be released as solely heat (if the reaction is carried out in an open container) or as a mixture of heat and work (if the reaction is carried out in the cylinder of an internal combustion engine). Because heat and work are the only two ways in which energy can be transferred between a system and its surroundings, any change in the internal energy of the system is the sum of the heat transferred (q) and the work done (w):

$$\Delta U_{sys} = q + w \tag{10.2.6}$$

Although q and w are not state functions on their own, their sum (ΔU_{sys}) is independent of the path taken and is therefore a state function. A major task for the designers of any machine that converts energy to work is to maximize the amount of work obtained and minimize the amount of energy released to the environment as heat. An example is the combustion of coal to produce electricity. Although the maximum amount of energy available from the process is fixed by the energy content of the reactants and the products, the fraction of that energy that can be used to perform useful work is not fixed.

Because we focus almost exclusively on the changes in the energy of a system, we will not use “sys” as a subscript unless we need to distinguish explicitly between a system and its surroundings.

> Although q and w are not state functions, their sum (ΔU_{sys}) is independent of the path taken and therefore is a state function.

Thus, because of the first law, we can determine ΔU for any process if we can measure both q and w. Heat, q, may be calculated by measuring a change in temperature of the surroundings. Work, w, may come in different forms, but it too can be measured. One important form of work for chemistry is *pressure-volume work* done by an expanding gas. At a constant external pressure (for example, atmospheric pressure)

$$w = -P\Delta V \tag{10.2.7}$$

The negative sign associated with PV work done indicates that the system loses energy when the volume increases. That is, an expanding gas does work on its surroundings, while a gas that is compressed has work done on it by the surroundings.

✔ Example 10.2.1

A sample of an ideal gas in the cylinder of an engine is compressed from 400 mL to 50.0 mL during the compression stroke against a constant pressure of 8.00 atm. At the same time, 140 J of energy is transferred from the gas to the surroundings as heat. What is the total change in the internal energy (ΔU) of the gas in joules?

Given: initial volume, final volume, external pressure, and quantity of energy transferred as heat

Asked for: total change in internal energy

Strategy:

A. Determine the sign of q to use in Equation 10.2.6.

B. From Equation 10.2.7 calculate w from the values given. Substitute this value into Equation 10.2.6 to calculate ΔU.

Solution

A From Equation 10.2.6, we know that ΔU = q + w. We are given the magnitude of q (140 J) and need only determine its sign. Because energy is transferred from the system (the gas) to the surroundings, q is negative by convention.

B Because the gas is being compressed, we know that work is being done on the system, so w must be positive. From Equation 10.2.6,

$$w = -P_{\text{ext}}\Delta V = -8.00\ \text{atm}(0.0500\ \text{L} - 0.400\ \text{L})\left(\frac{101.3\ \text{J}}{\text{L}\cdot\text{atm}}\right) = 284\ \text{J}$$

Thus

$$\begin{aligned}\Delta U &= q + w \\ &= -140\ J + 284\ J \\ &= 144\ J\end{aligned}$$

In this case, although work is done on the gas, increasing its internal energy, heat flows from the system to the surroundings, decreasing its internal energy by 144 J. The work done and the heat transferred can have opposite signs.

? Exercise 10.2.1

A sample of an ideal gas is allowed to expand from an initial volume of 0.200 L to a final volume of 3.50 L against a constant external pressure of 0.995 atm. At the same time, 117 J of heat is transferred from the surroundings to the gas. What is the total change in the internal energy (ΔU) of the gas in joules?

Answer

−216 J

By convention (to chemists), both heat flow and work have a negative sign when energy is transferred from a system to its surroundings and vice versa.

Summary

In chemistry, the small part of the universe that we are studying is the **system**, and the rest of the universe is the **surroundings**. **Open systems** can exchange both matter and energy with their surroundings, **closed systems** can exchange energy but not matter with their surroundings, and **isolated systems** can exchange neither matter nor energy with their surroundings. A **state function** is a property of a system that depends on only its present **state**, not its history. A reaction or process in which heat is transferred from a system to its surroundings is **exothermic**. A reaction or process in which heat is transferred to a system from its surroundings is **endothermic**. The first law of thermodynamics states that the energy of the universe is constant. The change in the internal energy of a system is the sum of the heat transferred and the work done. The heat flow is equal to the change in the internal energy of the system plus the PV work done. When the volume of a system is constant, changes in its internal energy can be calculated by substituting the ideal gas law into the equation for ΔU.

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10.3: Enthalpy

Learning Objectives

- To know the key features of a state function.
- To use Hess's law and thermochemical cycles to calculate enthalpy changes of chemical reactions.

Both heat and work represent energy transfer mechanisms. As discussed previously, the term "heat" refers to a *process* in which a body (the contents of a tea kettle, for example) acquires or loses energy as a direct consequence of its having a *different temperature* than its surroundings. Similarly, work refers to the transfer of energy that does not involve temperature differences. Hence, work, like energy, can take various forms, the most familiar being mechanical and electrical.

- *Mechanical work* arises when an object moves a distance Δx against an opposing force f:

$$w_{mechanical} = f\ \Delta x$$

- *Electrical work* is done when a body having a charge q moves through a potential difference ΔV.

$$w_{electrical} = q\Delta V$$

The unit of work is Joules. Work, like heat, exists only when energy is being transferred. When two bodies are placed in thermal contact and energy flows from the warmer body to the cooler one, this process is called "heat". A transfer of energy to or from a system by any means other than heat is called "work".

Enthalpy as a Composite Function

To further understand the relationship between heat flow (q) and the resulting change in internal energy (ΔU), we can look at two sets of limiting conditions: reactions that occur at constant volume and reactions that occur at constant pressure. We will assume that PV work is the only kind of work possible for the system, so we can substitute its definition $w = -P\Delta V$ into the first Law of Thermodynamics ($\Delta U = q + w$) to obtain the following:

$$\Delta U = q - P\Delta V \tag{10.3.1}$$

where the subscripts have been deleted.

If the reaction occurs in a closed vessel, the volume of the system is fixed, and ΔV is zero. Under these conditions, the heat flow (often given the symbol q_v to indicate constant volume) must equal ΔU:

$$\underset{\text{constant volume}}{q_v = \Delta U} \tag{10.3.2}$$

> *At constant volume, no PV work can be done, and the change in the internal energy of the system is equal to the amount of heat transferred from the system to the surroundings or vice versa.*

Many chemical reactions are not, however, carried out in sealed containers at constant volume but in open containers at a more or less constant pressure of about 1 atm. The heat flow under these conditions is given the symbol q_p to indicate constant pressure. Replacing q in Equation 10.3.2by q_p and rearranging to solve for q_p,

$$\underset{\text{constant pressure}}{q_p = \Delta U + P\Delta V} \tag{10.3.3}$$

Thus, at constant pressure, the heat flow for any process is equal to the change in the internal energy of the system plus the PV work done.

Because conditions of constant pressure are so important in chemistry, a new state function called enthalpy (H) is defined as

$$H = U + PV$$

At constant pressure, the change in the enthalpy of a system is as follows:

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + P\Delta V \tag{10.3.4}$$

Comparing the previous two equations shows that at constant pressure, the change in the enthalpy of a system is equal to the heat flow: $\Delta H = q_p$. This expression is consistent with our definition of enthalpy, where we stated that enthalpy is the heat absorbed or produced during any process that occurs at constant pressure.

> *At constant pressure, the change in the enthalpy of a system is equal to the heat flow:* $\Delta H = q_p$.

Example 10.3.1

The molar enthalpy of fusion for ice at 0.0°C and a pressure of 1.00 atm is 6.01 kJ, and the molar volumes of ice and water at 0°C are 0.0197 L and 0.0180 L, respectively. Calculate ΔH and ΔU for the melting of ice at 0.0°C.

Given: enthalpy of fusion for ice, pressure, and molar volumes of ice and water

Asked for: ΔH and ΔU for ice melting at 0.0°C

Strategy:

A. Determine the sign of q and set this value equal to ΔH.
B. Calculate Δ(PV) from the information given.
C. Determine ΔU by substituting the calculated values into Equation 10.3.4.

Solution

A Because 6.01 kJ of heat is absorbed from the surroundings when 1 mol of ice melts, q = +6.01 kJ. When the process is carried out at constant pressure, $q = q_p = \Delta H = 6.01$ kJ.

B To find ΔU using Equation ???, we need to calculate Δ(PV). The process is carried out at a constant pressure of 1.00 atm, so

$$\Delta(PV) = P\Delta V = P(V_f - V) = (1.00\ \text{atm})(0.0180\ \text{L} - 0.0197\ \text{L}) \tag{10.3.5}$$

$$= (-1.7 \times 10^{-3}\ \text{L}\cdot\text{atm})(101.3\ \text{J/L}\cdot\text{atm}) = -0.0017\ \text{J} \tag{10.3.6}$$

C Substituting the calculated values of ΔH and PΔV into Equation 18.11,

$$\Delta U = \Delta H - P\Delta V = 6010\ \text{J} - (-0.0017\ \text{J}) = 6010\ \text{J} = 6.01\ \text{kJ}$$

Exercise 10.3.1

At 298 K and 1 atm, the conversion of graphite to diamond requires the input of 1.850 kJ of heat per mole of carbon. The molar volumes of graphite and diamond are 0.00534 L and 0.00342 L, respectively. Calculate ΔH and ΔU for the conversion of C (graphite) to C (diamond) under these conditions.

Answer a

ΔH = 1.85 kJ/mol

Answer b

ΔU = 1.85 kJ/mol

The Relationship between ΔH and ΔU

If ΔH for a reaction is known, we can use the change in the enthalpy of the system (Equation 10.3.4) to calculate its change in internal energy. When a reaction involves only solids, liquids, liquid solutions, or any combination of these, the volume does not change appreciably (ΔV = 0). Under these conditions, we can simplify Equation 10.3.4 to ΔH = ΔU. If gases are involved, however, ΔH and ΔU can differ significantly. We can calculate ΔU from the measured value of ΔH by using the right side of Equation 10.3.4 together with the ideal gas law, PV = nRT. Recognizing that Δ(PV) = Δ(nRT), we can rewrite Equation 10.3.4 as follows:

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + \Delta(nRT) \tag{10.3.7}$$

At constant temperature, Δ(nRT) = RTΔn, where Δn is the difference between the final and initial numbers of moles of gas. Thus

$$\Delta U = \Delta H - RT\Delta n \tag{10.3.8}$$

For reactions that result in a net production of gas, Δn > 0, so ΔU < ΔH. Conversely, endothermic reactions (ΔH > 0) that result in a net consumption of gas have Δn < 0 and ΔU > ΔH. The relationship between ΔH and ΔU for systems involving gases is illustrated in Example 10.3.2

For reactions that result in a net production of gas, ΔU < ΔH. For endothermic reactions that result in a net consumption of gas, ΔU > ΔH.

Example 10.3.2: The Relationship Between ΔH and ΔU in Gas Evolving Reactions

The combustion of graphite to produce carbon dioxide is described by the equation

$$C_{(graphite,s)} + O_{2(g)} \rightarrow CO_{2(g)}$$

At 298 K and 1.0 atm, ΔH = −393.5 kJ/mol of graphite for this reaction, and the molar volume of graphite is 0.0053 L. What is ΔU for the reaction?

Given: balanced chemical equation, temperature, pressure, ΔH, and molar volume of reactant

Asked for: ΔU

Strategy:

A. Use the balanced chemical equation to calculate the change in the number of moles of gas during the reaction.
B. Substitute this value and the data given into Equation 10.3.8 to obtain ΔU.

Solution

A In this reaction, 1 mol of gas (CO_2) is produced, and 1 mol of gas (O_2) is consumed. Thus Δn = 1 − 1 = 0.

B Substituting this calculated value and the given values into Equation 10.3.8,

$$\begin{aligned}\Delta U &= \Delta H - RT\Delta n = (-393.5\text{ kJ/mol}) - [8.314\text{ J/(mol·K)}](298\text{ K})(0)\\ &= (-393.5\text{ kJ/mol}) - (0\text{ J/mol}) = -393.5\text{ kJ/mol}\end{aligned}$$

To understand why only the change in the volume of the gases needs to be considered, notice that the molar volume of graphite is only 0.0053 L. A change in the number of moles of gas corresponds to a volume change of 22.4 L/mol of gas at standard temperature and pressure (STP), so the volume of gas consumed or produced in this case is (1)(22.4 L) = 22.4 L, which is much, much greater than the volume of 1 mol of a solid such as graphite.

Exercise 10.3.2

Calculate ΔU for the conversion of oxygen gas to ozone at 298 K:

$$3O_2(g) \rightarrow 2O_3(g).$$

The value of ΔH for the reaction is 285.4 kJ.

Answer

288 kJ

As Example 10.3.2 illustrates, the magnitudes of ΔH and ΔU for reactions that involve gases are generally rather similar, even when there is a net production or consumption of gases.

Summary

Enthalpy is a state function, and the change in enthalpy of a system is equal to the sum of the change in the internal energy of the system and the PV work done. Enthalpy is a state function whose change indicates the amount of heat transferred from a system to its surroundings or vice versa, at constant pressure. The change in the internal energy of a system is the sum of the heat transferred and the work done. At constant pressure, heat flow (q) and internal energy (U) are related to the system's enthalpy (H). The heat

flow is equal to the change in the internal energy of the system plus the PV work done. When the volume of a system is constant, changes in its internal energy can be calculated by substituting the ideal gas law into the equation for ΔU.

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10.4: Enthalpy of Reaction

Learning Objectives

- To understand how enthalpy pertains to chemical reactions

We have stated that the change in energy (ΔU) is equal to the sum of the heat produced and the work performed. Work done by an expanding gas is called *pressure-volume work*, (or just PV *work)*. Consider, for example, a reaction that produces a gas, such as dissolving a piece of copper in concentrated nitric acid. The chemical equation for this reaction is as follows:

$$\mathrm{Cu(s) + 4\,HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2\,H_2O(l) + 2\,NO_2(g)}$$

If the reaction is carried out in a closed system that is maintained at constant pressure by a movable piston, the piston will rise as nitrogen dioxide gas is formed (Figure 10.4.1). The system is performing work by lifting the piston against the downward force exerted by the atmosphere (i.e., *atmospheric pressure*). We find the amount of PV work done by multiplying the external pressure P by the change in volume caused by movement of the piston (ΔV). At a constant external pressure (here, atmospheric pressure),

$$w = -P\Delta V \tag{10.4.1}$$

The negative sign associated with PV work done indicates that the system loses energy when the volume increases. If the volume increases at constant pressure ($\Delta V > 0$), the work done by the system is negative, indicating that a system has lost energy by performing work on its surroundings. Conversely, if the volume decreases ($\Delta V < 0$), the work done by the system is positive, which means that the surroundings have performed work on the system, thereby increasing its energy.

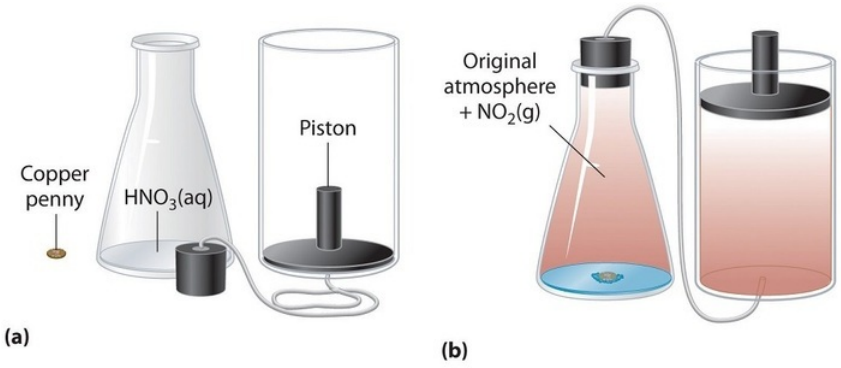


Figure 10.4.1: An Example of Work Performed by a Reaction Carried Out at Constant Pressure. (a) Initially, the system (a copper penny and concentrated nitric acid) is at atmospheric pressure. (b) When the penny is added to the nitric acid, the volume of NO_2 gas that is formed causes the piston to move upward to maintain the system at atmospheric pressure. In doing so, the system is performing work on its surroundings. (CC BY-NC-SA; anonymous)

The internal energy U of a system is the sum of the kinetic energy and potential energy of all its components. It is the change in internal energy that produces heat plus work. To measure the energy changes that occur in chemical reactions, chemists usually use a related thermodynamic quantity called **enthalpy** (H) (from the Greek *enthalpein*, meaning "to warm"). The enthalpy of a system is defined as the sum of its internal energy U plus the product of its pressure P and volume V:

\[H =U + PV \label{5.4.3} \]

Because internal energy, pressure, and volume are all state functions, enthalpy is also a state function. So we can define a change in enthalpy (ΔH) accordingly

$$\Delta H = H_{final} - H_{initial}$$

If a chemical change occurs at constant pressure (i.e., for a given P, $\Delta P = 0$), the change in enthalpy (ΔH) is

$$\Delta H = \Delta(U + PV) \tag{10.4.2}$$

$$= \Delta U + \Delta PV \tag{10.4.3}$$

$$= \Delta U + P\Delta V \tag{10.4.4}$$

Substituting $q + w$ for ΔU (First Law of Thermodynamics) and $-w$ for $P\Delta V$ (Equation 10.4.1) into Equation 10.4.4, we obtain

$$\Delta H = \Delta U + P\Delta V \tag{10.4.5}$$

$$= q_p + \cancel{w} - \cancel{w} \tag{10.4.6}$$

$$= q_p \tag{10.4.7}$$

The subscript p is used here to emphasize that this equation is true only for a process that occurs at constant pressure. From Equation 10.4.7 we see that at constant pressure the change in enthalpy, ΔH of the system, is equal to the heat gained or lost.

$$\Delta H = H_{final} - H_{initial} \tag{10.4.8}$$

$$= q_p \tag{10.4.9}$$

Just as with ΔU, because enthalpy is a state function, the magnitude of ΔH depends on only the initial and final states of the system, not on the path taken. Most important, the enthalpy change is the same even if the process does *not* occur at constant pressure.

> *To find ΔH for a reaction, measure q_p.*

When we study energy changes in chemical reactions, the most important quantity is usually the enthalpy of reaction (ΔH_{rxn}), the change in enthalpy that occurs during a reaction (such as the dissolution of a piece of copper in nitric acid). If heat flows from a system to its surroundings, the enthalpy of the system decreases, so ΔH_{rxn} is negative. Conversely, if heat flows from the surroundings to a system, the enthalpy of the system increases, so ΔH_{rxn} is positive. Thus:

- $\Delta H_{rxn} < 0$ for an *exothermic reaction*, and
- $\Delta H_{rxn} > 0$ for an *endothermic reaction*.

In chemical reactions, bond breaking requires an input of energy and is therefore an endothermic process, whereas bond making releases energy, which is an exothermic process. The sign conventions for heat flow and enthalpy changes are summarized in the following table:

sign conventions for heat flow and enthalpy changes

Reaction Type	q	ΔH_{rxn}
exothermic	< 0	< 0 (heat flows from a system to its surroundings)
endothermic	> 0	> 0 (heat flows from the surroundings to a system)

If ΔH_{rxn} is negative, then the enthalpy of the products is less than the enthalpy of the reactants; that is, *an exothermic reaction is energetically downhill* (Figure 10.4.2*a*). Conversely, if ΔH_{rxn} is positive, then the enthalpy of the products is greater than the enthalpy of the reactants; thus, *an endothermic reaction is energetically uphill* (Figure 10.4.2*b*). Two important characteristics of enthalpy and changes in enthalpy are summarized in the following discussion.

> *Bond breaking **ALWAYS** requires an input of energy; bond making **ALWAYS** releases energy.y.*

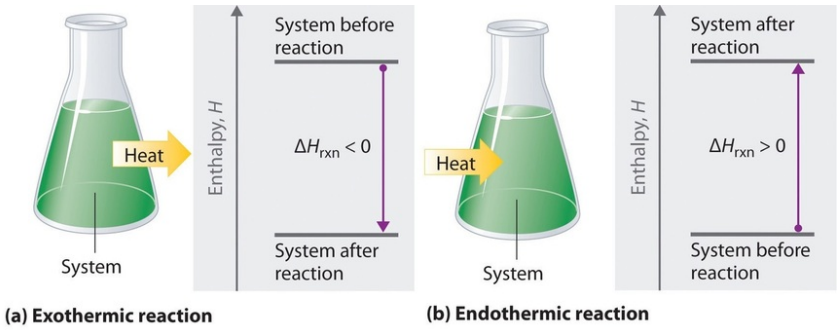


Figure 10.4.2: The Enthalpy of Reaction. Energy changes in chemical reactions are usually measured as changes in enthalpy. (a) If heat flows from a system to its surroundings, the enthalpy of the system decreases, ΔH_{rxn} is negative, and the reaction is exothermic; it is energetically downhill. (b) Conversely, if heat flows from the surroundings to a system, the enthalpy of the system increases, ΔH_{rxn} is positive, and the reaction is endothermic; it is energetically uphill. (CC BY-NC-SA; anonymous)

- **Reversing a reaction or a process changes the sign of Δ*H*.** Ice *absorbs* heat when it melts (electrostatic interactions are broken), so liquid water must *release* heat when it freezes (electrostatic interactions are formed):

$$heat + H_2O(s) \rightarrow H_2O(l) \qquad \Delta H > 0$$
$$H_2O(l) \rightarrow H_2O(s) + heat \qquad \Delta H < 0$$

  In both cases, the *magnitude* of the enthalpy change is the same; only the *sign* is different.

- **Enthalpy is an extensive property (like mass).** The magnitude of ΔH for a reaction is proportional to the amounts of the substances that react. For example, a large fire produces more heat than a single match, even though the chemical reaction—the combustion of wood—is the same in both cases. For this reason, the enthalpy change for a reaction is usually given in kilojoules per mole of a particular reactant or product. Consider Equation 10.4.10, which describes the reaction of aluminum with iron(III) oxide (Fe_2O_3) at constant pressure. According to the reaction stoichiometry, 2 mol of Fe, 1 mol of Al_2O_3, and 851.5 kJ of heat are produced for every 2 mol of Al and 1 mol of Fe_2O_3 consumed:

$$2\,\mathrm{Al(s)} + \mathrm{Fe_2O_3(s)} \longrightarrow 2\,\mathrm{Fe(s)} + \mathrm{Al_2O_3(s)} + 815.5\ kJ \tag{10.4.10}$$

  Thus Δ*H* = −851.5 kJ/mol of Fe_2O_3. We can also describe Δ*H* for the reaction as −425.8 kJ/mol of Al: because 2 mol of Al are consumed in the balanced chemical equation, we divide −851.5 kJ by 2. When a value for Δ*H*, in kilojoules rather than kilojoules per mole, is written after the reaction, as in Equation 10.4.11, it is the value of Δ*H* corresponding to the reaction of the molar quantities of reactants as given in the balanced chemical equation:

$$2\,\mathrm{Al(s)} + \mathrm{Fe_2O_3(s)} \longrightarrow 2\,\mathrm{Fe(s)} + \mathrm{Al_2O_3(s)} \quad \Delta H_{rxn} = -851.5\ kJ \tag{10.4.11}$$

  If 4 mol of Al and 2 mol of Fe_2O_3 react, the change in enthalpy is 2 × (−851.5 kJ) = −1703 kJ. We can summarize the relationship between the amount of each substance and the enthalpy change for this reaction as follows:

$$-\frac{851.5\ kJ}{2\ mol\ Al} = -\frac{425.8\ kJ}{1\ mol\ Al} = -\frac{1703\ kJ}{4\ mol\ Al} \tag{10.4.12}$$

The relationship between the magnitude of the enthalpy change and the mass of reactants is illustrated in Example 10.4.1.

✔ Example 10.4.1: Melting Icebergs

Certain parts of the world, such as southern California and Saudi Arabia, are short of freshwater for drinking. One possible solution to the problem is to tow icebergs from Antarctica and then melt them as needed. If ΔH is 6.01 kJ/mol for the reaction at 0°C and constant pressure:

$$\mathrm{H_2O(s) \rightarrow H_2O(l)}$$

How much energy would be required to melt a moderately large iceberg with a mass of 1.00 million metric tons (1.00×10^6 metric tons)? (A metric ton is 1000 kg.)

Given: energy per mole of ice and mass of iceberg

Asked for: energy required to melt iceberg

Strategy:

A. Calculate the number of moles of ice contained in 1 million metric tons (1.00×10^6 metric tons) of ice.

B. Calculate the energy needed to melt the ice by multiplying the number of moles of ice in the iceberg by the amount of energy required to melt 1 mol of ice.

Solution:

A Because enthalpy is an extensive property, the amount of energy required to melt ice depends on the amount of ice present. We are given ΔH for the process—that is, the amount of energy needed to melt 1 mol (or 18.015 g) of ice—so we need to calculate the number of moles of ice in the iceberg and multiply that number by ΔH (+6.01 kJ/mol):

$$moles\ H_2O = 1.00 \times 10^6\ \cancel{\text{metric ton}}\ \text{H}_2\text{O} \left(\frac{1000\ \cancel{kg}}{1\ \cancel{\text{metric ton}}}\right)\left(\frac{1000\ \cancel{g}}{1\ \cancel{kg}}\right)\left(\frac{1\ mol\ H_2O}{18.015\ \cancel{g\ H_2O}}\right)$$

$$= 5.55 \times 10^{10}\ mol\,\text{H}_2\text{O}$$

B The energy needed to melt the iceberg is thus

$$\left(\frac{6.01\ kJ}{\cancel{mol\ H_2O}}\right)\left(5.55 \times 10^{10}\ \cancel{mol\ H_2O}\right) = 3.34 \times 10^{11}\ kJ$$

Because so much energy is needed to melt the iceberg, this plan would require a relatively inexpensive source of energy to be practical. To give you some idea of the scale of such an operation, the amounts of different energy sources equivalent to the amount of energy needed to melt the iceberg are shown below.

Possible sources of the approximately $3.34 \times 10^{11}\ kJ$ needed to melt a 1.00×10^6 metric ton iceberg

- Combustion of 3.8×10^3 ft^3 of natural gas
- Combustion of 68,000 barrels of oil
- Combustion of 15,000 tons of coal
- 1.1×10^8 kilowatt-hours of electricity

Alternatively, we can rely on ambient temperatures to slowly melt the iceberg. The main issue with this idea is the cost of dragging the iceberg to the desired place.

? Exercise 10.4.1: Thermite Reaction

If 17.3 g of powdered aluminum are allowed to react with excess Fe_2O_3, how much heat is produced?

Answer

273 kJ

Enthalpies of Reaction

One way to report the heat absorbed or released would be to compile a massive set of reference tables that list the enthalpy changes for all possible chemical reactions, which would require an incredible amount of effort. Fortunately, since enthalpy is a state function, all we have to know is the initial and final states of the reaction. This allows us to calculate the enthalpy change for virtually any conceivable chemical reaction using a relatively small set of tabulated data, such as the following:

- Enthalpy of combustion (ΔH_{comb}) The change in enthalpy that occurs during a combustion reaction. Enthalpy changes have been measured for the combustion of virtually any substance that will burn in oxygen; these values are usually reported as the enthalpy of combustion per mole of substance.
- Enthalpy of fusion (ΔH_{fus}) The enthalpy change that acompanies the melting (fusion) of 1 mol of a substance. The enthalpy change that accompanies the melting, or fusion, of 1 mol of a substance; these values have been measured for almost all the elements and for most simple compounds.
- Enthalpy of vaporization (ΔH_{vap}) The enthalpy change that accompanies the vaporization of 1 mol of a substance. The enthalpy change that accompanies the vaporization of 1 mol of a substance; these values have also been measured for nearly all the

elements and for most volatile compounds.

- Enthalpy of solution (ΔH_{soln}) The change in enthalpy that occurs when a specified amount of solute dissolves in a given quantity of solvent. The enthalpy change when a specified amount of solute dissolves in a given quantity of solvent.

Table 10.4.1: Enthalpies of Vaporization and Fusion for Selected Substances at Their Boiling Points and Melting Points

Substance	ΔH_{vap} (kJ/mol)	ΔH_{fus} (kJ/mol)
argon (Ar)	6.3	1.3
methane (CH_4)	9.2	0.84
ethanol (CH_3CH_2OH)	39.3	7.6
benzene (C_6H_6)	31.0	10.9
water (H_2O)	40.7	6.0
mercury (Hg)	59.0	2.29
iron (Fe)	340	14

> The sign convention is the same for all enthalpy changes: negative if heat is released by the system and positive if heat is absorbed by the system.



Enthalpy of Reaction: Enthalpy of Reaction, YouTube(opens in new window) [youtu.be]

Summary

For a chemical reaction, the **enthalpy of reaction** (ΔH_{rxn}) is the difference in enthalpy between products and reactants; the units of ΔH_{rxn} are kilojoules per mole. Reversing a chemical reaction reverses the sign of ΔH_{rxn}.

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10.5: Heat Capacity, Enthalpy, and Calorimetry

Learning Objectives

- Explain the technique of calorimetry
- Calculate and interpret heat and related properties using typical calorimetry data
- To use calorimetric data to calculate enthalpy changes.

Heat Capacity

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)

$$C = \frac{q}{\Delta T} \tag{10.5.1}$$

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 18,140 J of energy to raise the temperature of the pan by 50.0 °C

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

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

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

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

$$c = \frac{q}{m\Delta T} \tag{10.5.2}$$

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:

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

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

$$c_{iron} = \frac{90,700 J}{(4,040\ g)(50.0\ ^\circ C)} = 0.449\ J/g\ ^\circ C$$

Although the large pan is more massive than the small pan, since both are made of the same material, they both yield the same value for specific heat (for the material of construction, iron). Note that specific heat is measured in units of energy per temperature per mass and is an intensive property, being derived from a ratio of two extensive properties (heat and mass). The molar heat capacity, also an intensive property, is the heat capacity per mole of a particular substance and has units of J/mol °C (Figure 10.5.1).



Figure 10.5.1: Due to its larger mass, a large frying pan has a larger heat capacity than a small frying pan. Because they are made of the same material, both frying pans have the same specific heat. (CC BY; Mark Blaser via OpenStax).

The heat capacity of an object depends on both its *mass* and its *composition*. For example, doubling the mass of an object doubles its heat capacity. Consequently, the amount of substance must be indicated when the heat capacity of the substance is reported. The molar heat capacity (C_p) is the amount of energy needed to increase the temperature of 1 mol of a substance by 1°C; the units of C_p are thus J/(mol•°C).The subscript *p* indicates that the value was measured at constant pressure. The specific heat (c_s) is the amount of energy needed to increase the temperature of 1 g of a substance by 1°C; its units are thus J/(g•°C).

We can relate the quantity of a substance, the amount of heat transferred, its heat capacity, and the temperature change either via moles (Equation 10.5.3) or mass (Equation 10.5.4):

$$q = nc_p\Delta T \tag{10.5.3}$$

where

- n is the number of moles of substance and
- c_p is the *molar heat capacity* (i.e., heat capacity per **mole** of substance), and
- $\Delta T = T_{final} - T_{initial}$ is the temperature change.

$$q = mc_s\Delta T \tag{10.5.4}$$

where

- m is the mass of substance in grams,
- c_s is the *specific heat* (i.e., heat capacity per **gram** of substance), and
- $\Delta T = T_{final} - T_{initial}$ is the temperature change.

Both Equations 10.5.3 and 10.5.4 are under constant pressure (which matters) and both show that we know the amount of a substance and its specific heat (for mass) or molar heat capcity (for moles), 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.

The specific heats of some common substances are given in Table 10.5.1. Note that the specific heat values of most solids are less than 1 J/(g•°C), whereas those of most liquids are about 2 J/(g•°C). Water in its solid and liquid states is an exception. The heat capacity of ice is twice as high as that of most solids; the heat capacity of liquid water, 4.184 J/(g•°C), is one of the highest known. 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 10.5.1.

Table 10.5.1: 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

Substance	Symbol (state)	Specific Heat (J/g °C)
nitrogen	$N_2(g)$	1.040
air	mixture	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
quartz	$SiO_2(s)$	0.730

The value of C is intrinsically a positive number, but ΔT and q can be either positive or negative, and they both must have the same sign. If ΔT and q are positive, then *heat flows from the surroundings into an object*. If ΔT and q are negative, then *heat flows from an object into its surroundings*.

If a substance gains thermal energy, its temperature increases, its final temperature is higher than its initial temperature, then $\Delta T > 0$ and q is positive. If a substance loses thermal energy, its temperature decreases, the final temperature is lower than the initial temperature, so $\Delta T < 0$ and q is negative.

Example 10.5.1: Measuring Heat

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

Solution

To answer this question, consider these factors:

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

The specific heat of water is 4.184 J/g °C (Table 10.5.1), so to heat 1 g of water by 1 °C requires 4.184 J. We note that since 4.184 J is required to heat 1 g of water by 1 °C, we will need 800 times as much to heat 800 g of water by 1 °C. Finally, we observe that since 4.184 J are required to heat 1 g of water by 1 °C, we will need 64 times as much to heat it by 64 °C (that is, from 21 °C to 85 °C).

This can be summarized using Equation 10.5.4:

$$\begin{aligned} q &= mc_s\Delta T \\ &= mc_s(T_{\text{final}} - T_{\text{initial}}) \\ &= (4.184\ \text{J}/\cancel{\text{g}}^\circ\text{C}) \times (800\ \cancel{\text{g}}) \times (85-21)^\circ\text{C} \\ &= (4.184\ \text{J}/\cancel{\text{g}}^\circ\cancel{\text{C}}) \times (800\ \cancel{\text{g}}) \times (64)^\circ\cancel{\text{C}} \\ &= 210,000\ \text{J} (= 210\ \text{kJ}) \end{aligned}$$

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

Exercise 10.5.1

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

Answer

$5.07 \times 10^4\ J$

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 10.5.2: 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 Equation 10.5.4:

$$q = mc_s\Delta T \qquad = mc_s(T_{final} - T_{initial})$$

Substituting the known values:

$$6,640\ J = (348\ g)c_s(43.6 - 22.4)\ ^\circ C$$

Solving:

$$c = \frac{6,640\ J}{(348\ g)(21.2^\circ C)} = 0.900\ J/g\ ^\circ C$$

Comparing this value with the values in Table 10.5.1, this value matches the specific heat of aluminum, which suggests that the unknown metal may be aluminum.

Exercise 10.5.2

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

$c = 0.45\ J/g\ ^\circ C$; the metal is likely to be iron from checking Table 10.5.1

Example 10.5.3: Solar Heating

A home solar energy storage unit uses 400 L of water for storing thermal energy. On a sunny day, the initial temperature of the water is 22.0°C. During the course of the day, the temperature of the water rises to 38.0°C as it circulates through the water wall. How much energy has been stored in the water? (The density of water at 22.0°C is 0.998 g/mL.)



Passive solar system. During the day (a), sunlight is absorbed by water circulating in the water wall. At night (b), heat stored in the water wall continues to warm the air inside the house.

Given: volume and density of water and initial and final temperatures

Asked for: amount of energy stored

Strategy:

A. Use the density of water at 22.0°C to obtain the mass of water (m) that corresponds to 400 L of water. Then compute ΔT for the water.
B. Determine the amount of heat absorbed by substituting values for m, c_s, and ΔT into Equation 10.5.1.

Solution:

A The mass of water is

$$mass\ of\ H_2O = 400\ \cancel{L}\left(\frac{1000\ \cancel{mL}}{1\ \cancel{L}}\right)\left(\frac{0.998\ g}{1\ \cancel{mL}}\right) = 3.99\times10^5 g\ H_2O$$

The temperature change (ΔT) is 38.0°C − 22.0°C = +16.0°C.

B From Table 10.5.1, the specific heat of water is 4.184 J/(g•°C). From Equation 10.5.4, the heat absorbed by the water is thus

$$q = mc_s\Delta T = \left(3.99\times10^5\ \cancel{g}\right)\left(\frac{4.184\ J}{\cancel{g}\cdot\cancel{^\circ C}}\right)\left(16.0\ \cancel{^\circ C}\right) = 2.67\times10^7 J = 2.67\times10^4 kJ$$

Both q and ΔT are positive, consistent with the fact that the water has absorbed energy.

? Exercise 10.5.3: Solar Heating

Some solar energy devices used in homes circulate air over a bed of rocks that absorb thermal energy from the sun. If a house uses a solar heating system that contains 2500 kg of sandstone rocks, what amount of energy is stored if the temperature of the rocks increases from 20.0°C to 34.5°C during the day? Assume that the specific heat of sandstone is the same as that of quartz (SiO_2) in Table 10.5.1.

Answer

$2.7\times10^4\ kJ$

Even though the mass of sandstone is more than six times the mass of the water in Example 10.5.1, the amount of thermal energy stored is the same to two significant figures.

Heat "Flow" to Thermal Equilibrium

When two objects at different temperatures are placed in contact, heat flows from the warmer object to the cooler one until the temperature of both objects is the same. The law of conservation of energy says that the total energy cannot change during this

process:

$$q_{cold} + q_{hot} = 0 \tag{10.5.5}$$

The equation implies that the amount of heat that flows *from* a warmer object is the same as the amount of heat that flows *into* a cooler object. Because the direction of heat flow is opposite for the two objects, the sign of the heat flow values must be opposite:

$$q_{cold} = -q_{hot} \tag{10.5.6}$$

Thus heat is conserved in any such process, consistent with the law of conservation of energy.

> *The amount of heat lost by a warmer object equals the amount of heat gained by a cooler object.*

Substituting for q from Equation 10.5.4 gives

$$[mc_s\Delta T]_{cold} + [mc_s\Delta T]_{hot} = 0$$

which can be rearranged to give

$$[mc_s\Delta T]_{cold} = -[mc_s\Delta T]_{hot} \tag{10.5.7}$$

When two objects initially at different temperatures are placed in contact, we can use Equation 10.5.7 to calculate the final temperature if we know the chemical composition and mass of the objects.

Example 10.5.4: Thermal Equilibration of Copper and Water

If a 30.0 g piece of copper pipe at 80.0°C is placed in 100.0 g of water at 27.0°C, what is the final temperature? Assume that no heat is transferred to the surroundings.

Given: mass and initial temperature of two objects

Asked for: final temperature

Strategy: Using Equation 10.5.7 and writing $\Delta T = T_{final} - T_{initial}$ for both the copper and the water, substitute the appropriate values of m, c_s, and $T_{initial}$ into the equation and solve for T_{final}.

Solution

We can adapt Equation 10.5.7 to solve this problem, remembering that $\Delta T = T_{final} - T_{initial}$:

$$[mc_s\,(T_{final} - T_{initial})]_{Cu} + [mc_s\,(T_{final} - T_{initial})]_{H_2O} = 0$$

Substituting the data provided in the problem and Table 10.5.1 gives

$$\begin{aligned}(30\ g)\,(0.385\ J/(g^\circ C))(T_{final} - 80^\circ C) + (100\ g)(4.184\ J/(g^\circ C))(T_{final} - 27.0^\circ C) &= 0\\ T_{final}\,(11.6\ J/^oC) - 924\ J + T_{final}\,(418.4\ J/^oC) - 11,300\ J &= 0\\ T_{final}\,(430\ J/\,(g\cdot^o C)) &= 12,224\ J\\ T_{final} &= 28.4\ ^oC\end{aligned}$$

Exercise 10.5.4A: Thermal Equilibration of Gold and Water

If a 14.0 g chunk of gold at 20.0°C is dropped into 25.0 g of water at 80.0°C, what is the final temperature if no heat is transferred to the surroundings?

Answer

80.0°C

Exercise 10.5.4B: Thermal Equilibration of Aluminum and Water

A 28.0 g chunk of aluminum is dropped into 100.0 g of water with an initial temperature of 20.0°C. If the final temperature of the water is 24.0°C, what was the initial temperature of the aluminum? (Assume that no heat is transferred to the surroundings.)

Answer

90.6°C

Measuring Heat "Flow"

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

A calorimeter is a device used to measure the amount of heat involved in a chemical or physical process.

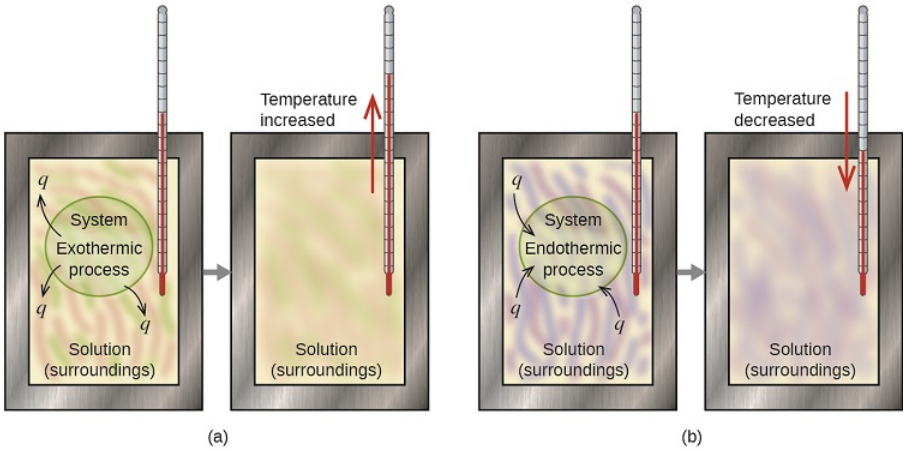


Figure 10.5.2: In a calorimetric determination, either (a) an exothermic process occurs and heat, q, is negative, indicating that thermal energy is transferred from the system to its surroundings, or (b) an endothermic process occurs and heat, q, is positive, indicating that thermal energy is transferred from the surroundings to the system.

The thermal energy change accompanying a chemical reaction is responsible for the change in temperature that takes place in a calorimeter. If the reaction releases heat ($q_{rxn} < 0$), then heat is absorbed by the calorimeter ($q_{calorimeter} > 0$) and its temperature increases. Conversely, if the reaction absorbs heat ($q_{rxn} > 0$), then heat is transferred from the calorimeter to the system ($q_{calorimeter} < 0$) and the temperature of the calorimeter decreases. In both cases, *the amount of heat absorbed or released by the calorimeter is equal in magnitude and opposite in sign to the amount of heat produced or consumed by the reaction*. The heat capacity of the calorimeter or of the reaction mixture may be used to calculate the amount of heat released or absorbed by the chemical reaction. The amount of heat released or absorbed per gram or mole of reactant can then be calculated from the mass of the reactants.

> *The amount of heat absorbed or released by the calorimeter is equal in magnitude and opposite in sign to the amount of heat produced or consumed by the reaction.*

Constant-Pressure Calorimetry

Because ΔH is defined as the heat flow at constant pressure, measurements made using a constant-pressure calorimeter (a device used to measure enthalpy changes in chemical processes at constant pressure) give ΔH values directly. This device is particularly well suited to studying reactions carried out in solution at a constant atmospheric pressure. A “student” version, called a *coffee-cup*

calorimeter (Figure 10.5.3), is often encountered in general chemistry laboratories. Commercial calorimeters operate on the same principle, but they can be used with smaller volumes of solution, have better thermal insulation, and can detect a change in temperature as small as several millionths of a degree (10^{-6} °C).

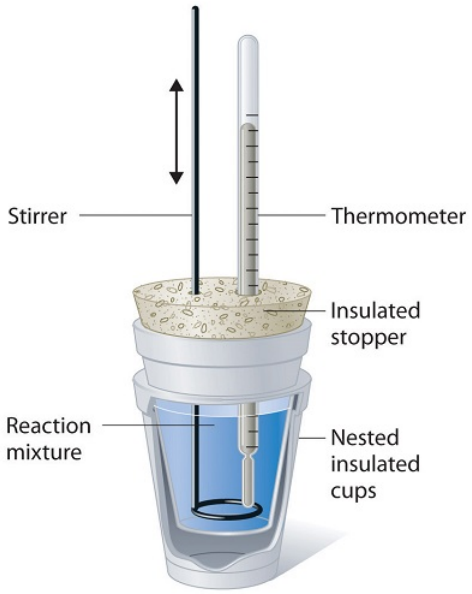


Figure 10.5.3: A Coffee-Cup Calorimeter. This simplified version of a constant-pressure calorimeter consists of two Styrofoam cups nested and sealed with an insulated stopper to thermally isolate the system (the solution being studied) from the surroundings (the air and the laboratory bench). Two holes in the stopper allow the use of a thermometer to measure the temperature and a stirrer to mix the reactants.

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

$$q_{\text{substance M}} + q_{\text{substance W}} = 0 \tag{10.5.8}$$

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

$$q_{\text{substance M}} = -q_{\text{substance W}} \tag{10.5.9}$$

The magnitude of the heat (change) is therefore the same for both substances, and the negative sign merely shows that $q_{substance\ M}$ and $q_{substance\ W}$ 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, $q_{substance\ M}$ is a negative value and $q_{\text{substance W}}$ is positive, since heat is transferred from M to W.

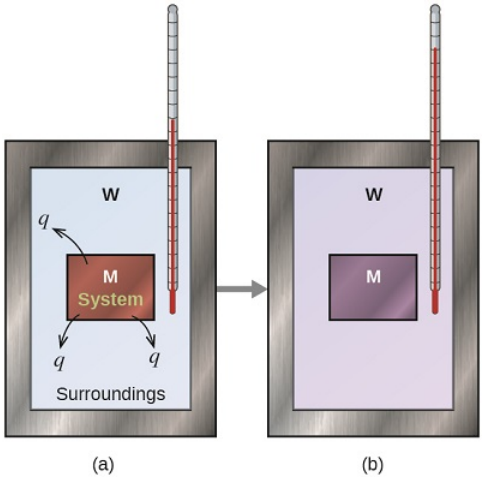


Figure 10.5.4: In a simple calorimetry process, (a) heat, q, is transferred from the hot metal, M, to the cool water, W, until (b) both are at the same temperature.

Example 10.5.5: Heat between Substances at Different Temperatures

A 360-g piece of rebar (a steel rod used for reinforcing concrete) is dropped into 425 mL of water at 24.0 °C. The final temperature of the water was measured as 42.7 °C. Calculate the initial temperature of the piece of rebar. Assume the specific heat of steel is approximately the same as that for iron (Table T4), and that all heat transfer occurs between the rebar and the water (there is no heat exchange with the surroundings).

Solution

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

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

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

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

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

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

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

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

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

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

Exercise 10.5.5A

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 10.5.5B

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 38.8 °C.

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

Example 10.5.6: Identifying a Metal by Measuring Specific Heat

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

Solution

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

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

In expanded form, this is:

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

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

$$(c_{\text{metal}})(59.7\text{ g})(28.5^\circ\text{C} - 100.0^\circ\text{C}) = -(4.18\text{ J/g }^\circ\text{C})(60.0\text{ g})(28.5^\circ\text{C} - 22.0^\circ\text{C})$$

Solving this:

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

Comparing this with values in Table T4, our experimental specific heat is closest to the value for copper (0.39 J/g °C), so we identify the metal as copper.

Exercise 10.5.6

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

$$c_{metal} = 0.13\ J/g\ ^\circ C$$

This specific heat is close to that of either gold or lead. It would be difficult to determine which metal this was based solely on the numerical values. However, the observation that the metal is silver/gray in addition to the value for the specific heat indicates that the metal is lead.

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

or consumed in the reaction (the "system"), q_{reaction}, plus the heat absorbed or lost by the solution (the "surroundings"), q_{solution}, must add up to zero:

$$q_{\text{reaction}} + q_{\text{solution}} = 0 \tag{10.5.10}$$

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

$$q_{\text{reaction}} = -q_{\text{solution}} \tag{10.5.11}$$

This concept lies at the heart of all calorimetry problems and calculations. Because the heat released or absorbed at constant pressure is equal to ΔH, the relationship between heat and ΔH_{rxn} is

$$\Delta H_{rxn} = q_{rxn} = -q_{calorimater} = -mc_s\Delta T \tag{10.5.12}$$

The use of a constant-pressure calorimeter is illustrated in Example 10.5.7.

Example 10.5.7: Heat of Solution

When 5.03 g of solid potassium hydroxide are dissolved in 100.0 mL of distilled water in a coffee-cup calorimeter, the temperature of the liquid increases from 23.0°C to 34.7°C. The density of water in this temperature range averages 0.9969 g/cm^3. What is ΔH_{soln} (in kilojoules per mole)? Assume that the calorimeter absorbs a negligible amount of heat and, because of the large volume of water, the specific heat of the solution is the same as the specific heat of pure water.

Given: mass of substance, volume of solvent, and initial and final temperatures

Asked for: ΔH_{soln}

Strategy:

A. Calculate the mass of the solution from its volume and density and calculate the temperature change of the solution.
B. Find the heat flow that accompanies the dissolution reaction by substituting the appropriate values into Equation 10.5.1.
C. Use the molar mass of KOH to calculate ΔH_{soln}.

Solution:

A To calculate ΔH_{soln}, we must first determine the amount of heat released in the calorimetry experiment. The mass of the solution is

$$\left(100.0\ \cancel{mL}\ \text{H}_2\text{O}\right)\left(0.9969\ g/\ \cancel{mL}\right) + 5.03\ g\ KOH = 104.72\ g$$

The temperature change is (34.7°C − 23.0°C) = +11.7°C.

B Because the solution is not very concentrated (approximately 0.9 M), we assume that the specific heat of the solution is the same as that of water. The heat flow that accompanies dissolution is thus

$$\begin{aligned} q_{calorimater} &= mc_s\Delta T \\ &= \left(104.72\ \cancel{g}\right)\left(\frac{4.184\ J}{\cancel{g}\cdot\cancel{^\circ C}}\right)\left(11.7\ \cancel{^\circ C}\right) \\ &= 5130\ J \\ &= 5.13\ kJ \end{aligned}$$

The temperature of the solution increased because heat was absorbed by the solution ($q > 0$). Where did this heat come from? It was released by KOH dissolving in water. From Equation 10.5.1, we see that

$$\Delta H_{rxn} = -q_{calorimeter} = -5.13\ kJ$$

This experiment tells us that dissolving 5.03 g of KOH in water is accompanied by the *release* of 5.13 kJ of energy. Because the temperature of the solution increased, the dissolution of KOH in water must be exothermic.

C The last step is to use the molar mass of KOH to calculate ΔH_{soln} - the heat associated when dissolving 1 mol of KOH:

$$\Delta H_{soln} = \left(\frac{5.13\ kJ}{5.03\ \cancel{g}}\right)\left(\frac{56.11\ \cancel{g}}{1\ mol}\right)$$
$$= -57.2\ kJ/mol$$

? Exercise 10.5.7: Heat of Dissolving

A coffee-cup calorimeter contains 50.0 mL of distilled water at 22.7°C. Solid ammonium bromide (3.14 g) is added and the solution is stirred, giving a final temperature of 20.3°C. Using the same assumptions as in Example 10.5.7, find ΔH_{soln} for NH_4Br (in kilojoules per mole).

Answer

16.6 kJ/mol

Constant-Volume Calorimetry

Constant-pressure calorimeters are not very well suited for studying reactions in which one or more of the reactants is a gas, such as a combustion reaction. The enthalpy changes that accompany combustion reactions are therefore measured using a constant-volume calorimeter, such as the bomb calorimeter (A device used to measure energy changes in chemical processes. shown schematically in Figure 10.5.4). The reactant is placed in a steel cup inside a steel vessel with a fixed volume (the "bomb"). The bomb is then sealed, filled with excess oxygen gas, and placed inside an insulated container that holds a known amount of water. Because combustion reactions are exothermic, the temperature of the bath and the calorimeter increases during combustion. If the heat capacity of the bomb and the mass of water are known, the heat released can be calculated.

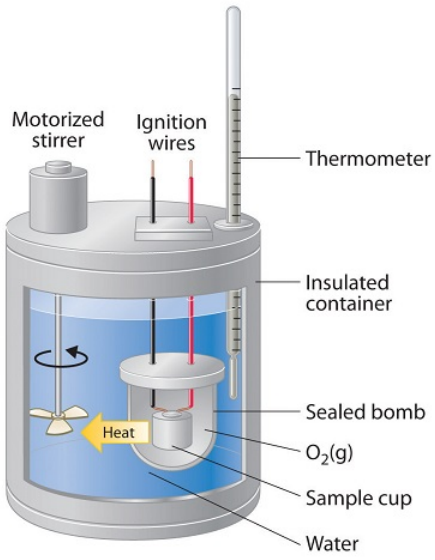


Figure 10.5.4: A Bomb Calorimeter. After the temperature of the water in the insulated container has reached a constant value, the combustion reaction is initiated by passing an electric current through a wire embedded in the sample. Because this calorimeter operates at constant volume, the heat released is not precisely the same as the enthalpy change for the reaction. (CC BY-SA-NC; anonymous)

Because the volume of the system (the inside of the bomb) is fixed, the combustion reaction occurs under conditions in which the volume, but not the pressure, is constant. The heat released by a reaction carried out at constant volume is identical to the change in *internal energy* (ΔU) rather than the enthalpy change (ΔH); ΔU is related to Δ*H* by an expression that depends on the change in the number of moles of gas during the reaction. The difference between the heat flow measured at constant volume and the enthalpy change is usually quite small, however (on the order of a few percent). Assuming that $\Delta U < \Delta H$, the relationship between the measured temperature change and ΔH_{comb} is given in Equation 10.5.13, where C_{bomb} is the total heat capacity of the steel bomb and the water surrounding it

$$\Delta H_{comb} < q_{comb} = q_{calorimater} = C_{bomb}\Delta T \tag{10.5.13}$$

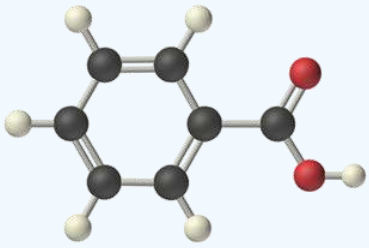
To measure the heat capacity of the calorimeter, we first burn a carefully weighed mass of a standard compound whose enthalpy of combustion is accurately known. Benzoic acid ($C_6H_5CO_2H$) is often used for this purpose because it is a crystalline solid that can be obtained in high purity. The combustion of benzoic acid in a bomb calorimeter releases 26.38 kJ of heat per gram (i.e., its ΔH_{comb} = −26.38 kJ/g). This value and the measured increase in temperature of the calorimeter can be used to determine C_{bomb}. The use of a bomb calorimeter to measure the ΔH_{comb} of a substance is illustrated in Example 10.5.8



Video* 10.5.1*: *Video of view how a bomb calorimeter is prepared for action.*

Example 10.5.8: Combustion of Glucose

The combustion of 0.579 g of benzoic acid in a bomb calorimeter caused a 2.08°C increase in the temperature of the calorimeter. The chamber was then emptied and recharged with 1.732 g of glucose and excess oxygen. Ignition of the glucose resulted in a temperature increase of 3.64°C. What is the ΔH_{comb} of glucose?



Benzoic acid

Given: mass and ΔT for combustion of standard and sample

Asked for: ΔH_{comb} of glucose

Strategy:

A. Calculate the value of q_{rxn} for benzoic acid by multiplying the mass of benzoic acid by its ΔH_{comb}. Then use Equation 10.5.1 to determine the heat capacity of the calorimeter (C_{bomb}) from q_{comb} and ΔT.

B. Calculate the amount of heat released during the combustion of glucose by multiplying the heat capacity of the bomb by the temperature change. Determine the ΔH_{comb} of glucose by multiplying the amount of heat released per gram by the molar mass of glucose.

Solution:

The first step is to use Equation 10.5.1 and the information obtained from the combustion of benzoic acid to calculate C_{bomb}. We are given ΔT, and we can calculate q_{comb} from the mass of benzoic acid:

$$q_{comb} = \left(0.579 \ \cancel{g}\right)\left(-26.38 \ kJ/\cancel{g}\right) = -15.3 \ kJ$$

From Equation 10.5.1,

$$-C_{bomb} = \frac{q_{comb}}{\Delta T} = \frac{-15.3\ kJ}{2.08\ ^oC} = -7.34\ kJ/^oC$$

B According to the strategy, we can now use the heat capacity of the bomb to calculate the amount of heat released during the combustion of glucose:

$$q_{comb} = -C_{bomb}\Delta T = (-7.34\ kJ/^oC)\,(3.64\ ^oC) = -26.7\ kJ$$

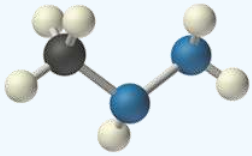
Because the combustion of 1.732 g of glucose released 26.7 kJ of energy, the ΔH_{comb} of glucose is

$$\Delta H_{comb} = \left(\frac{-26.7\ kJ}{1.732\ \cancel{g}}\right)\left(\frac{180.16\ \cancel{g}}{mol}\right) = -2780\ kJ/mol = 2.78 \times 10^3\ kJ/mol$$

This result is in good agreement (< 1% error) with the value of $\Delta H_{comb} = -2803\ kJ/mol$ that calculated using enthalpies of formation.

? Exercise 10.5.8: Combustion of Benzoic Acid

When 2.123 g of benzoic acid is ignited in a bomb calorimeter, a temperature increase of 4.75°C is observed. When 1.932 g of methylhydrazine (CH_3NHNH_2) is ignited in the same calorimeter, the temperature increase is 4.64°C. Calculate the ΔH_{comb} of methylhydrazine, the fuel used in the maneuvering jets of the US space shuttle.



Methylhydrazine

Answer

-1.30×10^3 kJ/mol

Summary

Calorimetry measures enthalpy changes during chemical processes, where the magnitude of the temperature change depends on the amount of heat released or absorbed and on the heat capacity of the system. **Calorimetry** is the set of techniques used to measure enthalpy changes during chemical processes. It uses devices called *calorimeters*, which measure the change in temperature when a chemical reaction is carried out. The magnitude of the temperature change depends on the amount of heat released or absorbed and on the heat capacity of the system. The **heat capacity (*C*)** of an object is the amount of energy needed to raise its temperature by 1°C; its units are joules per degree Celsius. The **specific heat** (c_s) of a substance is the amount of energy needed to raise the temperature of 1 g of the substance by 1°C, and the **molar heat capacity** (c_p) is the amount of energy needed to raise the temperature of 1 mol of a substance by 1°C. Liquid water has one of the highest specific heats known. Heat flow measurements can be made with either a **constant-pressure calorimeter**, which gives ΔH values directly, or a **bomb calorimeter**, which operates at constant volume and is particularly useful for measuring enthalpies of combustion.

Thermal energy itself cannot be measured easily, but the temperature change caused by the flow of thermal energy between objects or substances can be measured. Calorimetry describes a set of techniques employed to measure enthalpy changes in chemical processes using devices called *calorimeters*. To have any meaning, the quantity that is actually measured in a calorimetric experiment, the change in the temperature of the device, must be related to the heat evolved or consumed in a chemical reaction. We begin this section by explaining how the flow of thermal energy affects the temperature of an object.

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10.6: Calorimetry

Learning Objectives

- To use calorimetric data to calculate enthalpy changes.

Thermal energy itself cannot be measured easily, but the temperature change caused by the flow of thermal energy between objects or substances can be measured. Calorimetry describes a set of techniques employed to measure enthalpy changes in chemical processes using devices called *calorimeters*. To have any meaning, the quantity that is actually measured in a calorimetric experiment, the change in the temperature of the device, must be related to the heat evolved or consumed in a chemical reaction. We begin this section by explaining how the flow of thermal energy affects the temperature of an object.

Heat Capacity

We have seen that the temperature of an object changes when it absorbs or loses thermal energy. The *magnitude* of the temperature change depends on both the *amount* of thermal energy transferred (q) and the *heat capacity* of the object. Its heat capacity (C) is the amount of energy needed to raise the temperature of the object exactly 1°C; the units of C are joules per degree Celsius (J/°C). Note that a degree Celsius is exactly the same as a Kelvin, so the heat capacities can be expresses equally well, and perhaps a bit more correctly in SI, as joules per Kelvin, J/K

The change in temperature (ΔT) is

$$\Delta T = \frac{q}{C} \tag{10.6.1}$$

where q is the amount of heat (in joules), C is the heat capacity (in joules per degree Celsius), and ΔT is $T_{final} - T_{initial}$ (in degrees Celsius). Note that ΔT is *always* written as the final temperature minus the initial temperature.

Which Temperature units to use

Since the scaling for Kelvin (K) and degrees Celsius (°C) are exactly the same, the DIFFERENCE

$$\Delta T = T_{final} - T_{initial}$$

is the same is either is used for temperature calculations, but make sure not to mix these two temperature units for BOTH T_{final} and $T_{initial}$.

The value of C is intrinsically a positive number, but ΔT and q can be either positive or negative, and they both must have the *same* sign. If ΔT and q are positive, then *heat flows from the surroundings into an object*. If ΔT and q are negative, then *heat flows from an object into its surroundings*.

The heat capacity of an object depends on both its *mass* and its *composition*. For example, doubling the mass of an object doubles its heat capacity. Consequently, the amount of substance must be indicated when the heat capacity of the substance is reported. The molar heat capacity (C_p) is the amount of energy needed to increase the temperature of 1 mol of a substance by 1°C; the units of C_p are thus J/(mol•°C).The subscript p indicates that the value was measured at constant pressure. The specific heat (C_s) is the amount of energy needed to increase the temperature of 1 g of a substance by 1°C; its units are thus J/(g•°C).

We can relate the quantity of a substance, the amount of heat transferred, its heat capacity, and the temperature change either via **moles**:

$$q = nC_p\Delta T \tag{10.6.2}$$

where n is the number of moles of substance and C_p is the molar heat capacity or via **mass**:

$$q = mC_s\Delta T \tag{10.6.3}$$

where m is the mass of substance in grams and C_s is the specific heat.

The specific heats of some common substances are given in Table $10.6.1$. Note that the specific heat values of most solids are less than 1 J/(g•°C), whereas those of most liquids are about 2 J/(g•°C). Water in its solid and liquid states is an exception. The heat

capacity of ice is twice as high as that of most solids; the heat capacity of liquid water, 4.184 J/(g•°C), is one of the highest known.

Table 10.6.1: Specific Heats of Selected Substances at 25°C

Compound	Specific Heat [J/(g•°C)]	Compound	Specific Heat [J/(g•°C)]
H_2O (s)	2.108	Al(s)	0.897
H_2O (l)	4.184	Fe(s)	0.449
H_2O (g)	2.062	Cu(s)	0.385
CH_3OH (methanol)	2.531	Au(s)	0.129
CH_3CH_2OH (ethanol)	2.438	Hg(l)	0.140
n-C_6H_{14} (*n*-hexane)	2.270	NaCl(s)	0.864
C_6H_6 (benzene)	1.745	MgO(s)	0.921
C(s) (graphite)	0.709	SiO_2(s) (quartz)	0.742
C(s) (diamond)	0.509	$CaCO_3$(s) (calcite)	0.915

The high specific heat of liquid water has important implications for life on Earth. A given mass of water releases more than five times as much heat for a 1°C temperature change as does the same mass of limestone or granite. Consequently, coastal regions of our planet tend to have less variable climates than regions in the center of a continent. After absorbing large amounts of thermal energy from the sun in summer, the water slowly releases the energy during the winter, thus keeping coastal areas warmer than otherwise would be expected (Figure 10.6.1). Water's capacity to absorb large amounts of energy without undergoing a large increase in temperature also explains why swimming pools and waterbeds are usually heated. Heat must be applied to raise the temperature of the water to a comfortable level for swimming or sleeping and to maintain that level as heat is exchanged with the surroundings. Moreover, because the human body is about 70% water by mass, a great deal of energy is required to change its temperature by even 1 °C. Consequently, the mechanism for maintaining our body temperature at about 37 °C does not have to be as finely tuned as would be necessary if our bodies were primarily composed of a substance with a lower specific heat.

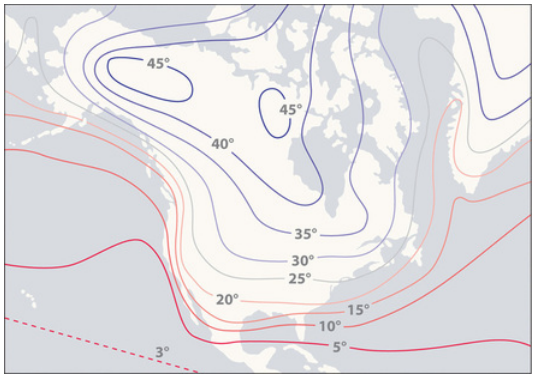


Figure 10.6.1: The High Specific Heat of Liquid Water Has Major Effects on Climate. Regions that are near very large bodies of water, such as oceans or lakes, tend to have smaller temperature differences between summer and winter months than regions in the center of a continent. The contours on this map show the difference between January and July monthly mean surface temperatures (in degrees Celsius).

Example 10.6.1: Solar Heating

A home solar energy storage unit uses 400 L of water for storing thermal energy. On a sunny day, the initial temperature of the water is 22.0 °C. During the course of the day, the temperature of the water rises to 38.0 °C as it circulates through the water wall. How much energy has been stored in the water? (The density of water at 22.0 °C is 0.998 g/mL.)



Passive solar system. During the day (a), sunlight is absorbed by water circulating in the water wall. At night (b), heat stored in the water wall continues to warm the air inside the house.

Given: volume and density of water and initial and final temperatures

Asked for: amount of energy stored

Strategy:

A. Use the density of water at 22.0 °C to obtain the mass of water (m) that corresponds to 400 L of water. Then compute ΔT for the water.

B. Determine the amount of heat absorbed by substituting values for m, C_s, and ΔT into Equation 10.6.1.

Solution:

A The mass of water is

$$\text{mass of } H_2O = 400 \ \cancel{L}\left(\frac{1000 \ \cancel{mL}}{1 \ \cancel{L}}\right)\left(\frac{0.998 \ g}{1 \ \cancel{mL}}\right)$$

$$= 3.99 \times 10^5 g \ H_2O$$

The temperature change (ΔT) is

$$38.0^oC - 22.0^oC = +16.0^oC.$$

B From Table 10.6.1, the specific heat of water is 4.184 J/(g•°C). From Equation 10.6.3, the heat absorbed by the water is thus

$$q = mC_s\Delta T$$

$$= \left(3.99 \times 10^5 \ \cancel{g}\right)\left(\frac{4.184 \ J}{\cancel{g} \cdot \ \cancel{^oC}}\right)\left(16.0 \ \cancel{^oC}\right)$$

$$= 2.67 \times 10^7 \ J = 2.67 \times 10^4 \ kJ$$

Both q and ΔT are positive, consistent with the fact that the water has absorbed energy.

? Exercise 10.6.1: Solar Heating

Some solar energy devices used in homes circulate air over a bed of rocks that absorb thermal energy from the sun. If a house uses a solar heating system that contains 2500 kg of sandstone rocks, what amount of energy is stored if the temperature of the rocks increases from 20.0 °C to 34.5 °C during the day? Assume that the specific heat of sandstone is the same as that of quartz (SiO_2) in Table 10.6.1.

Answer

$2.7 \times 10^4 \ kJ$

Even though the mass of sandstone is more than six times the mass of the water in Example 10.6.1, the amount of thermal energy stored is the same to two significant figures.

When two objects at different temperatures are placed in contact, heat flows from the warmer object to the cooler one until the temperature of both objects is the same. The law of conservation of energy says that the total energy cannot change during this process:

$$q_{cold} + q_{hot} = 0 \tag{10.6.4}$$

The equation implies that the amount of heat that flows *from* a warmer object is the same as the amount of heat that flows *into* a cooler object. Because the direction of heat flow is opposite for the two objects, the sign of the heat flow values must be opposite:

$$q_{cold} = -q_{hot} \tag{10.6.5}$$

Thus heat is conserved in any such process, consistent with the law of conservation of energy.

> *Equation 10.6.5 argues that the amount of heat lost by a warmer object equals the amount of heat gained by a cooler object.*

Substituting for *q* from Equation 10.6.2 into Equation 10.6.5 gives

$$[mC_s\Delta T]_{cold} + [mC_s\Delta T]_{hot} = 0 \tag{10.6.6}$$

which can be rearranged to give

$$[mC_s\Delta T]_{cold} = -[mC_s\Delta T]_{hot} \tag{10.6.7}$$

When two objects initially at different temperatures are placed in contact, we can use Equation 10.6.7 to calculate the final temperature if we know the chemical composition and mass of the objects.

Example 10.6.2: Thermal Equilibration of Copper and Water

If a 30.0 g piece of copper pipe at 80.0 °C is placed in 100.0 g of water at 27.0 °C, what is the final temperature? Assume that no heat is transferred to the surroundings.

Given: mass and initial temperature of two objects

Asked for: final temperature

Strategy: Using Equation 10.6.6 and writing ΔT as $T_{final} - T_{initial}$ for both the copper and the water, substitute the appropriate values of m, C_s, and $T_{initial}$ into the equation and solve for T_{final}.

Solution

We can adapt Equation 10.6.6 to solve this problem, remembering that ΔT is defined as $T_{final} - T_{initial}$:

$$[mC_s\,(T_{final} - T_{initial})]_{Cu} + [mC_s\,(T_{final} - T_{initial})]_{H_2O} = 0$$

Substituting the data provided in the problem and Table 10.6.1 gives

$$\begin{aligned}[(30\ g)\,(0.385\ J)\,(T_{final} - 80.0\,^\circ\text{C})]_{Cu} + [(100\,g)(4.18\,J/\,^\circ\text{C})\,(T_{final} - 27.0\,^\circ\text{C})]_{\text{H}_2\text{O}} &= 0\\ [T_{final}\,(11.6\ J/\,^\circ\text{C}) - 924\ J] + [T_{final}\,(418.4\ J/\,^\circ\text{C}) - 11,300\ J] &= 0\\ T_{final}\,(430\ J/\,(g\cdot\,^\circ\text{C})) &= 12,224\ J\\ T_{final} &= 28.4\ ^\circ\text{C}\end{aligned}$$

It is expected that the water will increase in temperature since the added copper pipe was hotter. However, the amount of the increase is not great and that is because there is more mass of water (three-fold), but mostly because the greater specific heat of water (order of magnitude) vs. copper.

Exercise 10.6.2A: Thermal Equilibration of Gold and Water

If a 14.0 g chunk of gold at 20.0°C is dropped into 25.0 g of water at 80.0 °C, what is the final temperature if no heat is transferred to the surroundings?

Answer

80.0°C

? Exercise 10.6.2B: Thermal Equilibration of Aluminum and Water

A 28.0 g chunk of aluminum is dropped into 100.0 g of water with an initial temperature of 20.0 °C. If the final temperature of the water is 24.0 °C, what was the initial temperature of the aluminum? (Assume that no heat is transferred to the surroundings.)

Answer

90.6°C

In Example 10.6.1, radiant energy from the sun was used to raise the temperature of water. A calorimetric experiment uses essentially the same procedure, except that the thermal energy change accompanying a chemical reaction is responsible for the change in temperature that takes place in a calorimeter. If the reaction releases heat ($q_{rxn} < 0$), then heat is absorbed by the calorimeter ($q_{calorimeter} > 0$) and its temperature increases. Conversely, if the reaction absorbs heat ($q_{rxn} > 0$), then heat is transferred from the calorimeter to the system ($q_{calorimeter} < 0$) and the temperature of the calorimeter decreases. In both cases, *the amount of heat absorbed or released by the calorimeter is equal in magnitude and opposite in sign to the amount of heat produced or consumed by the reaction*. The heat capacity of the calorimeter or of the reaction mixture may be used to calculate the amount of heat released or absorbed by the chemical reaction. The amount of heat released or absorbed per gram or mole of reactant can then be calculated from the mass of the reactants.



Conservation of Energy: The Movement of Heat between Substances: Conservation of Energy: The Movement of Heat between Substances, YouTube(opens in new window) [youtu.be]

Constant-Pressure Calorimetry

Because ΔH is defined as the heat flow at constant pressure, measurements made using a constant-pressure calorimeter (a device used to measure enthalpy changes in chemical processes at constant pressure) give ΔH values directly. This device is particularly well suited to studying reactions carried out in solution at a constant atmospheric pressure. A "student" version, called a *coffee-cup calorimeter* (Figure 10.6.2), is often encountered in general chemistry laboratories. Commercial calorimeters operate on the same principle, but they can be used with smaller volumes of solution, have better thermal insulation, and can detect a change in temperature as small as several millionths of a degree (10^{-6} °C). Because the heat released or absorbed at constant pressure is equal to ΔH, the relationship between heat and ΔH_{rxn} is

$$\Delta H_{rxn} = q_{rxn} = -q_{calorimater} = -mC_s\Delta T \tag{10.6.8}$$

The use of a constant-pressure calorimeter is illustrated in Example 10.6.3.

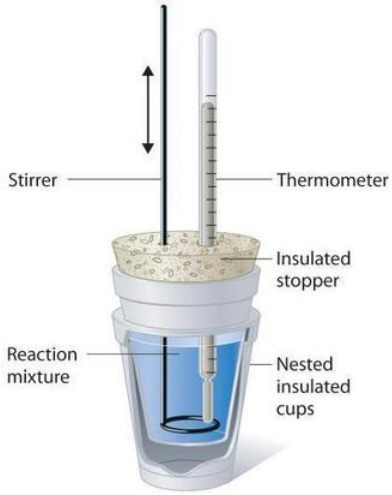


Figure 10.6.2: A Coffee-Cup Calorimeter. This simplified version of a constant-pressure calorimeter consists of two Styrofoam cups nested and sealed with an insulated stopper to thermally isolate the system (the solution being studied) from the surroundings (the air and the laboratory bench). Two holes in the stopper allow the use of a thermometer to measure the temperature and a stirrer to mix the reactants.

Example 10.6.3: Heat of solution for Potassium Hydroxide

When 5.03 g of solid potassium hydroxide are dissolved in 100.0 mL of distilled water in a coffee-cup calorimeter, the temperature of the liquid increases from 23.0 °C to 34.7 °C. The density of water in this temperature range averages 0.9969 g/cm^3. What is ΔH_{soln} (in kilojoules per mole)? Assume that the calorimeter absorbs a negligible amount of heat and, because of the large volume of water, the specific heat of the solution is the same as the specific heat of pure water.

Given: mass of substance, volume of solvent, and initial and final temperatures

Asked for: ΔH_{soln}

Strategy:

A. Calculate the mass of the solution from its volume and density and calculate the temperature change of the solution.
B. Find the heat flow that accompanies the dissolution reaction by substituting the appropriate values into Equation 10.6.8.
C. Use the molar mass of KOH to calculate ΔH_{soln}.

Solution:

A To calculate ΔH_{soln}, we must first determine the amount of heat released in the calorimetry experiment. The mass of the solution is

$$\left(100.0\ \cancel{mL}\ \text{H}_2\text{O}\right)\left(0.9969\ g/\ \cancel{mL}\right) + 5.03\ g\ \text{KOH} = 104.72\ g$$

The temperature change is therefor

$$(34.7\,^oC - 23.0\,^oC) = +11.7\,^oC.$$

B Because the solution is not very concentrated (approximately 0.9 M), we assume that the specific heat of the solution is the same as that of water. The heat flow that accompanies dissolution is thus

$$\begin{aligned} q_{calorimater} &= mC_s\Delta T \\ &= \left(104.72\ \cancel{g}\right)\left(\frac{4.184\ J}{\cancel{g}\cdot\ \cancel{^oC}}\right)(11.7\ ^oC) \\ &= 5130\ J = 5.13\ kJ \end{aligned}$$

The temperature of the solution increased because heat was absorbed by the solution ($q > 0$). Where did this heat come from? It was released by KOH dissolving in water. From Equation 10.6.1, we see that

$$\Delta H_{rxn} = -q_{calorimeter} = -5.13\ kJ$$

This experiment tells us that dissolving 5.03 g of KOH in water is accompanied by the *release* of 5.13 kJ of energy. Because the temperature of the solution increased, the dissolution of KOH in water must be exothermic.

C The last step is to use the molar mass of KOH to calculate ΔH_{soln}, i.e., the heat released when dissolving 1 mol of KOH:

$$\Delta H_{soln} = \left(\frac{5.13\ kJ}{5.03\ \cancel{g}}\right)\left(\frac{56.11\ \cancel{g}}{1\ mol}\right)$$
$$= -57.2\ kJ/mol$$

? Exercise 10.6.3: Heat of solution for ammonium bromide

A coffee-cup calorimeter contains 50.0 mL of distilled water at 22.7 °C. Solid ammonium bromide (3.14 g) is added and the solution is stirred, giving a final temperature of 20.3°C. Using the same assumptions as in Example 10.6.3, find ΔH_{soln} for NH_4Br (in kilojoules per mole).

Answer

16.6 kJ/mol



Conservation of Energy: Coffee Cup Calorimetry: Conservation of Energy: Coffee Cup Calorimetry, YouTube(opens in new window) [youtu.be] (opens in new window)

Constant-Volume Calorimetry

Constant-pressure calorimeters are not very well suited for studying reactions in which one or more of the reactants is a gas, such as a combustion reaction. The enthalpy changes that accompany combustion reactions are therefore measured using a constant-volume calorimeter, such as the bomb calorimeter(A device used to measure energy changes in chemical processes. shown schematically in Figure 10.6.3). The reactant is placed in a steel cup inside a steel vessel with a fixed volume (the “bomb”). The bomb is then sealed, filled with excess oxygen gas, and placed inside an insulated container that holds a known amount of water. Because combustion reactions are exothermic, the temperature of the bath and the calorimeter increases during combustion. If the heat capacity of the bomb and the mass of water are known, the heat released can be calculated.

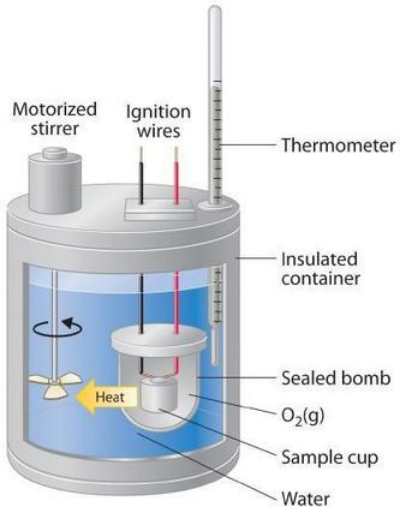


Figure 10.6.3: A Bomb Calorimeter. After the temperature of the water in the insulated container has reached a constant value, the combustion reaction is initiated by passing an electric current through a wire embedded in the sample. Because this calorimeter operates at constant volume, the heat released is not precisely the same as the enthalpy change for the reaction.

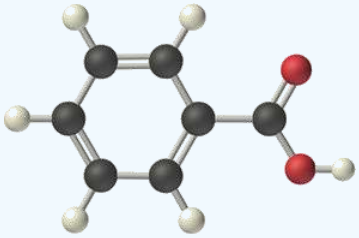
Because the volume of the system (the inside of the bomb) is fixed, the combustion reaction occurs under conditions in which the volume, but not the pressure, is constant. The heat released by a reaction carried out at constant volume is identical to the change in *internal energy* (ΔU) rather than the enthalpy change (ΔH); ΔU is related to ΔH by an expression that depends on the change in the number of moles of gas during the reaction. The difference between the heat flow measured at constant volume and the enthalpy change is usually quite small, however (on the order of a few percent). Assuming that $\Delta U < \Delta H$, the relationship between the measured temperature change and ΔH_{comb} is given in Equation 10.6.9, where C_{bomb} is the total heat capacity of the steel bomb and the water surrounding it:

$$\Delta H_{comb} < q_{comb} = q_{calorimater} = C_{bomb}\Delta T \tag{10.6.9}$$

To measure the heat capacity of the calorimeter, we first burn a carefully weighed mass of a standard compound whose enthalpy of combustion is accurately known. Benzoic acid ($C_6H_5CO_2H$) is often used for this purpose because it is a crystalline solid that can be obtained in high purity. The combustion of benzoic acid in a bomb calorimeter releases 26.38 kJ of heat per gram (i.e., its $\Delta H_{comb} = -26.38\ kJ/g$). This value and the measured increase in temperature of the calorimeter can be used in Equation 10.6.9 to determine C_{bomb}. The use of a bomb calorimeter to measure the ΔH_{comb} of a substance is illustrated in Example 10.6.4

Example 10.6.4: Combustion of Glucose

The combustion of 0.579 g of benzoic acid in a bomb calorimeter caused a 2.08 °C increase in the temperature of the calorimeter. The chamber was then emptied and recharged with 1.732 g of glucose and excess oxygen. Ignition of the glucose resulted in a temperature increase of 3.64°C. What is the ΔH_{comb} of glucose?



Benzoic acid

Given: mass and ΔT for combustion of standard and sample

Asked for: ΔH_{comb} of glucose

Strategy:

A. Calculate the value of q_{rxn} for benzoic acid by multiplying the mass of benzoic acid by its ΔH_{comb}. Then use Equation $ref5.5.9$ to determine the heat capacity of the calorimeter (C_{bomb}) from q_{comb} and ΔT.

B. Calculate the amount of heat released during the combustion of glucose by multiplying the heat capacity of the bomb by the temperature change. Determine the ΔH_{comb} of glucose by multiplying the amount of heat released per gram by the molar mass of glucose.

Solution:

The first step is to use Equation 10.6.9 and the information obtained from the combustion of benzoic acid to calculate C_{bomb}. We are given ΔT, and we can calculate q_{comb} from the mass of benzoic acid:

$$\begin{aligned} q_{comb} &= \left(0.579 \ \cancel{g}\right)\left(-26.38 \ kJ/\ \cancel{g}\right) \\ &= -15.3 \ kJ \end{aligned}$$

From Equation 10.6.9,

$$\begin{aligned} -C_{bomb} &= \frac{q_{comb}}{\Delta T} \\ &= \frac{-15.3 \ kJ}{2.08 \ ^oC} \\ &= -7.34 \ kJ/^oC \end{aligned}$$

B According to the strategy, we can now use the heat capacity of the bomb to calculate the amount of heat released during the combustion of glucose:

$$\begin{aligned} q_{comb} &= -C_{bomb}\Delta T \\ &= (-7.34 \ kJ/^oC)\,(3.64 \ ^oC) \\ &= -26.7 \ kJ \end{aligned}$$

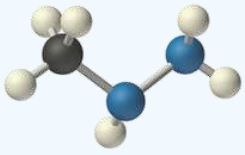
Because the combustion of 1.732 g of glucose released 26.7 kJ of energy, the ΔH_{comb} of glucose is

$$\begin{aligned} \Delta H_{comb} &= \left(\frac{-26.7 \ kJ}{1.732 \ \cancel{g}}\right)\left(\frac{180.16 \ \cancel{g}}{mol}\right) \\ &= -2780 \ kJ/mol \\ &= 2.78 \times 10^3 \ J/mol \end{aligned}$$

This result is in good agreement (< 1% error) with the value of $\Delta H_{comb} = -2803 \, kJ/mol$ that calculated using enthalpies of formation.

? Exercise 10.6.4: Combustion of Benzoic Acid

When 2.123 g of benzoic acid is ignited in a bomb calorimeter, a temperature increase of 4.75 °C is observed. When 1.932 g of methylhydrazine (CH_3NHNH_2) is ignited in the same calorimeter, the temperature increase is 4.64 °C. Calculate the ΔH_{comb} of methylhydrazine, the fuel used in the maneuvering jets of the US space shuttle.



Methylhydrazine

Answer

-1.30×10^3 kJ/mol



Conservation of Energy: Bomb Calorimetry: Conservation of Energy: Bomb Calorimetry, YouTube(opens in new window) [youtu.be]

Summary

Enthalpy is a state function used to measure the heat transferred from a system to its surroundings or vice versa at constant pressure. Only the **change in enthalpy (Δ*H*)** can be measured. A negative Δ*H* means that heat flows from a system to its surroundings; a positive Δ*H* means that heat flows into a system from its surroundings. Calorimetry measures enthalpy changes during chemical processes, where the magnitude of the temperature change depends on the amount of heat released or absorbed and on the heat capacity of the system. **Calorimetry** is the set of techniques used to measure enthalpy changes during chemical processes. It uses devices called *calorimeters*, which measure the change in temperature when a chemical reaction is carried out. The magnitude of the temperature change depends on the amount of heat released or absorbed and on the heat capacity of the system. The **heat capacity (*C*)** of an object is the amount of energy needed to raise its temperature by 1°C; its units are joules per degree Celsius. The **specific heat (C_s)** of a substance is the amount of energy needed to raise the temperature of 1 g of the substance by 1°C, and the **molar heat capacity (C_p)** is the amount of energy needed to raise the temperature of 1 mol of a substance by 1°C. Liquid water has one of the highest specific heats known. Heat flow measurements can be made with either a **constant-pressure calorimeter**, which gives Δ*H* values directly, or a **bomb calorimeter**, which operates at constant volume and is particularly useful for measuring enthalpies of combustion.

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10.7: Hess's Law

Learning Objectives

- To use Hess's law and thermochemical cycles to calculate enthalpy changes of chemical reactions.

Because enthalpy is a state function, the enthalpy change for a reaction depends on only two things: (1) the masses of the reacting substances and (2) the physical states of the reactants and products. It does not depend on the path by which reactants are converted to products. If you climbed a mountain, for example, the altitude change would not depend on whether you climbed the entire way without stopping or you stopped many times to take a break. If you stopped often, the overall change in altitude would be the sum of the changes in altitude for each short stretch climbed. Similarly, when we add two or more balanced chemical equations to obtain a net chemical equation, ΔH for the net reaction is the sum of the ΔH values for the individual reactions. This principle is called Hess's law, after the Swiss-born Russian chemist Germain Hess (1802–1850), a pioneer in the study of thermochemistry. Hess's law allows us to calculate ΔH values for reactions that are difficult to carry out directly by adding together the known ΔH values for individual steps that give the overall reaction, even though the overall reaction may not actually occur via those steps.

> *Hess's Law argues that ΔH for the net reaction is the sum of the ΔH values for the individual reactions. This is nothing more than arguing that ΔH is a state function.*

We can illustrate Hess's law using the thermite reaction. The overall reaction shown in Equation 5.6.1 can be viewed as occurring in three distinct steps with known ΔH values. As shown in Figure 5.6.1, the first reaction produces 1 mol of solid aluminum oxide (Al_2O_3) and 2 mol of liquid iron at its melting point of 1758°C (part (a) in Equation 5.6.1); the enthalpy change for this reaction is −732.5 kJ/mol of Fe_2O_3. The second reaction is the conversion of 2 mol of liquid iron at 1758°C to 2 mol of solid iron at 1758°C (part (b) in Equation 5.6.1); the enthalpy change for this reaction is −13.8 kJ/mol of Fe (−27.6 kJ per 2 mol Fe). In the third reaction, 2 mol of solid iron at 1758°C is converted to 2 mol of solid iron at 25°C (part (c) in Equation 5.6.1); the enthalpy change for this reaction is −45.5 kJ/mol of Fe (−91.0 kJ per 2 mol Fe). As you can see in Figure 5.6.1, the overall reaction is given by the longest arrow (shown on the left), which is the sum of the three shorter arrows (shown on the right). Adding parts (a), (b), and (c) in Equation 5.6.1 gives the overall reaction, shown in part (d):

$$\begin{array}{rcll} 2\,\mathrm{Al(s,25\,^\circ C)} + \mathrm{Fe_2O_3(s,25\,^\circ C)} & \longrightarrow & 2\,\mathrm{Fe(l,1758\,^\circ C)} + \mathrm{Al_2O_3(s,1758\,^\circ C)} & \Delta H = -732.5\,\mathrm{kJ} \quad \text{(a)} \\ 2\,\mathrm{Fe(l,1758\,^\circ C)} & \longrightarrow & 2\,\mathrm{Fe(s,1758\,^\circ C)} & \Delta H = -\ 27.6\,\mathrm{kJ} \quad \text{(b)} \\ 2\,\mathrm{Fe(s,1758\,^\circ C)} + \mathrm{Al_2O_3(s,1758\,^\circ C)} & \longrightarrow & 2\,\mathrm{Fe(s,25\,^\circ C)} + \mathrm{Al_2O_3(s,25\,^\circ C)} & \Delta H = -\ 91.0\,\mathrm{kJ} \quad \text{(c)} \\ \hline 2\,\mathrm{Al(s,25\,^\circ C)} + \mathrm{Fe_2O_3(s,25\,^\circ C)} & \longrightarrow & \mathrm{Al_2O_3(s,25\,^\circ C)} + 2\,\mathrm{Fe(s,25\,^\circ C)} & \Delta H = -851.1\,\mathrm{kJ} \quad \text{(d)} \end{array} \tag{5.6.1}$$

The net reaction in part (d) in Equation 5.6.1 is identical to the equation for the thermite reaction that we saw in a previous section. By Hess's law, the enthalpy change for part (d) is the sum of the enthalpy changes for parts (a), (b), and (c). In essence, Hess's law enables us to calculate the enthalpy change for the sum of a series of reactions without having to draw a diagram like that in Figure 10.7.1

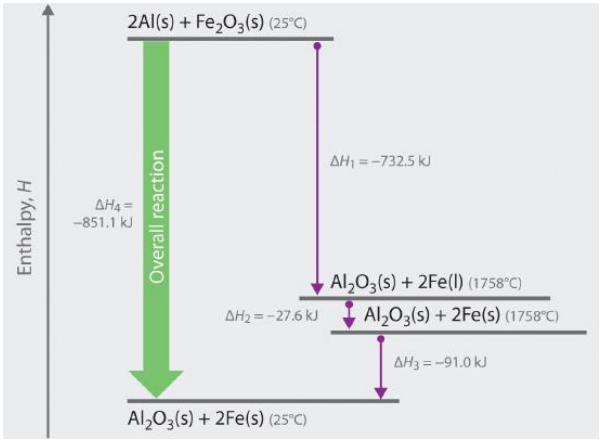


Figure 10.7.1: Energy Changes accompanying the thermite reaction. Because enthalpy is a state function, the overall enthalpy change for the reaction of 2 mol of Al(s) with 1 mol of Fe_2O_3(s) is −851.1 kJ, whether the reaction occurs in a single step (ΔH_4, shown on the left) or in three hypothetical steps (shown on the right) that involve the successive formation of solid Al_2O_3 and liquid iron (ΔH_1), solid iron at 1758°C (ΔH_2), and solid iron at 25°C (ΔH_3). Thus $\Delta H_4 = \Delta H_1 + \Delta H_2 + \Delta H_3$, as stated by Hess's law.

Comparing parts (a) and (d) in Equation 5.6.1 also illustrates an important point: The magnitude of ΔH for a reaction depends on the physical states of the reactants and the products (gas, liquid, solid, or solution). When the product is liquid iron at its melting point (part (a) in Equation 5.6.1), only 732.5 kJ of heat are released to the surroundings compared with 852 kJ when the product is solid iron at 25°C (part (d) in Equation 5.6.1). The difference, 120 kJ, is the amount of energy that is released when 2 mol of liquid iron solidifies and cools to 25°C. It is important to specify the physical state of all reactants and products when writing a thermochemical equation.

When using Hess's law to calculate the value of ΔH for a reaction, follow this procedure:

1. Identify the equation whose ΔH value is unknown and write individual reactions with known ΔH values that, when added together, will give the desired equation. We illustrate how to use this procedure in Example 10.7.1.
2. Arrange the chemical equations so that the reaction of interest is the sum of the individual reactions.
3. If a reaction must be reversed, change the sign of ΔH for that reaction. Additionally, if a reaction must be multiplied by a factor to obtain the correct number of moles of a substance, multiply its ΔH value by that same factor.
4. Add together the individual reactions and their corresponding ΔH values to obtain the reaction of interest and the unknown ΔH.

✔ Example 10.7.1

When carbon is burned with limited amounts of oxygen gas (O_2), carbon monoxide (CO) is the main product:

$$(1)\ 2\,C(s) + O_2(g) \longrightarrow 2\,CO(g) \quad \Delta H = -221.0\ kJ$$

When carbon is burned in excess O_2, carbon dioxide (CO_2) is produced:

$$(2)\ C(s) + O_2(g) \longrightarrow CO_2(g) \quad \Delta H = -393.5\ kJ$$

Use this information to calculate the enthalpy change per mole of CO for the reaction of CO with O_2 to give CO_2.

Given: two balanced chemical equations and their ΔH values

Asked for: enthalpy change for a third reaction

Strategy:

A. After balancing the chemical equation for the overall reaction, write two equations whose ΔH values are known and that, when added together, give the equation for the overall reaction. (Reverse the direction of one or more of the equations as necessary, making sure to also reverse the sign of ΔH.)

B. Multiply the equations by appropriate factors to ensure that they give the desired overall chemical equation when added together. To obtain the enthalpy change per mole of CO, write the resulting equations as a sum, along with the enthalpy change for each.

Solution:

A We begin by writing the balanced chemical equation for the reaction of interest:

$$(3)\ \ \mathrm{CO(g)} + \tfrac{1}{2}\mathrm{O_2(g)} \longrightarrow \mathrm{CO_2(g)} \quad \Delta H_{rxn} = ?$$

There are at least two ways to solve this problem using Hess's law and the data provided. The simplest is to write two equations that can be added together to give the desired equation and for which the enthalpy changes are known. Observing that CO, a reactant in Equation 3, is a product in Equation 1, we can reverse Equation (1) to give

$$2\,\mathrm{CO(g)} \longrightarrow 2\,\mathrm{C(s)} + \mathrm{O_2(g)} \quad \Delta H = +221.0\ \mathrm{kJ}$$

Because we have reversed the direction of the reaction, the sign of ΔH is changed. We can use Equation 2 as written because its product, CO_2, is the product we want in Equation 3:

$$\mathrm{C(s)} + \mathrm{O_2(g)} \longrightarrow \mathrm{CO_2(s)} \quad \Delta H = -393.5\ \mathrm{kJ}$$

B Adding these two equations together does not give the desired reaction, however, because the numbers of C(s) on the left and right sides do not cancel. According to our strategy, we can multiply the second equation by 2 to obtain 2 mol of C(s) as the reactant:

$$2\,\mathrm{C(s)} + 2\,\mathrm{O_2(g)} \longrightarrow 2\,\mathrm{CO_2(s)} \quad \Delta H = -787.0\ \mathrm{kJ}$$

Writing the resulting equations as a sum, along with the enthalpy change for each, gives

$$\begin{array}{rcll} 2\,\mathrm{CO(g)} & \longrightarrow & 2\,\cancel{\mathrm{C(s)}} + \cancel{\mathrm{O_2(g)}} & \Delta H = -\Delta H_1 = +221.0\ \mathrm{kJ} \\ \cancel{2\,\mathrm{C(s)}} + \cancel{2}\,\mathrm{O_2(g)} & \longrightarrow & 2\,\mathrm{CO_2(g)} & \Delta H = -2\Delta H_2 = -787.0\ \mathrm{kJ} \\ \hline 2\,\mathrm{CO(g)} + \mathrm{O_2(g)} & \longrightarrow & 2\,\mathrm{CO_2(g)} & \Delta H = -566.0\ \mathrm{kJ} \end{array}$$

Note that the overall chemical equation and the enthalpy change for the reaction are both for the reaction of 2 mol of CO with O_2, and the problem asks for the amount per mole of CO. Consequently, we must divide both sides of the final equation and the magnitude of ΔH by 2:

$$\mathrm{CO(g)} + \tfrac{1}{2}\mathrm{O_2(g)} \longrightarrow \mathrm{CO_2(g)} \quad \Delta H = -283.0\ \mathrm{kJ}$$

An alternative and equally valid way to solve this problem is to write the two given equations as occurring in steps. Note that we have multiplied the equations by the appropriate factors to allow us to cancel terms:

$$\begin{array}{lrll} \mathrm{(A)} & 2\,\mathrm{C(s)} + \mathrm{O_2(g)} \longrightarrow 2\,\cancel{\mathrm{CO(g)}} & \Delta H_A = \Delta H_1 & = +221.0\ \mathrm{kJ} \\ \mathrm{(B)} & \cancel{2\,\mathrm{CO(g)}} + \mathrm{O_2(g)} \longrightarrow 2\,\mathrm{CO_2(g)} & \Delta H_B & = ? \\ \mathrm{(C)} & 2\,\mathrm{C(s)} + 2\,\mathrm{O_2(g)} \longrightarrow 2\,\mathrm{CO_2(g)} & \Delta H = 2\Delta H_2 = 2 \times (-393.5\ \mathrm{kJ}) & = -787.0\ \mathrm{kJ} \end{array}$$

The sum of reactions A and B is reaction C, which corresponds to the combustion of 2 mol of carbon to give CO_2. From Hess's law, $\Delta H_A + \Delta H_B = \Delta H_C$, and we are given ΔH for reactions A and C. Substituting the appropriate values gives

$$-221.0\ kJ + \Delta H_B = -787.0\ kJ$$
$$\Delta H_B = -566.0$$

This is again the enthalpy change for the conversion of 2 mol of CO to CO_2. The enthalpy change for the conversion of 1 mol of CO to CO_2 is therefore −566.0 ÷ 2 = −283.0 kJ/mol of CO, which is the same result we obtained earlier. As you can see, there may be more than one correct way to solve a problem.

? Exercise 10.7.1

The reaction of acetylene (C_2H_2) with hydrogen (H_2) can produce either ethylene (C_2H_4) or ethane (C_2H_6):

$$C_2H_2\,(g) + H_2\,(g) \rightarrow C_2H_4\,(g) \quad \Delta H = -175.7\ kJ/mol\ C_2H_2$$
$$C_2H_2\,(g) + 2H_2\,(g) \rightarrow C_2H_6\,(g) \quad \Delta H = -312.0\ kJ/mol\ C_2H_2$$

What is ΔH for the reaction of C_2H_4 with H_2 to form C_2H_6?

Answer

−136.3 kJ/mol of C_2H_4



Hess’s Law: Hess's Law, YouTube(opens in new window) [youtu.be]

Summary

Hess's law is arguing the overall enthalpy change for a series of reactions is the sum of the enthalpy changes for the individual reactions. For a chemical reaction, the **enthalpy of reaction (ΔH_{rxn})** is the difference in enthalpy between products and reactants; the units of ΔH_{rxn} are kilojoules per mole. Reversing a chemical reaction reverses the sign of ΔH_{rxn}. The magnitude of ΔH_{rxn} also depends on the physical state of the reactants and the products because processes such as melting solids or vaporizing liquids are also accompanied by enthalpy changes: the **enthalpy of fusion (ΔH_{fus})** and the **enthalpy of vaporization (ΔH_{vap})**, respectively. The overall enthalpy change for a series of reactions is the sum of the enthalpy changes for the individual reactions, which is **Hess’s law**. The **enthalpy of combustion (ΔH_{comb})** is the enthalpy change that occurs when a substance is burned in excess oxygen.

Contributors and Attributions

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10.8: Enthalpies of Formation

Learning Objectives

- To understand Enthalpies of Formation and be able to use them to calculate Enthalpies of Reaction

One way to report the heat absorbed or released by chemical reactions would be to compile a massive set of reference tables that list the enthalpy changes for all possible chemical reactions, which would require an incredible amount of effort. Fortunately, Hess's law allows us to calculate the enthalpy change for virtually any conceivable chemical reaction using a relatively small set of tabulated data, starting from the elemental forms of each atom at 25 °C and 1 atm pressure.

Enthalpy of formation (ΔH_f) is the enthalpy change for the formation of 1 mol of a compound from its component elements, such as the formation of carbon dioxide from carbon and oxygen. The formation of any chemical can be as a reaction from the corresponding elements:

$$\text{elements} \rightarrow \text{compound}$$

which in terms of the the Enthalpy of formation becomes

$$\Delta H_{rxn} = \Delta H_f \tag{10.8.1}$$

For example, consider the combustion of carbon:

$$\mathrm{C(s) + O_2(g) \longrightarrow CO_2(g)}$$

then

$$\Delta H_{rxn} = \Delta H_f \left[CO_2\left(g\right)\right]$$

The sign convention for ΔH_f is the same as for any enthalpy change: $\Delta H_f < 0$ if heat is released when elements combine to form a compound and $\Delta H_f > 0$ if heat is absorbed.

> The sign convention is the same for all enthalpy changes: negative if heat is released by the system and positive if heat is absorbed by the system.

Standard Enthalpies of Formation

The magnitude of ΔH for a reaction depends on the physical states of the reactants and the products (gas, liquid, solid, or solution), the pressure of any gases present, and the temperature at which the reaction is carried out. To avoid confusion caused by differences in reaction conditions and ensure uniformity of data, the scientific community has selected a specific set of conditions under which enthalpy changes are measured. These standard conditions serve as a reference point for measuring differences in enthalpy, much as sea level is the reference point for measuring the height of a mountain or for reporting the altitude of an airplane.

The standard conditions for which most thermochemical data are tabulated are a *pressure* of 1 atmosphere (atm) for all gases and a *concentration* of 1 M for all species in solution (1 mol/L). In addition, each pure substance must be in its standard state, which is usually its most stable form at a pressure of 1 atm at a specified temperature. We assume a temperature of 25°C (298 K) for all enthalpy changes given in this text, unless otherwise indicated. Enthalpies of formation measured under these conditions are called **standard enthalpies of formation** (ΔH_f^o) The enthalpy change for the formation of 1 mol of a compound from its component elements when the component elements are each in their standard states. The standard enthalpy of formation of any element in its most stable form is zero by definition.

> *The standard enthalpy of formation of any element in its standard state is zero by definition.*

For example, although oxygen can exist as ozone (O_3), atomic oxygen (O), and molecular oxygen (O_2), O_2 is the most stable form at 1 atm pressure and 25°C. Similarly, hydrogen is H_2(g), not atomic hydrogen (H). Graphite and diamond are both forms of elemental carbon, but because graphite is more stable at 1 atm pressure and 25°C, the standard state of carbon is graphite (Figure 10.8.1). Therefore, $\mathrm{O_2(g)}$, $\mathrm{H_2(g)}$, and graphite have ΔH_f^o values of zero.

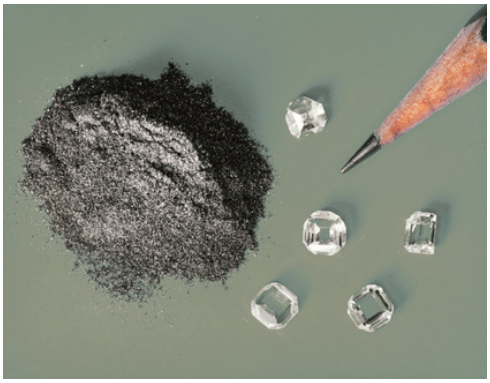


Figure 10.8.1: Elemental Carbon. Although graphite and diamond are both forms of elemental carbon, graphite is slightly more stable at 1 atm pressure and 25°C than diamond is. Given enough time, diamond will revert to graphite under these conditions. Hence graphite is the standard state of carbon.

The standard enthalpy of formation of glucose from the elements at 25°C is the enthalpy change for the following reaction:

$$6C\,(s, graphite) + 6H_2\,(g) + 3O_2\,(g) \rightarrow C_6H_{12}O_6\,(s) \quad \Delta H_f^o = -1273.3\ kJ \tag{10.8.2}$$

It is not possible to measure the value of $\Delta H^o o_f$ for glucose, −1273.3 kJ/mol, by simply mixing appropriate amounts of graphite, O_2, and H_2 and measuring the heat evolved as glucose is formed since the reaction shown in Equation 10.8.2 does not occur at a measurable rate under any known conditions. Glucose is not unique; most compounds cannot be prepared by the chemical equations that define their standard enthalpies of formation. Instead, values of $\Delta H^o o_f$ are obtained using **Hess's law** and standard enthalpy changes that have been measured for other reactions, such as combustion reactions. Values of ΔH_f^o for an extensive list of compounds are given in Table T1. Note that ΔH_f^o values are always reported in kilojoules per mole of the substance of interest. Also notice in Table T1 that the standard enthalpy of formation of O_2(g) is zero because it is the most stable form of oxygen in its standard state.

Example 10.8.1: Enthalpy of Formation

For the formation of each compound, write a balanced chemical equation corresponding to the standard enthalpy of formation of each compound.

a. $HCl(g)$
b. $MgCO_3(s)$
c. $CH_3(CH_2)_{14}CO_2H(s)$ (*palmitic acid*)

Given:

compound formula and phase.

Asked for:

balanced chemical equation for its formation from elements in standard states

Strategy:

Use Table T1 to identify the standard state for each element. Write a chemical equation that describes the formation of the compound from the elements in their standard states and then balance it so that 1 mol of product is made.

Solution:

To calculate the standard enthalpy of formation of a compound, we must start with the elements in their standard states. The standard state of an element can be identified in Table T1: by a ΔH_f^o value of 0 kJ/mol.

Hydrogen chloride contains one atom of hydrogen and one atom of chlorine. Because the standard states of elemental hydrogen and elemental chlorine are $H_2(g)$ and $Cl_2(g)$, respectively, the unbalanced chemical equation is

$$H_2(g) + Cl_2(g) \rightarrow HCl(g)$$

Fractional coefficients are required in this case because ΔH^o_f values are reported for *1 mol* of the product, HCl. Multiplying both $H_2(g)$ and $Cl_2(g)$ by 1/2 balances the equation:

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) \rightarrow HCl(g)$$

The standard states of the elements in this compound are $\mathrm{Mg(s)}$, $\mathrm{C(s,\,graphite)}$, and $\mathrm{O_2(g)}$. The unbalanced chemical equation is thus

$$\mathrm{Mg(s) + C(s,\,graphite) + O_2(g) \rightarrow MgCO_3(s)}$$

This equation can be balanced by inspection to give

$$\mathrm{Mg(s) + C(s,\,graphite) + \tfrac{3}{2}O_2(g) \rightarrow MgCO_3(s)}$$

Palmitic acid, the major fat in meat and dairy products, contains hydrogen, carbon, and oxygen, so the unbalanced chemical equation for its formation from the elements in their standard states is as follows:

$$\mathrm{C(s,\,graphite) + H_2(g) + O_2(g) \rightarrow CH_3(CH_2)_{14}CO_2H(s)}$$

There are 16 carbon atoms and 32 hydrogen atoms in 1 mol of palmitic acid, so the balanced chemical equation is

$$\mathrm{16\,C(s,\,graphite) + 16\,H_2(g) + O_2(g) \longrightarrow CH_3(CH_2)_{14}CO_2H(s)}$$

? Exercise 10.8.1

For the formation of each compound, write a balanced chemical equation corresponding to the standard enthalpy of formation of each compound.

a. $\mathrm{NaCl(s)}$
b. $\mathrm{H_2SO_4(l)}$
c. $\mathrm{CH_3CO_2H(l)}$ (*acetic acid*)

Answer a

$$\mathrm{Na(s) + \tfrac{1}{2}Cl_2(g) \rightarrow NaCl(s)}$$

Answer b

$$\mathrm{H_2(g) + \tfrac{1}{8}S_8(s) + 2\,O_2(g) \rightarrow H_2SO_4(l)}$$

Answer c

$$\mathrm{2\,C(s) + O_2(g) + 2\,H_2(g) \longrightarrow CH_3CO_2H(l)}$$



Definition of Heat of Formation Reactions: https://youtu.be/A20k0CK4doI

Standard Enthalpies of Reaction

Tabulated values of standard enthalpies of formation can be used to calculate enthalpy changes for *any* reaction involving substances whose ΔH_f^o values are known. The standard enthalpy of reaction ΔH_{rxn}^o is the enthalpy change that occurs when a reaction is carried out with all reactants and products in their standard states. Consider the general reaction

$$aA + bB \rightarrow cC + dD \tag{10.8.3}$$

where A, B, C, and D are chemical substances and a, b, c, and d are their stoichiometric coefficients. The magnitude of ΔH^o is the sum of the standard enthalpies of formation of the products, each multiplied by its appropriate coefficient, minus the sum of the standard enthalpies of formation of the reactants, also multiplied by their coefficients:

$$\Delta H^o_{rxn} = \underbrace{\left[c\Delta H^o_f(C) + d\Delta H^o_f(D)\right]}_{\text{products}} - \underbrace{\left[a\Delta H^o_f(A) + b\Delta H^o_f(B)\right]}_{\text{reactants}} \tag{10.8.4}$$

More generally, we can write

$$\Delta H^o_{rxn} = \sum m\Delta H^o_f(products) - \sum n\Delta H^o_f(reactants) \tag{10.8.5}$$

where the symbol $\sum$ means "sum of" and m and n are the stoichiometric coefficients of each of the products and the reactants, respectively. "Products minus reactants" summations such as Equation 10.8.5 arise from the fact that enthalpy is a state function. Because many other thermochemical quantities are also state functions, "products minus reactants" summations are very common in chemistry; we will encounter many others in subsequent chapters.

> "Products minus reactants" summations are typical of state functions.

To demonstrate the use of tabulated ΔH^o values, we will use them to calculate ΔH_{rxn} for the combustion of glucose, the reaction that provides energy for your brain:

$$C_6H_{12}O_6(s) + 6\,O_2(g) \rightarrow 6\,CO_2(g) + 6\,H_2O(l) \tag{10.8.6}$$

Using Equation 10.8.5, we write

$$\Delta H^o_f = \left\{6\Delta H^o_f[CO_2(g)] + 6\Delta H^o_f[H_2O(g)]\right\} - \left\{\Delta H^o_f[C_6H_{12}O_6(s)] + 6\Delta H^o_f[O_2(g)]\right\} \tag{10.8.7}$$

From Table T1, the relevant ΔH^o_f values are $\Delta H^o_f[CO_2(g)]$ = -393.5 kJ/mol, $\Delta H^o_f[H_2O(l)]$ = -285.8 kJ/mol, and $\Delta H^o_f[C_6H_{12}O_6(s)]$ = -1273.3 kJ/mol. Because $O_2(g)$ is a pure element in its standard state, $\Delta H^o_f[O_2(g)]$ = 0 kJ/mol. Inserting these values into Equation 10.8.7 and changing the subscript to indicate that this is a combustion reaction, we obtain

$$\Delta H^o_{comb} = [6(-393.5\ kJ/mol) + 6(-285.8\ kJ/mol)] - [-1273.3 + 6(0\ kJ\ mol)] \tag{10.8.8}$$

$$= -2802.5\ kJ/mol \tag{10.8.9}$$

As illustrated in Figure 10.8.2, we can use Equation 10.8.8 to calculate ΔH^o_f for glucose because enthalpy is a state function. The figure shows two pathways from reactants (middle left) to products (bottom). The more direct pathway is the downward green arrow labeled ΔH^o_{comb}. The alternative hypothetical pathway consists of **four separate reactions** that convert the reactants to the elements in their standard states (upward purple arrow at left) and then convert the elements into the desired products (downward purple arrows at right). The reactions that convert the reactants to the elements are the reverse of the equations that define the ΔH^o_f values of the reactants. Consequently, the enthalpy changes are

$$\begin{aligned}
\Delta H^o_1 &= \Delta H^o_f[glucose(s)] \\
&= -1\ \cancel{mol\ glucose}\left(\frac{1273.3\ kJ}{1\ \cancel{mol\ glucose}}\right) \\
&= +1273.3\ kJ \\
\Delta H^o_2 &= 6\Delta H^o_f[O_2(g)] \\
&= 6\ \cancel{mol\ O_2}\left(\frac{0\ kJ}{1\ \cancel{mol\ O_2}}\right) \\
&= 0\ kJ
\end{aligned} \tag{10.8.10}$$

> *Recall that when we reverse a reaction, we must also reverse the* ***sign*** *of the accompanying enthalpy change (Equation 10.8.4 since the products are now reactants and vice versa.*

The overall enthalpy change for conversion of the reactants (1 mol of glucose and 6 mol of O_2) to the elements is therefore +1273.3 kJ.

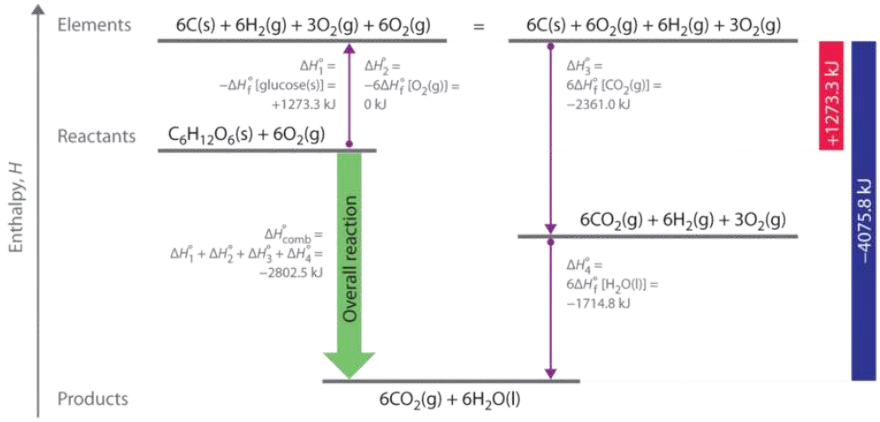


Figure 10.8.1: A Thermochemical Cycle for the Combustion of Glucose. Two hypothetical pathways are shown from the reactants to the products. The green arrow labeled ΔH^o_{comb} indicates the combustion reaction. Alternatively, we could first convert the reactants to the elements via the reverse of the equations that define their standard enthalpies of formation (the upward arrow, labeled ΔH^o_1 and ΔH^o_2). Then we could convert the elements to the products via the equations used to define their standard enthalpies of formation (the downward arrows, labeled ΔH^o_3 and ΔH^o_4). Because enthalpy is a state function, ΔH^o_{comb} is equal to the sum of the enthalpy changes $\Delta H^o_1 + \Delta H^o_2 + \Delta H^o_3 + \Delta H^o_4$.

The reactions that convert the elements to final products (downward purple arrows in Figure 10.8.2) are identical to those used to define the ΔH^o_f values of the products. Consequently, the enthalpy changes (from Table T1) are

$$\Delta H^o_3 = \Delta H^o_f\,[CO_2\,(g)] = 6\ \cancel{mol\ CO_2}\left(\frac{393.5\ kJ}{1\ \cancel{mol\ CO_2}}\right) = -2361.0\ kJ$$
$$\Delta H^o_4 = 6\Delta H^o_f\,[H_2O\,(l)] = 6\ \cancel{mol\ H_2O}\left(\frac{-285.8\ kJ}{1\ \cancel{mol\ H_2O}}\right) = -1714.8\ kJ \tag{10.8.11}$$

The overall enthalpy change for the conversion of the elements to products (6 mol of carbon dioxide and 6 mol of liquid water) is therefore −4075.8 kJ. Because enthalpy is a state function, the difference in enthalpy between an initial state and a final state can be computed using *any* pathway that connects the two. Thus the enthalpy change for the combustion of glucose to carbon dioxide and water is the sum of the enthalpy changes for the conversion of glucose and oxygen to the elements (+1273.3 kJ) and for the conversion of the elements to carbon dioxide and water (−4075.8 kJ):

$$\Delta H^o_{comb} = +1273.3\ kJ + (-4075.8\ kJ) = -2802.5\ kJ \tag{10.8.12}$$

This is the same result we obtained using the "products minus reactants" rule (Equation 10.8.5) and ΔH^o_f values. The two results must be the same because Equation 10.8.12 is just a more compact way of describing the thermochemical cycle shown in Figure 10.8.1.

Example 10.8.2: Heat of Combustion

Long-chain fatty acids such as palmitic acid ($CH_3(CH_2)_{14}CO_2H$) are one of the two major sources of energy in our diet (ΔH^o_f =−891.5 kJ/mol). Use the data in Table T1 to calculate ΔH^o_{comb} for the combustion of palmitic acid. Based on the energy released in combustion *per gram*, which is the better fuel — glucose or palmitic acid?

Given: compound and ΔH^o_f values

Asked for: ΔH^o_{comb} per mole and per gram

Strategy:

A. After writing the balanced chemical equation for the reaction, use Equation 10.8.5 and the values from Table T1 to calculate ΔH^o_{comb} the energy released by the combustion of 1 mol of palmitic acid.

B. Divide this value by the molar mass of palmitic acid to find the energy released from the combustion of 1 g of palmitic acid. Compare this value with the value calculated in Equation 10.8.8 for the combustion of glucose to determine which is the better fuel.

Solution:

A To determine the energy released by the combustion of palmitic acid, we need to calculate its ΔH^o_f. As always, the first requirement is a balanced chemical equation:

$$C_{16}H_{32}O_{2(s)} + 23O_{2(g)} \rightarrow 16CO_{2(g)} + 16H_2O_{(l)}$$

Using Equation 10.8.5 ("products minus reactants") with ΔH^o_f values from Table T1 (and omitting the physical states of the reactants and products to save space) gives

$$\begin{aligned}\Delta H^o_{comb} &= \sum m\Delta H^o_f\,(products) - \sum n\Delta H^o_f\,(reactants)\\ &= [16\,(-393.5\ kJ/mol\ CO_2) + 16\,(-285.8\ kJ/mol\ H_2O\,)]\\ &\quad - [-891.5\ kJ/mol\ C_{16}H_{32}O_2 + 23\,(0\ kJ/mol\ O_2\,)]\\ &= -9977.3\ kJ/mol\end{aligned}$$

This is the energy released by the combustion of 1 mol of palmitic acid.

B The energy released by the combustion of 1 g of palmitic acid is

$$\Delta H^o_{comb}\ per\ gram = \left(\frac{9977.3\ kJ}{1\ \cancel{mol}}\right)\left(\frac{1\ \cancel{mol}}{256.42\ g}\right) = -38.910\ kJ/g$$

As calculated in Equation 10.8.8, \(ΔH^o_f\) of glucose is −2802.5 kJ/mol. The energy released by the combustion of 1 g of glucose is therefore

$$\Delta H^o_{comb}\ per\ gram = \left(\frac{-2802.5\ kJ}{1\ \cancel{mol}}\right)\left(\frac{1\ \cancel{mol}}{180.16\ g}\right) = -15.556\ kJ/g$$

The combustion of fats such as palmitic acid releases more than twice as much energy per gram as the combustion of sugars such as glucose. This is one reason many people try to minimize the fat content in their diets to lose weight.

? Exercise 10.8.2: Water–gas shift reaction

Use Table T1 to calculate ΔH^o_{rxn} for the *water–gas shift reaction*, which is used industrially on an enormous scale to obtain H_2(g):

$$CO(g) + H_2O(g) \longrightarrow CO_2(g) + H_2(g)$$

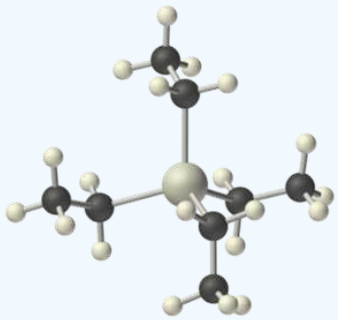
Answer

−41.2 kJ/mol

We can also measure the enthalpy change for another reaction, such as a combustion reaction, and then use it to calculate a compound's ΔH^o_f which we cannot obtain otherwise. This procedure is illustrated in Example 10.8.3.

✓ Example 10.8.3: Tetraethyllead

Beginning in 1923, tetraethyllead $[(C_2H_5)_4Pb]$ was used as an antiknock additive in gasoline in the United States. Its use was completely phased out in 1986 because of the health risks associated with chronic lead exposure. Tetraethyllead is a highly poisonous, colorless liquid that burns in air to give an orange flame with a green halo. The combustion products are CO_2(g), H_2O(l), and red PbO(s). What is the standard enthalpy of formation of tetraethyllead, given that ΔH^o_f is −19.29 kJ/g for the combustion of tetraethyllead and ΔH^o_f of red PbO(s) is −219.0 kJ/mol?



Tetraethyllead

Given: reactant, products, and ΔH^o_{comb} values

Asked for: ΔH_f^o of the reactants

Strategy:

A. Write the balanced chemical equation for the combustion of tetraethyl lead. Then insert the appropriate quantities into Equation 10.8.5 to get the equation for ΔH^o_f of tetraethyl lead.
B. Convert ΔH^o_{comb} per gram given in the problem to ΔH^o_{comb} per mole by multiplying ΔH^o_{comb} per gram by the molar mass of tetraethyllead.
C. Use Table T1 to obtain values of ΔH_f^o for the other reactants and products. Insert these values into the equation for ΔH_f^o of tetraethyl lead and solve the equation.

Solution:

A The balanced chemical equation for the combustion reaction is as follows:

$$2\,(\mathrm{C_2H_5})_4\mathrm{Pb(l)} + 27\,\mathrm{O_2(g)} \rightarrow 2\,\mathrm{PbO(s)} + 16\,\mathrm{CO_2(g)} + 20\,\mathrm{H_2O(l)}$$

Using Equation 10.8.5 gives

$$\Delta H^o_{comb} = \left[2\Delta H^o_f\,(PbO) + 16\Delta H^o_f\,(CO_2) + 20\Delta H^o_f\,(H_2O)\right] - \left[2\Delta H^o_f\,((C_2H_5)_4Pb) + 27\Delta H^o_f\,(O_2)\right]$$

Solving for $\Delta H^o_f[(\mathrm{C_2H_5})_4\mathrm{Pb}]$ gives

$$\Delta H^o_f\,((C_2H_5)_4Pb) = \Delta H^o_f\,(PbO) + 8\Delta H^o_f\,(CO_2) + 10\Delta H^o_f\,(H_2O) - \frac{27}{2}\Delta H^o_f\,(O_2) - \frac{\Delta H^o_{comb}}{2}$$

The values of all terms other than $\Delta H^o_f[(\mathrm{C_2H_5})_4\mathrm{Pb}]$ are given in Table T1.

B The magnitude of ΔH^o_{comb} is given in the problem in kilojoules per *gram* of tetraethyl lead. We must therefore multiply this value by the molar mass of tetraethyl lead (323.44 g/mol) to get ΔH^o_{comb} for 1 mol of tetraethyl lead:

$$\Delta H^o_{comb} = \left(\frac{-19.29\ kJ}{\cancel{g}}\right)\left(\frac{323.44\ \cancel{g}}{mol}\right)$$
$$= -6329\ kJ/mol$$

Because the balanced chemical equation contains 2 mol of tetraethyllead, ΔH^o_{rxn} is

$$\Delta H^o_{rxn} = 2\ \ mol\ \cancel{(C_2H5)_4Pb}\left(\frac{-6329\ kJ}{1\ \ mol\ \cancel{(C_2H5)_4Pb}}\right)$$
$$= -12,480\ kJ$$

C Inserting the appropriate values into the equation for $\Delta H^o_f[(\mathrm{C_2H_5})_4\mathrm{Pb}]$ gives

$$\Delta H^o_f\,[(C_2H_4)_4Pb] = [1\ mol\ PbO\ \times 219.0\ kJ/mol] + [8\ mol\ CO_2 \times (-393.5\ kJ/mol)] + [10\ mol\ H_2O \times (-285.8\ kJ/mol)]$$
$$+ [-27/2\ mol\ O_2) \times 0\ kJ/mol\ O_2]\ [12,480.2\ kJ/mol\ (C_2H_5)_4Pb]$$
$$= -219.0\ kJ - 3148\ kJ - 2858kJ - 0kJ + 6240\ kJ = 15kJ/mol$$

? Exercise 10.8.3

Ammonium sulfate, $(\mathrm{NH_4})_2\mathrm{SO_4}$, is used as a fire retardant and wood preservative; it is prepared industrially by the highly exothermic reaction of gaseous ammonia with sulfuric acid:

$$2\,\mathrm{NH_3(g)} + \mathrm{H_2SO_4(aq)} \rightarrow (\mathrm{NH_4})_2\mathrm{SO_4(s)}$$

The value of ΔH^o_{rxn} is -179.4 kJ/mole $\mathrm{H_2SO_4}$. Use the data in Table T1 to calculate the standard enthalpy of formation of ammonium sulfate (in kilojoules per mole).

Answer

−1181 kJ/mol



Calculating DH° using DHf°: https://youtu.be/Y3aJJno9W2c

Summary

- The standard state for measuring and reporting enthalpies of formation or reaction is 25 ^{o}C and 1 atm.
- The elemental form of each atom is that with the lowest enthalpy in the standard state.
- The standard state heat of formation for the elemental form of each atom is zero.

The **enthalpy of formation** (ΔH_f) is the enthalpy change that accompanies the formation of a compound from its elements. **Standard enthalpies of formation** (ΔH_f^o) are determined under **standard conditions**: a pressure of 1 atm for gases and a concentration of 1 M for species in solution, with all pure substances present in their **standard states** (their most stable forms at 1 atm pressure and the temperature of the measurement). The standard heat of formation of any element in its most stable form is defined to be zero. The **standard enthalpy of reaction** (ΔH_{rxn}^o) can be calculated from the sum of the **standard enthalpies of formation** of the products (each multiplied by its stoichiometric coefficient) minus the sum of the standard enthalpies of formation of the reactants (each multiplied by its stoichiometric coefficient)—the "products minus reactants" rule. The **enthalpy of solution** (ΔH_{soln}) is the heat released or absorbed when a specified amount of a solute dissolves in a certain quantity of solvent at constant pressure.

Contributors and Attributions

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10.9: Foods and Fuels

Learning Objectives

- To understand the relationship between thermochemistry and nutrition.

The thermochemical quantities that you probably encounter most often are the caloric values of food. Food supplies the raw materials that your body needs to replace cells and the energy that keeps those cells functioning. About 80% of this energy is released as heat to maintain your body temperature at a sustainable level to keep you alive. The nutritional Calorie (with a capital C) that you see on food labels is equal to 1 kcal (kilocalorie). The caloric content of food is determined from its enthalpy of combustion (ΔH_{comb}) per gram, as measured in a bomb calorimeter, using the general reaction

$$\text{food} + \text{excess } \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) + \text{N}_2(\text{g}) \tag{10.9.1}$$

There are two important differences, however, between the caloric values reported for foods and the ΔH_{comb} of the same foods burned in a calorimeter. First, the ΔH_{comb} described in joules (or kilojoules) are negative for all substances that can be burned. In contrast, the caloric content of a food is always expressed as a *positive* number because it is *stored energy*. Therefore,

$$\text{caloric content} = -\Delta H_{\text{comb}} \tag{10.9.2}$$

Second, when foods are burned in a calorimeter, any nitrogen they contain (largely from proteins, which are rich in nitrogen) is transformed to N_2. In the body, however, nitrogen from foods is converted to urea [$(H_2N)_2C{=}O$], rather than N_2 before it is excreted. The ΔH_{comb} of urea measured by bomb calorimetry is −632.0 kJ/mol. Consequently, the enthalpy change measured by calorimetry for any nitrogen-containing food is greater than the amount of energy the body would obtain from it. The difference in the values is equal to the ΔH_{comb} of urea multiplied by the number of moles of urea formed when the food is broken down. This point is illustrated schematically in the following equations:

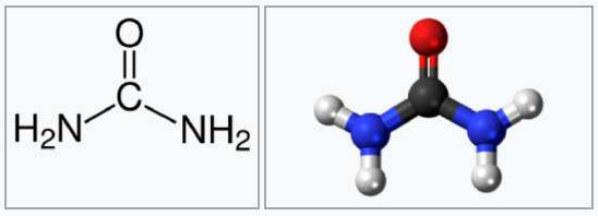
$$\text{food} + \text{excess } \text{O}_2(\text{g}) \xrightarrow{\Delta H_1 < 0} \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) + \cancel{(\text{H}_2\text{N})_2\text{C}{=}\text{O}(\text{s})}$$

$$\cancel{(\text{H}_2\text{N})_2\text{C}{=}\text{O}(\text{s})} + \tfrac{3}{2}\text{O}_2(\text{g}) \xrightarrow{\Delta H_2 = 632.0\,\text{kJ/mol}} \text{CO}_2(\text{g}) + 2\,\text{H}_2\text{O}(\text{l}) + \text{N}_2(\text{g})$$

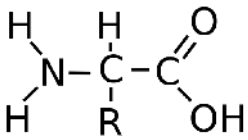
which adds up to

$$\text{food} + \text{excess } \text{O}_2(\text{g}) \xrightarrow{\Delta H_3 = \Delta H_1 + \Delta H_2 < 0} 2\,\text{CO}_2(\text{g}) + 3\,\text{H}_2\text{O}(\text{l}) + \text{N}_2(\text{g})$$

All three ΔH values are negative, and, by Hess's law, $\Delta H_3 = \Delta H_1 + \Delta H_2$. The magnitude of ΔH_1 must be less than ΔH_3, the calorimetrically measured ΔH_{comb} for a food. By producing urea rather than N_2, therefore, humans are excreting some of the energy that was stored in their food.



Because of their different chemical compositions, foods vary widely in caloric content. As we saw previously, for instance, a fatty acid such as palmitic acid produces about 39 kJ/g during combustion, while a sugar such as glucose produces 15.6 kJ/g. Fatty acids and sugars are the building blocks of fats and carbohydrates, respectively, two of the major sources of energy in the diet. Nutritionists typically assign average values of 38 kJ/g (about 9 Cal/g) and 17 kJ/g (about 4 Cal/g) for fats and carbohydrates, respectively, although the actual values for specific foods vary because of differences in composition. Proteins, the third major source of calories in the diet, vary as well. Proteins are composed of amino acids, which have the following general structure:



General structure of an amino acid. An amino acid contains an amine group ($-NH_2$) and a carboxylic acid group ($-CO_2H$).

In addition to their amine and carboxylic acid components, amino acids may contain a wide range of other functional groups: R can be hydrogen (–H); an alkyl group (e.g., $–CH_3$); an aryl group (e.g., $–CH_2C_6H_5$); or a substituted alkyl group that contains an amine, an alcohol, or a carboxylic acid (Figure 10.9.1). Of the 20 naturally occurring amino acids, 10 are required in the human diet; these 10 are called *essential amino acids* because our bodies are unable to synthesize them from other compounds. Because R can be any of several different groups, each amino acid has a different value of ΔH_{comb}. Proteins are usually estimated to have an average ΔH_{comb} of 17 kJ/g (about 4 Cal/g).

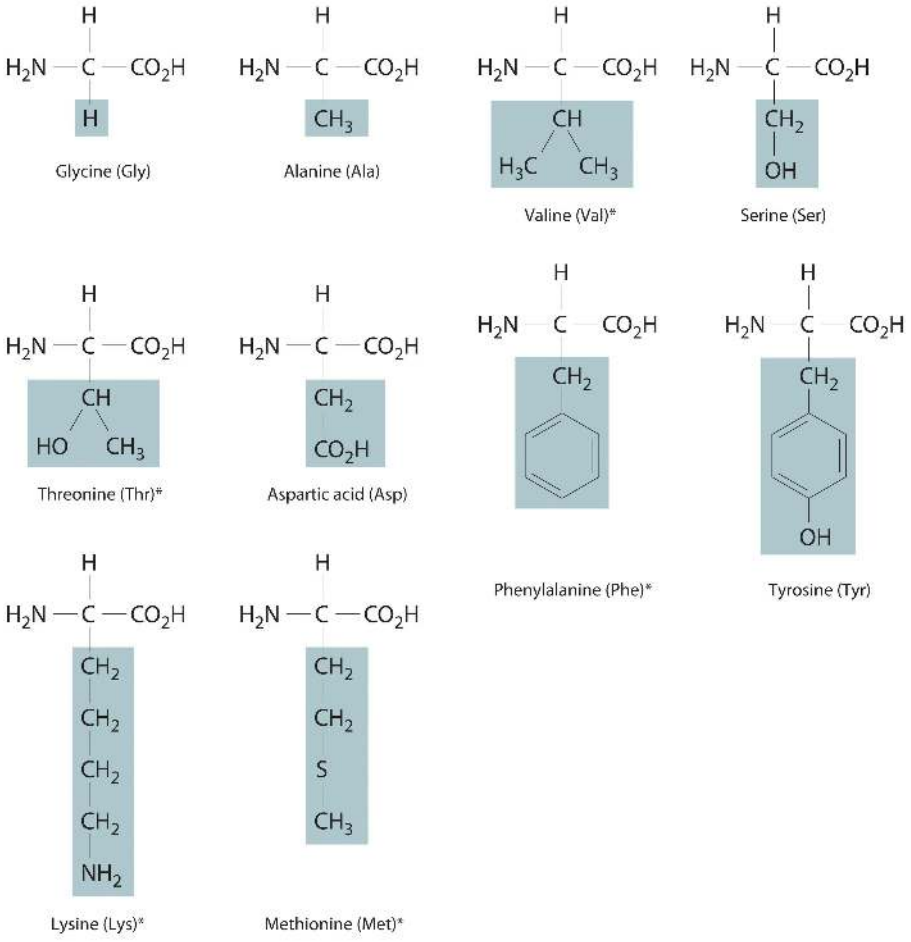
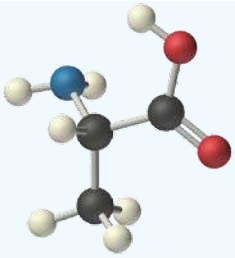


Figure 10.9.1: The Structures of 10 Amino Acids. Essential amino acids in this group are indicated with an asterisk.
Structures of glycine, alanine, valine, serine, threonine, aspartic acid, phenylalanine, tyrosine, lysine, methionine.

Example 10.9.1

Calculate the amount of available energy obtained from the biological oxidation of 1.000 g of alanine (an amino acid). Remember that the nitrogen-containing product is urea, not N_2, so biological oxidation of alanine will yield *less* energy than will combustion. The value of ΔH_{comb} for alanine is −1577 kJ/mol.



Alanine

Given: amino acid and ΔH_{comb} per mole

Asked for: caloric content per gram

Strategy:

A. Write balanced chemical equations for the oxidation of alanine to CO_2, H_2O, and urea; the combustion of urea; and the combustion of alanine. Multiply both sides of the equations by appropriate factors and then rearrange them to cancel urea from both sides when the equations are added.

B. Use Hess's law to obtain an expression for ΔH for the oxidation of alanine to urea in terms of the ΔH_{comb} of alanine and urea. Substitute the appropriate values of ΔH_{comb} into the equation and solve for ΔH for the oxidation of alanine to CO_2, H_2O, and urea.

C. Calculate the amount of energy released per gram by dividing the value of ΔH by the molar mass of alanine.

Solution:

The actual energy available biologically from alanine is less than its ΔH_{comb} because of the production of urea rather than N_2. We know the ΔH_{comb} values for alanine and urea, so we can use Hess's law to calculate ΔH for the oxidation of alanine to CO_2, H_2O, and urea.

A We begin by writing balanced chemical equations for (1) the oxidation of alanine to CO_2, H_2O, and urea; (2) the combustion of urea; and (3) the combustion of alanine. Because alanine contains only a single nitrogen atom, whereas urea and N_2 each contain two nitrogen atoms, it is easier to balance Equations 1 and 3 if we write them for the oxidation of 2 mol of alanine:

$$(1)\quad 2C_3H_7NO_2\,(s)+6O_2\,(g)\rightarrow 5CO_2\,(g)+5H_2O\,(l)+(H_2N)_2C=O\,(s)$$

$$(2)\quad (H_2N)_2C=O\,(s)+\frac{3}{2}O_2\,(g)\rightarrow CO_2\,(g)+2H_2O\,(l)+N_2\,(g)$$

$$(3)\quad (1)\quad 2C_3H_7NO_2\,(s)+\frac{15}{2}O_2\,(g)\rightarrow 6CO_2\,(g)+7H_2O\,(l)+N_2\,(g)$$

Adding Equations 1 and 2 and canceling urea from both sides give the overall chemical equation directly:

$$(1)\quad 2C_3H_7NO_2\,(s)+6O_2\,(g)\rightarrow 5CO_2\,(g)+5H_2O\,(l)+\cancel{(H_2N)_2C=O\,(s)}$$

$$(2)\quad \cancel{(H_2N)_2C=O\,(s)}+\frac{3}{2}O_2\,(g)\rightarrow CO_2\,(g)+2H_2O\,(l)+N_2\,(g)$$

$$(3)\quad (1)\quad 2C_3H_7NO_2\,(s)+\frac{15}{2}O_2\,(g)\rightarrow 6CO_2\,(g)+7H_2O\,(l)+N_2\,(g)$$

B By Hess's law, $\Delta H_3 = \Delta H_1 + \Delta H_2$. We know that $\Delta H_3 = 2\Delta H_{comb}$ (alanine), $\Delta H_2 = \Delta H_{comb}$ (urea), and $\Delta H_1 = 2\Delta H$ (alanine → urea). Rearranging and substituting the appropriate values gives

$$\Delta H_1=\Delta H_3-\Delta H_2$$

$$=2\,(-1577\ kJ/mol)-(-632.0\ kJ/mol)$$

= -2522 \; kJ/\left (2 \;mol\; analine \right) \nonumber \]

Thus ΔH (alanine → urea) = −2522 kJ/(2 mol of alanine) = −1261 kJ/mol of alanine. Oxidation of alanine to urea rather than to nitrogen therefore results in about a 20% decrease in the amount of energy released (−1261 kJ/mol versus −1577 kJ/mol).

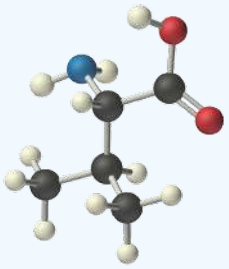
C The energy released per gram by the biological oxidation of alanine is

$$\left(\frac{-1261\ kJ}{1\ \cancel{mol}}\right)\left(\frac{1\ \cancel{mol}}{89.094\ g}\right) = -14.15\ kJ/g$$

This is equal to −3.382 Cal/g.

? Exercise 10.9.1

Calculate the energy released per gram from the oxidation of valine (an amino acid) to CO_2, H_2O, and urea. Report your answer to three significant figures. The value of ΔH_{comb} for valine is −2922 kJ/mol.



Valine

Answer

−22.2 kJ/g (−5.31 Cal/g)

The reported caloric content of foods does not include ΔH_{comb} for those components that are not digested, such as fiber. Moreover, meats and fruits are 50%−70% water, which cannot be oxidized by O_2 to obtain energy. So water contains no calories. Some foods contain large amounts of fiber, which is primarily composed of sugars. Although fiber can be burned in a calorimeter just like glucose to give carbon dioxide, water, and heat, humans lack the enzymes needed to break fiber down into smaller molecules that can be oxidized. Hence fiber also does not contribute to the caloric content of food.

Table 10.9.1: Approximate Composition and Fuel Value of an 8 oz Slice of Roast Beef

Composition	Calories
97.5 g of water	× 0 Cal/g = 0
58.7 g of protein	× 4 Cal/g = 235
69.3 g of fat	× 9 Cal/g = 624
0 g of carbohydrates	× 4 Cal/g = 0
1.5 g of minerals	× 0 Cal/g = 0
Total mass: 227.0 g	**Total calories: about 900 Cal**

We can determine the caloric content of foods in two ways. The most precise method is to dry a carefully weighed sample and carry out a combustion reaction in a bomb calorimeter. The more typical approach, however, is to analyze the food for protein, carbohydrate, fat, water, and “minerals” (everything that doesn’t burn) and then calculate the caloric content using the average values for each component that produces energy (9 Cal/g for fats, 4 Cal/g for carbohydrates and proteins, and 0 Cal/g for water and minerals). An example of this approach is shown in Table 10.9.1 for a slice of roast beef. The compositions and caloric contents of some common foods are given in Table 10.9.2

Table 10.9.2: Approximate Compositions and Fuel Values of Some Common Foods

Food (quantity)	Approximate Composition (%)	Food Value (Cal/g)	Calories

Food (quantity)	Approximate Composition (%)				Food Value (Cal/g)	Calories
	Water	**Carbohydrate**	**Protein**	**Fat**		
beer (12 oz)	92	3.6	0.3	0	0.4	150
coffee (6 oz)	100	~0	~0	~0	~0	~0
milk (1 cup)	88	4.5	3.3	3.3	0.6	150
egg (1 large)	75	2	12	12	1.6	80
butter (1 tbsp)	16	~0	~0	79	7.1	100
apple (8 oz)	84	15	~0	0.5	0.6	125
bread, white (2 slices)	37	48	8	4	2.6	130
brownie (40 g)	10	55	5	30	4.8	190
hamburger (4 oz)	54	0	24	21	2.9	326
fried chicken (1 drumstick)	53	8.3	22	15	2.7	195
carrots (1 cup)	87	10	1.3	~0	0.4	70

Because the Calorie represents such a large amount of energy, a few of them go a long way. An average 73 kg (160 lb) person needs about 67 Cal/h (1600 Cal/day) to fuel the basic biochemical processes that keep that person alive. This energy is required to maintain body temperature, keep the heart beating, power the muscles used for breathing, carry out chemical reactions in cells, and send the nerve impulses that control those automatic functions. Physical activity increases the amount of energy required but not by as much as many of us hope (Table 10.9.2). A moderately active individual requires about 2500−3000 Cal/day; athletes or others engaged in strenuous activity can burn 4000 Cal/day. Any excess caloric intake is stored by the body for future use, usually in the form of fat, which is the most compact way to store energy. When more energy is needed than the diet supplies, stored fuels are mobilized and oxidized. We usually exhaust the supply of stored carbohydrates before turning to fats, which accounts in part for the popularity of low-carbohydrate diets.

Table 10.9.3: Approximate Energy Expenditure by a 160 lb Person Engaged in Various Activities

Activity	**Cal/h**
sleeping	80
driving a car	120
standing	140
eating	150
walking 2.5 mph	210
mowing lawn	250
swimming 0.25 mph	300
roller skating	350
tennis	420
bicycling 13 mph	660
running 10 mph	900

Example 10.9.2

What is the minimum number of Calories expended by a 72.6 kg person who climbs a 30-story building? (Assume each flight of stairs is 14 ft high.) How many grams of glucose are required to supply this amount of energy? (The energy released during the combustion of glucose was calculated in Example 5.5.4).

Given: mass, height, and energy released by combustion of glucose

Asked for: calories expended and mass of glucose needed

Strategy:

A. Convert mass and height to SI units and then substitute these values into Equation 5.6 to calculate the change in potential energy (in kilojoules). Divide the calculated energy by 4.184 Cal/kJ to convert the potential energy change to Calories.

B. Use the value obtained in Example 5.5.4 for the combustion of glucose to calculate the mass of glucose needed to supply this amount of energy.

Solution:

The energy needed to climb the stairs equals the difference between the person's potential energy (*PE*) at the top of the building and at ground level.

A Recall that *PE* = *mgh*. Because *m* and *h* are given in non-SI units, we must convert them to kilograms and meters, respectively

$$PE = (72.6\ kg)\left(9.81\ m/s^2\right)(128m) = 8.55 \times 10^4\left(kg \cdot m^2/s^2\right) = 91.2kJ$$

To convert to Calories, we divide by 4.184 kJ/kcal:

$$PE = \left(91.2\ \cancel{kJ}\right)\left(\frac{1\ kcal}{4.184\ \cancel{kJ}}\right) = 21.8\ kcal = 21.8\ Cal$$

B Because the combustion of glucose produces 15.6 kJ/g (Example 5), the mass of glucose needed to supply 85.5 kJ of energy is

$$PE = \left(91.2\ \cancel{kJ}\right)\left(\frac{1\ g\ glucose}{15.6\ \cancel{kJ}}\right) = 5.85\ g\ glucose$$

This mass corresponds to only about a teaspoonful of sugar! Because the body is only about 30% efficient in using the energy in glucose, the actual amount of glucose required would be higher: (100%/30%) × 5.85 g = 19.5 g. Nonetheless, this calculation illustrates the difficulty many people have in trying to lose weight by exercise alone.

Exercise 10.9.2

Calculate how many times a 160 lb person would have to climb the tallest building in the United States, the 110-story Willis Tower in Chicago, to burn off 1.0 lb of stored fat. Assume that each story of the building is 14 ft high and use a calorie content of 9.0 kcal/g of fat.

Answer

About 55 times

The calculations in Example 5.8.2 ignore various factors, such as how fast the person is climbing. Although the rate is irrelevant in calculating the change in potential energy, it is very relevant to the amount of energy actually required to ascend the stairs. The calculations also ignore the fact that the body's conversion of chemical energy to mechanical work is significantly less than 100% efficient. According to the average energy expended for various activities listed in Table 5.8.3, a person must run more than 4.5 h at 10 mph or bicycle for 6 h at 13 mph to burn off 1 lb of fat (1.0 lb × 454 g/lb × 9.0 Cal/g = 4100 Cal). But if a person rides a bicycle at 13 mph for only 1 h per day 6 days a week, that person will burn off 50 lb of fat in the course of a year (assuming, of course, the cyclist doesn't increase his or her intake of calories to compensate for the exercise).

Summary

Thermochemical concepts can be applied to determine the actual energy available in food. The nutritional **Calorie** is equivalent to 1 kcal (4.184 kJ). The caloric content of a food is its ΔH_{comb} per gram. The combustion of nitrogen-containing substances produces $N_2(g)$, but the biological oxidation of such substances produces urea. Hence the actual energy available from nitrogen-containing substances, such as proteins, is less than the ΔH_{comb} of urea multiplied by the number of moles of urea produced. The typical caloric contents for food are 9 Cal/g for fats, 4 Cal/g for carbohydrates and proteins, and 0 Cal/g for water and minerals.

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10.E: Thermochemistry (Exercises)

5.1: The Nature of Energy

Conceptual Problems

1. What is the relationship between mechanical work and energy?
2. Does a person with a mass of 50 kg climbing a height of 15 m do work? Explain your answer. Does that same person do work while descending a mountain?
3. If a person exerts a force on an immovable object, does that person do work? Explain your answer.
4. Explain the differences between electrical energy, nuclear energy, and chemical energy.
5. The chapter describes thermal energy, radiant energy, electrical energy, nuclear energy, and chemical energy. Which form(s) of energy are represented by each of the following?
    1. sunlight
    2. the energy produced by a cathode ray tube, such as that found in a television
    3. the energy emitted from radioactivity
    4. the energy emitted from a burning candle
    5. the energy associated with a steam engine
    6. the energy emitted by a cellular phone
    7. the energy associated with a stick of dynamite
6. Describe the various forms of energy that are interconverted when a flashlight is switched on.
7. Describe the forms of energy that are interconverted when the space shuttle lifts off.
8. Categorize each of the following as representing kinetic energy or potential energy.
    1. the energy associated with a laptop computer sitting on the edge of a desk
    2. shoveling snow
    3. water pouring out of a fire hydrant
    4. the energy released by an earthquake
    5. the energy in a volcano about to erupt
    6. the energy associated with a coiled spring
9. Are the units for potential energy the same as the units for kinetic energy? Can an absolute value for potential energy be obtained? Explain your answer.
10. Categorize each of the following as representing kinetic energy or potential energy.
    1. water cascading over Niagara Falls
    2. a beaker balanced on the edge of a sink
    3. the energy released during a mudslide
    4. rollerblading
    5. the energy in a block of ice on a rooftop before a thaw
11. Why does hammering a piece of sheet metal cause the metal to heat up?

Conceptual Answers

3. Technically, the person is not doing any work, since the object does not move.

11. The kinetic energy of the hammer is transferred to the metal.

Numerical Problems

Please be sure you are familiar with the topics discussed in Essential Skills 4 before proceeding to the Numerical Problems.

1. Describe the mathematical relationship between (a) the thermal energy stored in an object and that object's mass and (b) the thermal energy stored in an object and that object's temperature.

2. How much energy (in kilojoules) is released or stored when each of the following occurs?
    1. A 230 lb football player is lifted to a height of 4.00 ft.
    2. An 11.8 lb cat jumps from a height of 6.50 ft.
    3. A 3.75 lb book falls off of a shelf that is 5.50 ft high.
3. Calculate how much energy (in kilojoules) is released or stored when each of the following occurs:
    1. A 130 lb ice skater is lifted 7.50 ft off the ice.
    2. A 48 lb child jumps from a height of 4.0 ft.
    3. An 18.5 lb light fixture falls from a 10.0 ft ceiling.
4. A car weighing 1438 kg falls off a bridge that is 211 ft high. Ignoring air resistance, how much energy is released when the car hits the water?
5. A 1 tn roller coaster filled with passengers reaches a height of 28 m before accelerating downhill. How much energy is released when the roller coaster reaches the bottom of the hill? Assume no energy is lost due to friction.

Numerical Answers

1.

a. The thermal energy content of an object is directly proportional to its mass.
b. The thermal energy content of an object is directly proportional to its temperature.

3.

a. 1.3 kJ stored
b. 0.26 kJ released
c. 0.251 kJ released

5.

1. 250 kJ released

5.2: The First Law of Thermodynamics

Conceptual Problems

1. Describe how a swinging pendulum that slows with time illustrates the first law of thermodynamics.
2. When air is pumped into a bicycle tire, the air is compressed. Assuming that the volume is constant, express the change in internal energy in terms of q and w.
3. What is the relationship between enthalpy and internal energy for a reaction that occurs at constant pressure?
4. An intrepid scientist placed an unknown salt in a small amount of water. All the salt dissolved in the water, and the temperature of the solution dropped several degrees.
    a. What is the sign of the enthalpy change for this reaction?
    b. Assuming the heat capacity of the solution is the same as that of pure water, how would the scientist calculate the molar enthalpy change?
    c. Propose an explanation for the decrease in temperature.
5. For years, chemists and physicists focused on enthalpy changes as a way to measure the spontaneity of a reaction. What arguments would you use to convince them not to use this method?
6. What is the relationship between enthalpy and internal energy for a reaction that occurs at constant volume?
7. The enthalpy of combustion (ΔH_{comb}) is defined thermodynamically as the enthalpy change for complete oxidation. The complete oxidation of hydrocarbons is represented by the following general equation: hydrocarbon + $O_2(g) \rightarrow CO_2(g) + H_2O(g)$. Enthalpies of combustion from reactions like this one can be measured experimentally with a high degree of precision. It has been found that the less stable the reactant, the more heat is evolved, so the more negative the value of ΔHcomb. In each pair of hydrocarbons, which member do you expect to have the greater (more negative) heat of combustion? Justify your answers.
    a. cyclopropane or cyclopentane

b. butane or 2-methylpropane
c. hexane or cyclohexane

8. Using a structural argument, explain why the trans isomer of 2-butene is more stable than the cis isomer. The enthalpies of formation of cis- and trans-2-butene are −7.1 kJ/mol and −11.4 kJ/mol, respectively.
9. Using structural arguments, explain why cyclopropane has a positive $\Delta H_f°$ (12.7 kJ/mol), whereas cyclopentane has a negative $\Delta H_f°$ (−18.4 kJ/mol). (Hint: consider bond angles.)

Conceptual Answers

3. At constant pressure, ΔH = ΔU + PΔV.
4.
5. In some simple case, when a reaction only involves solids, liquids or liquid solution, we can say that $\Delta H = \Delta U$. When a reaction involves gases, we can say that $\Delta U = \Delta H - RT\Delta n$. However, if we have a complicated case, it is hard to use ΔH to measure the spontaneity of a reaction. For example, when a reaction involved gases, liquid and solid, it is really hard for us to defined $\Delta(PV)$.
9. With bond angles of 60°, cyclopropane is highly strained, causing it to be less stable than cyclopentane, which has nearly ideal tetrahedral geometry at each carbon atom.

Numerical Problems

1. A block of CO_2 weighing 15 g evaporates in a 5.0 L container at 25°C. How much work has been done if the gas is allowed to expand against an external pressure of 0.98 atm under isothermal conditions? The enthalpy of sublimation of CO_2 is 25.1 kJ/mol. What is the change in internal energy (kJ/mol) for the sublimation of CO_2 under these conditions?
2. Zinc and HCl react according to the following equation:

$$Zn_{(s)} + 2HCl_{(aq)} \rightarrow Zn^{2+}_{(aq)} + 2Cl^{-}_{(aq)} + H_2(g) \tag{10.E.1}$$

When 3.00 g of zinc metal is added to a dilute HCl solution at 1.00 atm and 25°C, and this reaction is allowed to go to completion at constant pressure, 6.99 kJ of heat must be removed to return the final solution to its original temperature. What are the values of q and w, and what is the change in internal energy?

3. Acetylene torches, used industrially to cut and weld metals, reach flame temperatures as high as 3000°C. The combustion reaction is as follows:

$$2C_2H_{2\ (g)} + 5O_{2\ (g)} \rightarrow 4CO_{2\ (g)} + 2H_2O_{(l)} \qquad (\Delta H = -2599\ \text{kJ})$$

Calculate the amount of work done against a pressure of 1.0 atm when 4.0 mol of acetylene are allowed to react with 10 mol of O_2 at 1.0 atm at 20°C. What is the change in internal energy for the reaction?

4. When iron dissolves in 1.00 M aqueous HCl, the products are $FeCl_2$(aq) and hydrogen gas. Calculate the work done if 30 g of Fe react with excess hydrochloric acid in a closed vessel at 20°C. How much work is done if the reaction takes place in an open vessel with an external pressure of 1.0 atm?

Numerical Answers

1. −350 J; 8.2 kJ

5.3: Enthalpy

5.4: Enthalpy of Reaction

Conceptual Problems

Please be sure you are familiar with the topics discussed in Essential Skills 4 (Section 5.6 "Essential Skills 4") before proceeding to the Conceptual Problems.

1. Heat implies the flow of energy from one object to another. Describe the energy flow in an

a. exothermic reaction.

b. endothermic reaction.

2. When a thermometer is suspended in an insulated thermos that contains a block of ice, the temperature recorded on the thermometer drops. Describe the direction of heat flow.
3. In each scenario, the system is defined as the mixture of chemical substances that undergoes a reaction. State whether each process is endothermic or exothermic.
    1. Water is added to sodium hydroxide pellets, and the flask becomes hot.
    2. The body metabolizes glucose, producing carbon dioxide and water.
    3. Ammonium nitrate crystals are dissolved in water, causing the solution to become cool.
4. In each scenario, the system is defined as the mixture of chemical substances that undergoes a reaction. Determine whether each process is endothermic or exothermic.
    1. Concentrated acid is added to water in a flask, and the flask becomes warm.
    2. Water evaporates from your skin, causing you to shiver.
    3. A container of ammonium nitrate detonates.
5. Is Earth's environment an isolated system, an open system, or a closed system? Explain your answer.
6. Why is it impossible to measure the absolute magnitude of the enthalpy of an object or a compound?
7. Determine whether energy is consumed or released in each scenario. Explain your reasoning.
    1. A leaf falls from a tree.
    2. A motorboat maneuvers against a current.
    3. A child jumps rope.
    4. Dynamite detonates.
    5. A jogger sprints down a hill.
8. The chapter states that enthalpy is an extensive property. Why? Describe a situation that illustrates this fact.
9. The enthalpy of a system is affected by the physical states of the reactants and the products. Explain why.
10. Is the distance a person travels on a trip a state function? Why or why not?

5.5: Calorimetry

Conceptual Problems

1. Can an object have a negative heat capacity? Why or why not?
2. What two factors determine the heat capacity of an object? Does the specific heat also depend on these two factors? Explain your answer.
3. Explain why regions along seacoasts have a more moderate climate than inland regions do.
4. Although soapstone is more expensive than brick, soapstone is frequently the building material of choice for fireplaces, particularly in northern climates with harsh winters. Propose an explanation for this.

Numerical Problems

Please be sure you are familiar with the topics discussed in Essential Skills 4 (Section 9.9) before proceeding to the Numerical Problems.

1. Using Equation 9.6.2 and Equation 9.6.3, derive a mathematical relationship between C_s and C_p.
2. Complete the following table for 28.0 g of each element at an initial temperature of 22.0°C.

Element	q (J)	C_p [J/(mol·K)]	Final T (°C)
nickel	137	26.07	
silicon		19.789	3.0
zinc	603		77.5

Element	q (J)	C_p [J/(mol·K)]	Final T (°C)
mercury	137		57

3. Using Table 9.6.1, how much heat is needed to raise the temperature of a 2.5 g piece of copper wire from 20°C to 80°C? How much heat is needed to increase the temperature of an equivalent mass of aluminum by the same amount? If you were using one of these metals to channel heat away from electrical components, which metal would you use? Once heated, which metal will cool faster? Give the specific heat for each metal.
4. Gold has a molar heat capacity of 25.418 J/(mol·K), and silver has a molar heat capacity of 23.350 J/(mol·K).
    1. If you put silver and gold spoons of equal mass into a cup of hot liquid and wait until the temperature of the liquid is constant, which spoon will take longer to cool down when removed from the hot liquid?
    2. If 8.00 g spoons of each metal at 20.0°C are placed in an insulated mug with 50.0 g of water at 97.0°C, what will be the final temperature of the water after the system has equilibrated? (Assume that no heat is transferred to the surroundings.)
5. In an exothermic reaction, how much heat would need to be evolved to raise the temperature of 150 mL of water 7.5°C? Explain how this process illustrates the law of conservation of energy.
6. How much heat must be evolved by a reaction to raise the temperature of 8.0 oz of water 5.0°C? What mass of lithium iodide would need to be dissolved in this volume of water to produce this temperature change?
7. A solution is made by dissolving 3.35 g of an unknown salt in 150 mL of water, and the temperature of the water rises 3.0°C. The addition of a silver nitrate solution results in a precipitate. Assuming that the heat capacity of the solution is the same as that of pure water, use the information in Table 9.5.1 and solubility rules to identify the salt.
8. Using the data in Table 9.8.2, calculate the change in temperature of a calorimeter with a heat capacity of 1.78 kJ/°C when 3.0 g of charcoal is burned in the calorimeter. If the calorimeter is in a 2 L bath of water at an initial temperature of 21.5°C, what will be the final temperature of the water after the combustion reaction (assuming no heat is lost to the surroundings)?
9. A 3.00 g sample of TNT (trinitrotoluene, $C_7H_5N_3O_6$) is placed in a bomb calorimeter with a heat capacity of 1.93 kJ/°C; the ΔH_{comb} of TNT is −3403.5 kJ/mol. If the initial temperature of the calorimeter is 19.8°C, what will be the final temperature of the calorimeter after the combustion reaction (assuming no heat is lost to the surroundings)? What is the ΔH_f of TNT?

Answers

1. $C_p = C_s \times$ (molar mass)
2.
3. For Cu: q = 58 J; For Al: q = 130 J; Even though the values of the molar heat capacities are very similar for the two metals, the specific heat of Cu is only about half as large as that of Al, due to the greater molar mass of Cu versus Al: C_s = 0.385 and 0.897 *J*/(g•K) for Cu and Al, respectively. Thus loss of one joule of heat will cause almost twice as large a decrease in temperature of Cu versus Al.
4.
5. 4.7 kJ
6.
7. ΔH_{soln} = −0.56 kJ/g; based on reaction with $AgNO_3$, salt contains halide; dividing ΔH_{soln} values in Table 5.2 by molar mass of salts gives lithium bromide as best match, with −0.56 kJ/g.
8.
9. T_{final} = 43.1°C; the combustion reaction is

$$4C_7H_5N_3O_{6(s)} + 21O_{2(g)} \rightarrow 28CO_{2(g)} + 10H_2O_{(g)} + 6N_{2(g)} \tag{10.E.2}$$

with

$$\Delta_f^o H(TNT) = -65.5\ kJ/mol \tag{10.E.3}$$

5.6: Hess's Law

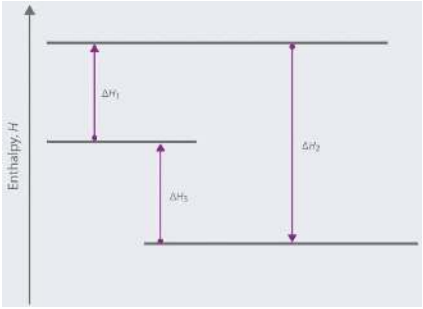
Conceptual Problems

Please be sure you are familiar with the topics discussed in Essential Skills 4 (Section 5.6 "Essential Skills 4") before proceeding to the Conceptual Problems.

1. Based on the following energy diagram,

   a. write an equation showing how the value of ΔH_2 could be determined if the values of ΔH_1 and ΔH_3 are known.

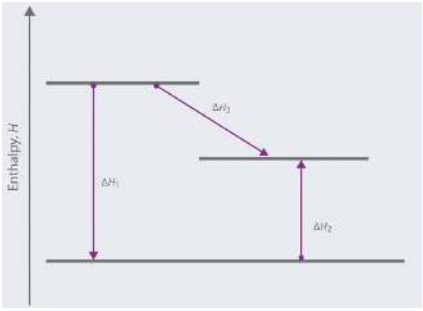
   b. identify each step as being exothermic or endothermic.



2. Based on the following energy diagram,

   a. write an equation showing how the value of ΔH_3 could be determined if the values of ΔH_1 and ΔH_2 are known.

   b. identify each step as being exothermic or endothermic.



3. Describe how Hess's law can be used to calculate the enthalpy change of a reaction that cannot be observed directly.
4. When you apply Hess's law, what enthalpy values do you need to account for each change in physical state?
   1. the melting of a solid
   2. the conversion of a gas to a liquid
   3. the solidification of a liquid
   4. the dissolution of a solid into water
5. In their elemental form, A_2 and B_2 exist as diatomic molecules. Given the following reactions, each with an associated $\Delta H°$, describe how you would calculate ΔH^o_f for the compound AB_2.

$$\begin{aligned} 2AB &\rightarrow A_2 + B_2 \quad \Delta H_1^o \\ 3AB &\rightarrow AB_2 + A_2B \quad \Delta H_2^o \\ 2A_2B &\rightarrow 2A_2 + B_2 \quad \Delta H_3^o \end{aligned}$$

Numerical Problems

Please be sure you are familiar with the topics discussed in Essential Skills 4 before proceeding to the Numerical Problems.

1. Methanol is used as a fuel in Indianapolis 500 race cars. Use the following table to determine whether methanol or 2,2,4-trimethylpentane (isooctane) releases more energy per liter during combustion.

Fuel	$\Delta H^o_{combustion}$(kJ/mol)	Density (g/mL)
methanol	−726.1	0.791
2,2,4-trimethylpentane	−5461.4	0.692

2.

a. Use the enthalpies of combustion given in the following table to determine which organic compound releases the greatest amount of energy per gram during combustion.

Fuel	$\Delta H^o_{combustion}$(kJ/mol)
methanol	−726.1
1-ethyl-2-methylbenzene	−5210.2
n-octane	−5470.5

b. Calculate the standard enthalpy of formation of 1-ethyl-2-methylbenzene.

3. Given the enthalpies of combustion, which organic compound is the best fuel per gram?

Fuel	ΔH^o_f(kJ/mol)
ethanol	−1366.8
benzene	−3267.6
cyclooctane	−5434.7

Numerical Answers

1.

2.

a. To one decimal place

methanol: ΔH/g = −22.6 kJ

C_9H_{12}: ΔH/g = −43.3 kJ

octane: ΔH/g = −47.9 kJ

Octane provides the largest amount of heat per gram upon combustion.

b, $\Delta H_f(C_9H_{17})$ = −46.1 kJ/mol

5.7: Enthalpies of Formation

Conceptual Problems

Please be sure you are familiar with the topics discussed in Essential Skills 4 (Section 5.6 "Essential Skills 4") before proceeding to the Conceptual Problems.

1. Describe how Hess's law can be used to calculate the enthalpy change of a reaction that cannot be observed directly.
2. When you apply Hess's law, what enthalpy values do you need to account for each change in physical state?
3. What is the difference between ΔH^o_f and ΔH_f?
4. How can ΔH^o_f of a compound be determined if the compound cannot be prepared by the reactions used to define its standard enthalpy of formation?
5. For the formation of each compound, write a balanced chemical equation corresponding to the standard enthalpy of formation of each compound.
   a. HBr

b. CH_3OH
c. $NaHCO_3$

6. Describe the distinction between ΔH_{soln} and ΔH_f.
7. The following table lists ΔH^o_{soln} values for some ionic compounds. If 1 mol of each solute is dissolved in 500 mL of water, rank the resulting solutions from warmest to coldest.

Compound	ΔH^o_{soln}(kJ/mol)
KOH	−57.61
$LiNO_3$	−2.51
$KMnO_4$	43.56
$NaC_2H_3O_2$	−17.32

Numerical Problems

Please be sure you are familiar with the topics discussed in Essential Skills 4 (Section 5.6 "Essential Skills 4") before proceeding to the Numerical Problems.

1. Using "Appendix A, calculate ΔH^o_{rxn} for each chemical reaction.
   a. $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$
   b. $CaCO_3(s, \text{calcite}) \rightarrow CaO(s) + CO_2(g)$
   c. $AgNO_3(s) + NaCl(s) \rightarrow AgCl(s) + NaNO_3(s)$
2. Using "Appendix A, determine ΔH^o_{rxn} for each chemical reaction.
   a. $2Na(s) + Pb(NO_3)_2(s) \rightarrow 2NaNO_3(s) + Pb(s)$
   b. $Na_2CO_3(s) + H_2SO_4(l) \rightarrow Na_2SO_4(s) + CO_2(g) + H_2O(l)$
   c. $2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$
3. Calculate ΔH^o_{rxn} for each chemical equation. If necessary, balance the chemical equations.
   a. $Fe(s) + CuCl_2(s) \rightarrow FeCl_2(s) + Cu(s)$
   b. $(NH_4)_2SO_4(s) + Ca(OH)_2(s) \rightarrow CaSO_4(s) + NH_3(g) + H_2O(l)$
   c. $Pb(s) + PbO_2(s) + H_2SO_4(l) \rightarrow PbSO_4(s) + H_2O(l)$
4. Calculate ΔH^o_{rxn} for each reaction. If necessary, balance the chemical equations.
   a. $4HBr(g) + O_2(g) \rightarrow 2H_2O(l) + 2Br_2(l)$
   b. $2KBr(s) + H_2SO_4(l) \rightarrow K_2SO_4(s) + 2HBr(g)$
   c. $4Zn(s) + 9HNO_3(l) \rightarrow 4Zn(NO_3)_2(s) + NH_3(g) + 3H_2O(l)$
5. Use the data in "Appendix A to calculate ΔH^o_f for the reaction $Sn(s, \text{white}) + 4HNO_3(l) \rightarrow SnO_2(s) + 4NO_2(g) + 2H_2O(l)$.
6. Use the data in "Appendix A to calculate ΔH^o_f for the reaction $P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(l)$.
7. How much heat is released or required in the reaction of 0.50 mol of HBr(g) with 1.0 mol of chlorine gas to produce bromine gas?
8. How much energy is released or consumed if 10.0 g of N_2O_5 is completely decomposed to produce gaseous nitrogen dioxide and oxygen?
9. In the mid-1700s, a method was devised for preparing chlorine gas from the following reaction:

$$NaCl(s) + H_2SO_4(l) + MnO_2(s) \rightarrow Na_2SO_4(s) + MnCl_2(s) + H_2O(l) + Cl_2(g)$$

   Calculate ΔH^o_{rxn} for this reaction. Is the reaction exothermic or endothermic?
10. Would you expect heat to be evolved during each reaction?

1. solid sodium oxide with gaseous sulfur dioxide to give solid sodium sulfite
2. solid aluminum chloride reacting with water to give solid aluminum oxide and hydrogen chloride gas

11. How much heat is released in preparing an aqueous solution containing 6.3 g of calcium chloride, an aqueous solution containing 2.9 g of potassium carbonate, and then when the two solutions are mixed together to produce potassium chloride and calcium carbonate.

Numerical Answers

1.
   a. −1203 kJ/mol O_2
   b. 179.2 kJ
   c. −59.3 kJ
2.
3.
4.
5. −174.1 kJ/mol
6.
7. −20.3 kJ
8.
9. −34.3 kJ/mol Cl_2; exothermic
10.
11. ΔH = −2.86 kJ $CaCl_2$: −4.6 kJ; K_2CO_3, −0.65 kJ; mixing, −0.28 kJ

5.8: Foods and Fuels

Conceptual Problems

1. Can water be considered a food? Explain your answer.
2. Describe how you would determine the caloric content of a bag of popcorn using a calorimeter.
3. Why do some people initially feel cold after eating a meal and then begin to feel warm?
4. In humans, one of the biochemical products of the combustion/digestion of amino acids is urea. What effect does this have on the energy available from these reactions? Speculate why conversion to urea is preferable to the generation of N_2.

Numerical Problems

Please be sure you are familiar with the topics discussed in Essential Skills 4 (Section 9.9) before proceeding to the Numerical Problems.

1. Determine the amount of energy available from the biological oxidation of 1.50 g of leucine (an amino acid, ΔH_{comb} = −3581.7 kJ/mol).

2. Calculate the energy released (in kilojoules) from the metabolism of 1.5 oz of vodka that is 62% water and 38% ethanol by volume, assuming that the total volume is equal to the sum of the volume of the two components. The density of ethanol is 0.824 g/mL. What is this enthalpy change in nutritional Calories?
3. While exercising, a person lifts an 80 lb barbell 7 ft off the ground. Assuming that the transformation of chemical energy to mechanical energy is only 35% efficient, how many Calories would the person use to accomplish this task? From Figure 9.4.2, how many grams of glucose would be needed to provide the energy to accomplish this task?

4. A 30 g sample of potato chips is placed in a bomb calorimeter with a heat capacity of 1.80 kJ/°C, and the bomb calorimeter is immersed in 1.5 L of water. Calculate the energy contained in the food per gram if, after combustion of the chips, the temperature of the calorimeter increases to 58.6°C from an initial temperature of 22.1°C.

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10.S: Thermochemistry (Summary)

- **thermodynamics** – study of energy and its transformations
- **thermochemistry** – relationships between chemical reactions and energy changes

5.1: The Nature of Energy

- **Force**: symbolized by *F*, any kind of push or pull exerted on an object
- **Work**: symbolized by *w*, movement of an object against some force

$$w = F \times d$$

- where *w* is work, *F* is force, and *d* is distance that the object is being moved
- **Heat**: energy that is transferred from one object to another because of difference in temperature
- **Energy**: the capacity to do work or to transfer heat

Kinetic and Potential Energy

Kinetic energy: energy of motion

$E_k = ½ mv^2$ where E_k is the kinetic energy, *m* is the mass, and *v* is the velocity.

Potential energy: energy that an object possesses as a result of its composition or its position with respect to another object

Energy Units

- **Joule**: SI unit for energy, 1J = kgm^2/s^2
- **Calorie**: abbreviated *cal*, originally defined as the amount of energy required to raise the temperature of 1 g of water by 1°C. 1 cal = 4.184 J

Systems and Surroundings

- **System**: portion singled out for study
- **Surroundings**: everything beyond the system

Systems exchanges energy with surroundings in the form of heat and work, but not matter

Lowering the Energy of the System

Systems tend to attain as low an energy as possible. Systems with a high potential energy are less stable and more likely to undergo change than systems with a low potential energy.

5.2: The First Law of Thermodynamics

First law of thermodynamics: aka **The Law of Conservation of Energy**; a statement of our experience that energy is conserved in any process. We can express the first law in many ways. One of the more useful expressions is that the change in internal energy, Δ*E*, of a system in any process is equal to the heat, *q*, added to the system, plus the work, *w*, done *on* the system by its surroundings: Δ*E* = *q* + *w*.

Internal Energy

The total energy of a system is the sum of all the kinetic and potential energies of its components parts.

Internal energy: total energy of the system (see above)

Because there are so many types of motion and interactions, we cannot determine the exact energy of any system. However, we can measure the changes *in internal energy that accompany chemical and physical processes.*

$?E = E_{final} - E_{initial}$

$E_{final} > E_{initial}$ = system has gained energy

$E_{final} < E_{initial}$ = system has lost energy

Initial state refers to reactants, final state to products.

Relating Δ*E* to Heat and Work

The internal energy of a system changes in magnitude as heat is added to or removed from the system, or as work is done on it or by it.

?E = q + w where ΔE is internal energy, q is heat, and w is work

Heat added to the system is assigned a positive sign. Likewise, work on the system is positive. On the other hand, both the heat lost by the system and the work done by the system on its surroundings are negative; they reduce the internal energy.

Ex. A system absorbs 50 J of heat and does 10 J of work on its surroundings, q = 50 J and w = 10 J. Thus, ΔE = 50 J + (10 J) = 40 J.

State Functions

The total energy of a system is proportional to the total quantity of matter in the system; energy is an extensive property.

State function: a property of a system that is determined by the state or condition of the system and not by how it got to that state; its value is fixed when temperature, pressure, composition, and physical form are specified. The internal energy of a system is a state function.

The value of a state function does not depend on the particular history of the sample, only on its present condition. Because E is a state function, ΔE depends only on the initial and final states of the system and not on how the change occurs.

However, the work done by a system in a given process is not a state function!!!

5.3: Enthalpy

Heat flows between system and surroundings until *both are at the same temperature*.

Endothermic process: a process in which a system absorbs heat from its surroundings

Exothermic process: a process in which a system releases heat to its surroundings

Enthalpy

Enthalpy: represented by *H*; deals with the amount of heat absorbed or released during a chemical reaction under constant pressure

The change in enthalpy, ΔH, equals the heat, q_p, added to or lost by the system when the process occurs under constant pressure:

?H = q_p

(The subscript P on q is a reminder that we are considering a special case where pressures is constant)

$\Delta H = H_{final} - H_{initial}$

$H_{final} > H_{initial}$ = positive Δ*H*; system has gained heat from surroundings (endothermic)

$H_{final} < H_{initial}$ = negative Δ*H*; system has lost heat to the surroundings (exothermic)

5.4: Enthalpy of Reaction

$$\Delta H = H(\text{products}) - H(\text{reactants})$$

Thermochemical equations: balanced chemical equations that show the associated enthalpy change

1. Enthalpy is an *extensive* property (depends on amount of matter present). *This fact means that the magnitude of ΔH is directly proportional to the amount of reactant consumed in the process*
2. The enthalpy change for a reaction is equal in magnitude but opposite in sign to ΔH for the reverse reaction. *When we reverse a reaction, the reactants become the products, and vice versa. Reversing the products and reactants leads to the same magnitude but a change in sign for ΔH.*
3. The enthalpy change for a reaction depends on the state of the reactants and products.

5.5: Calorimetry

Calorimetry: measurement of heat flow

Calorimeter: apparatus that measures heat flow

Heat Capacity and Specific Heat

Heat capacity: amount of energy required to raise the temperature of a given object by 1°C. The greater the capacity of a body, the more heat it requires to raise its temperature.

Molar heat capacity: when referring to pure substances; heat capacity of 1 mol of substance

Specific heat: heat capacity of 1 g of a substance (as opposed to a mole)

Specific heat= quantity of heat transferred / (grams of substance) X (temperature change)

= q / m X ΔT

q = (specific heat) X (grams of substance) X Δ*T*

ConstantPressure Calorimetry

Calorimeters are simple instruments to control pressure. Because the calorimeter prevents the gain or loss of heat from its surroundings, the heat released by the reaction, q_{rxn}, equals that gained by the solution, q_{soln}. Thus,

$q_{rxn} = q_{soln}$ = (specific heat) X (grams of solution) X Δ*T*

Bomb Calorimetry

Bomb calorimeter: device for measuring the heat evolved in the combustion of a substance under constant volume conditions. Most used for combustion reactions.

$q_{evolved} = C_{calorimeter}$ X Δ*T* , where $C_{calorimeter}$ is the heat capacity of the calorimeter

5.6: Hess's Law

Because enthalpy is a state function, the enthalpy change, Δ*H*, associated with any chemical process depends only on the *amount of matter that undergoes change*, and on the nature of the *initial state of the reactants* and the *final state of the products*.

$CH_{4\,(g)} + 2O_{2\,(g)}$? $CO_{2\,(g)} + 2H_2O_{\,(g)}$ Δ*H* = 802 kJ

(Add) $2H_2O_{\,(g)}$? $2H_2O_{\,(l)}$?*H* = 88 kJ

$CH_{4\,(g)} + 2O_{2\,(g)} + 2H_2O_{\,(g)} \rightarrow CO_{2\,(g)} + 2H_2O_{\,(l)} + 2H_2O_{\,(g)}$

Net equation:

$CH_{4\,(g)} + 2O_{2\,(g)}$? $CO_{2\,(g)} + 2H_2O_{\,(l)}$

To obtain the net equation, the sum of the reactants of the two equations is placed on one side of the arrow, and the sum of the products on the other side. Because $2H_2O_{\,(g)}$ occurs on both sides of the equation, it can be cancelled.

Hess's law: states that *if a reaction is carried out in a series of steps, Δ*H* for the reaction will be equal to the sum of the enthalpy changes for individual steps.* The overall enthalpy change for the process is independent of the number of steps or the particular nature of the path by which the reaction is carried out.

The first law of thermodynamics, in the form of Hess's law, teaches us that we can never expect to obtain more (or less) energy from a chemical reaction by changing the method of carrying out the reaction.

5.7: Enthalpies of Formation

- *Enthalpies of vaporization* (Δ*H* for converting liquids to gas)
- *Enthalpies of fusion* (Δ*H* for melting solids)
- *Enthalpies of combustion* (Δ*H* for combusting a substance in oxygen)

Enthalpy of formation: aka **Heat of formation**; enthalpy change that accompanies the formation of a substance from the most stable forms of its component elements. Labeled ΔH_f, where the subscript *f* indicates that the substance has been formed from its elements.

The magnitude of any enthalpy change depends on the conditions of temperature, pressure, and state (gas, liquid, solid) of the reactants and product.

Standard state: for a substance is the form most stable at the particular temperature of interest and at standard atmospheric pressure.

Standard enthalpy of formation: $\Delta H°_f$. change in enthalpy that accompanies the formation of 1 mol of that substance from its elements, with all substances in their standard states.

Using Enthalpies of Formation to Calculate Enthalpies of Reaction

$$\Delta H°_{rxn} = \sum n\Delta H°_f \text{ (products)} \sum m\Delta H°_f \text{ (reactants)}$$

$\sum$ = the sum of

m and n = stoichiometric coefficients of the chemical reaction

$C_3H_{8\,(g)} + 5O_{2\,(g)} \rightarrow 3CO_{2\,(g)} + 4H_2O_{\,(l)}$

$\Delta H°_{rxn} = [3\Delta H°_f\,(CO_2) + 4\Delta H°_f\,(H_2O)] - [\Delta H°_f\,(C_3H_8) + 5\Delta H°_f\,(O_2)]$

$\Delta H°_{rxn} = [(3 \text{ mol } CO_2)\,(393.5 \text{ kJ/mol}) + (4 \text{ mol } H_2O)\,(285.5 \text{ kJ/mol})]$

= (2324 kJ) – (103.85 kJ)

=2220 kJ

5.8: Foods and Fuels

Fuel value: energy released when 1g of a material is combusted

Foods

- Main sources of energy for the body are from carbohydrates and fat
- Breakdown of carbohydrates is rapid, so energy is quickly supplied to the body
- Fats are well suited for the body because (1) they are insoluble in water, which permits their storage in the human body. (2) they produce more energy per gram thatneither proteins or carbohydrates.

Fuels

- **Fossil fuels**: coal, petroleum, and natural gas
- **Natural gas**: consists of gaseous hydrocarbons, compounds of hydrogen and carbon
- **Petroleum**: liquid composed of hundreds of compounds
- **Coal**: solid; contains hydrocarbons of high molecular weight as well as compounds containing sulfur, oxygen, and nitrogen. Most abundant fossil fuel
- **Syngas**: synthetic gas abbreviation

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CHAPTER OVERVIEW

11: Spontaneous Processes and Thermodynamic Equilibrium

An General Chemistry Libretexts Textmap organized around the textbook

Principles of Modern Chemistry

by Oxtoby, Gillis, and Campion

Template:HideTOC

A spontaneous process is the time-evolution of a system in which it releases free energy and moves to a lower, more thermodynamically stable energy state.

11.1: The Nature of Spontaneous Processes
11.2: Entropy and Spontaneity - A Molecular Statistical Interpretation
11.3: Entropy and Heat - Experimental Basis of the Second Law of Thermodynamics
11.4: Entropy Changes in Reversible Processes
11.5: Entropy Changes and Spontaneity
11.6: The Third Law of Thermodynamics
11.7: The Gibbs Free Energy
11.8: Carnot Cycle, Efficiency, and Entropy
11.E: Spontaneous Processes (Exercises)

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11.1: The Nature of Spontaneous Processes

Learning Objectives

- Distinguish between spontaneous and nonspontaneous processes
- Describe the dispersal of matter and energy that accompanies certain spontaneous processes

In this section, consider the differences between two types of changes in a system: Those that occur spontaneously and those that occur only with the continuous input of energy. In doing so, we'll gain an understanding as to why some systems are naturally inclined to change in one direction under certain conditions. We'll also gain insight into how the spontaneity of a process affects the distribution of energy and matter within the system.

Spontaneous and Nonspontaneous 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. 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 11.1.1).

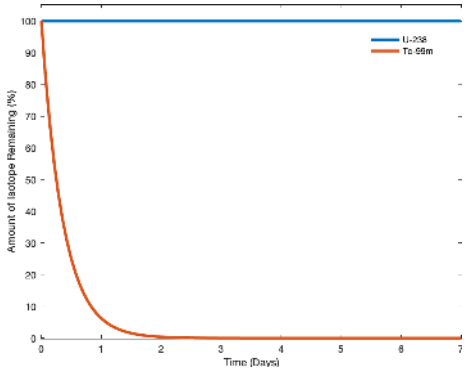


Figure 11.1.1: Both U-238 and Tc-99m undergo spontaneous radioactive decay, but at drastically different rates. Over the course of one week, essentially all of a Tc-99m sample and none of a U-238 sample will have decayed. (CC by 4.0; Morgan Johnson via LibreTexts)

Two curves are shown to represent U-238 and Tc-99m respectively. The vertical axes represents the percentage of isotope remaining and the horizontal axes is the time that has elapsed in days.

As another example, consider the conversion of diamond into graphite (Figure 11.1.2).

$$\mathrm{C(s,\,diamond)} \longrightarrow \mathrm{C(s,\,graphite)} \tag{11.1.1}$$

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, and 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.

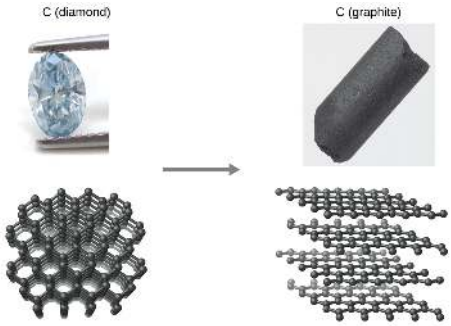


Figure 11.1.2: The conversion of carbon from the diamond allotrope to the graphite allotrope is spontaneous at ambient pressure, but its rate is immeasurably slow at low to moderate temperatures. This process is known as graphitization, and its rate can be increased to easily measurable values at temperatures 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)

Comparison of diamond and graphite shown in its physical form as well as its molecular arrangement respectively.

Dispersal of Matter and Energy

As we extend our 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 on the left and a vacuum on the right (Figure 11.1.3). When the valve is opened, the gas spontaneously expands to fill both flasks. 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.

$$w = -P\Delta V \tag{11.1.2}$$

$$= 0 \;\; (\mathrm{P} = 0 \text{ in a vaccum}) \tag{11.1.3}$$

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.

$$\Delta U = q + w \quad \text{(First Law of Thermodynamics)}$$
$$= 0 + 0 = 0 \quad (11.1.4)$$

The spontaneity of this process is therefore not a consequence of any change in energy that accompanies the process. Instead, the movement of the gas 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 process took place, the matter was distributed both more widely (occupying twice its original volume) and more uniformly (present in equal amounts in each flask).

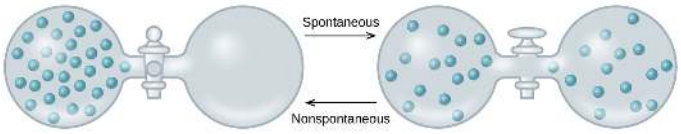


Figure 11.1.3: An isolated system consists of an ideal gas in one flask that is connected by a closed valve to a second flask containing a vacuum. Once the valve is opened, the gas spontaneously becomes evenly distributed between the flasks.
When the valve is closed, all of the gas molecules accumlating only in one side of the flask. The diagram with the open valve shows gas being equally distributed among the two flasks. The dispersion of the gas is labeled as spontaneous while the reverse is labeled as non spontaneous.

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 11.1.4). 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.

$$q_X < 0 \quad \text{and} \quad q_Y = -q_X > 0 \quad (11.1.5)$$

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 11.1.4:When two objects at different temperatures come in contact, heat spontaneously flows from the hotter to the colder object.
Two separated blocks. One is labeled X and the other labeled Y. The diagram next to it shows the two blocks in contact with one another.

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 11.1.1: Redistribution of Matter during a Spontaneous Process

Describe how matter and energy are 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 11.1.5:(credit a: modification of work by Jenny Downing; credit b: modification of work by “Fuzzy Gerdes”/Flickr; credit c: modification of work by Sahar Atwa)
This figure has three photos labeled, “a,” “b,” and “c.” Photo a shows a glass with dry ice in water. There is a thick vapor coming from the top of the glass. Photo b shows water forming outside of a glass containing cold beverage. Photo c shows a sealed container that holds a red liquid.

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. However, an input of energy from the surroundings ss required for the molecules to leave the solid phase and enter the gas phase.
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. As the gas molecules move together to form the droplets of liquid, they form intermolecular forces and thus release energy to the surroundings.
c. The process in question is *dilution*. The food dye molecules initially occupy a much smaller volume (the drop of dye solution) than they occupy once the process is complete (in the full glass of water). The process therefore entails a greater dispersal of matter. The process may also yield a more uniform dispersal of matter, since the initial state of the system involves two regions of different dye concentrations (high in the drop, zero in the water), and the final state of the system contains a single dye concentration throughout. This process can occur with out a change in energy because the molecules have kinetic energy relative to the temperature of the water, and so will be constantly in motion.

Exercise 11.1.1

Describe how matter and energy are redistributed when you empty a canister of compressed air into a room.

Answer

This process entails both a greater and more uniform dispersal of matter as the compressed air in the canister is permitted to expand into the lower-pressure air of the room. The process also requires an input of energy to disrupt the intermolecular forces between the closely-spaced gas molecules that are originally compressed into the container. If you were to touch the nozzle of the canister, you would notice that it is cold because the exiting molecules are taking energy away from their surroundings, and the canister is part of the surroundings.

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. In this section we have only discussed nuclear decay, physical changes of pure substances, and macroscopic events such as water flowing downhill. In the following sections we will discuss mixtures and chemical reactions, situations in which the description of sponteneity becomes more challenging.

Glossary

nonspontaneous process
process that requires continual input of energy from an external source

spontaneous change
process that takes place without a continuous input of energy from an external source

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11.2: Entropy and Spontaneity - A Molecular Statistical Interpretation

Learning Objectives

- The Learning Objective of this Module is to understand the relationship between internal energy and entropy.

We know that the first law of thermodynamics governs changes in the state function we called internal energy (U) and that changes in the internal energy (ΔU) are closely related to changes in the enthalpy (ΔH), which is a measure of the heat flow between a system and its surroundings at constant pressure. You also learned previously that the enthalpy change for a chemical reaction can be calculated using tabulated values of enthalpies of formation. This information, however, does not tell us whether a particular process or reaction will occur spontaneously.

Spontaneous Reactions

Let's consider a familiar example of spontaneous change. If a hot frying pan that has just been removed from the stove is allowed to come into contact with a cooler object, such as cold water in a sink, heat will flow from the hotter object to the cooler one, in this case usually releasing steam. Eventually both objects will reach the same temperature, at a value between the initial temperatures of the two objects. This transfer of heat from a hot object to a cooler one obeys the first law of thermodynamics: energy is conserved.

Now consider the same process in reverse. Suppose that a hot frying pan in a sink of cold water were to become hotter while the water became cooler. As long as the same amount of thermal energy was gained by the frying pan and lost by the water, the first law of thermodynamics would be satisfied. Yet we all know that such a process cannot occur: heat always flows from a hot object to a cold one, never in the reverse direction. That is, by itself the magnitude of the heat flow associated with a process does not predict whether the process will occur spontaneously.

For many years, chemists and physicists tried to identify a single measurable quantity that would enable them to predict whether a particular process or reaction would occur spontaneously. Initially, many of them focused on enthalpy changes and hypothesized that an exothermic process would always be spontaneous. But although it is true that many, if not most, spontaneous processes are exothermic, there are also many spontaneous processes that are not exothermic. For example, at a pressure of 1 atm, ice melts spontaneously at temperatures greater than 0°C, yet this is an endothermic process because heat is absorbed. Similarly, many salts (such as NH_4NO_3, NaCl, and KBr) dissolve spontaneously in water even though they absorb heat from the surroundings as they dissolve (i.e., $\Delta H_{soln} > 0$). Reactions can also be both spontaneous and highly endothermic, like the reaction of barium hydroxide with ammonium thiocyanate shown in Figure 11.2.1.



Figure 11.2.1: An Endothermic Reaction. The reaction of barium hydroxide with ammonium thiocyanate is spontaneous but highly endothermic, so water, one product of the reaction, quickly freezes into slush. When water is placed on a block of wood under the flask, the highly endothermic reaction that takes place in the flask freezes water that has been placed under the beaker, so the flask becomes frozen to the wood. For a full video: see www.youtube.com/watch?v=GQkJI-Nq3Os.

Thus enthalpy is not the only factor that determines whether a process is spontaneous. For example, after a cube of sugar has dissolved in a glass of water so that the sucrose molecules are uniformly dispersed in a dilute solution, they never spontaneously come back together in solution to form a sugar cube. Moreover, the molecules of a gas remain evenly distributed throughout the entire volume of a glass bulb and never spontaneously assemble in only one portion of the available volume. To help explain why

these phenomena proceed spontaneously in only one direction requires an additional state function called entropy (S), a thermodynamic property of all substances that is proportional to their degree of disorder.

> The direction of a spontaneous process is not governed by the internal energy change nor enthalpy change and thus the First Law of Thermodynamics cannot predict the direction of a natural process

Probabilities and Microstates

Chemical and physical changes in a system may be accompanied by either an increase or a decrease in the disorder of the system, corresponding to an increase in entropy ($\Delta S > 0$) or a decrease in entropy ($\Delta S < 0$), respectively. As with any other state function, the change in entropy is defined as the difference between the entropies of the final and initial states:

$$\Delta S = S_f - S_i \tag{11.2.1}$$

When a gas expands into a vacuum, its entropy increases because the increased volume allows for greater atomic or molecular disorder. The greater the number of atoms or molecules in the gas, the greater the disorder. The magnitude of the entropy of a system depends on the number of microscopic states, or microstates, associated with it (in this case, the number of atoms or molecules); that is, the greater the number of microstates, the greater the entropy.

How can we express disorder quantitatively? From the example of coins, you can probably see that simple statistics plays a role: the probability of obtaining three heads and seven tails after tossing ten coins is just the ratio of the number of ways that ten different coins can be arranged in this way, to the number of all possible arrangements of ten coins.



Using the language of molecular statistics, we say that a collection of coins in which a given fraction of its members are heads-up constitutes a *macroscopic state* of the system. Since we do not care which coins are heads-up, there are clearly numerous configurations of the individual coins which can result in this “macrostate”. Each of these configurations specifies a *microscopic state* of the system. The greater the number of microstates that correspond to a given macrostate (or configuration), the greater the probability of that macrostate. To see what this means, consider the possible outcomes of a toss of four coins (Table 11.2.1):

Table 11.2.1: Coin Toss Results

macrostate (Configuration)	ways	probability	microstates
0 heads	1	1/16	TTTT
1 head	4	4/16 = 1/4	HTTT THTT TTHT TTTH
2 heads	6	6/16 = 3/8	HHTT HTHT HTTH THHT TTHH THTH
3 heads	4	4/16 = 1/4	HHHT HTHH HHTH THHH
4 heads	1	1/16	HHHH

A toss of four coins will yield one of the five outcomes (macrostates) listed in the leftmost column of the table. The second column gives the number of “ways”— that is, the number of head/tail configurations of the set of coins (the number of microstates)— that can result in the macrostate. The probability of a toss resulting in a particular macrostate is proportional to the number of microstates corresponding to the macrostate, and is equal to this number, divided by the total number of possible microstates (in this example, 2^4 =16). An important assumption here is that all microstates are equally probable; that is, the toss is a “fair” one in which the many factors that determine the trajectory of each coin operate in an entirely random way.

> The greater the number of **microstates** that correspond to a given **macrostate**, the greater the probability of that **macrostate**.

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* possible for the system. A microstate (Ω) is a specific configuration of the locations and energies of the atoms or molecules that comprise a system like the following:

$$S = k \ln \Omega \tag{11.2.2}$$

Here k is the Boltzmann constant and has a value of 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:

$$\Delta S = S_\mathrm{f} - S_\mathrm{i} \tag{11.2.3}$$

$$= k \ln \Omega_\mathrm{f} - k \ln \Omega_\mathrm{i} \tag{11.2.4}$$

$$= k \ln \frac{\Omega_\mathrm{f}}{\Omega_\mathrm{i}} \tag{11.2.5}$$

For processes involving an increase in the number of microstates, $\Omega_f > \Omega_i$, the entropy of the system increases, $\Delta S > 0$. Conversely, processes that reduce the number of microstates, $\Omega_f < \Omega_i$, 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 11.2.2 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 (Equation 11.2.2), *the most probable distribution is therefore the one of greatest entropy*.

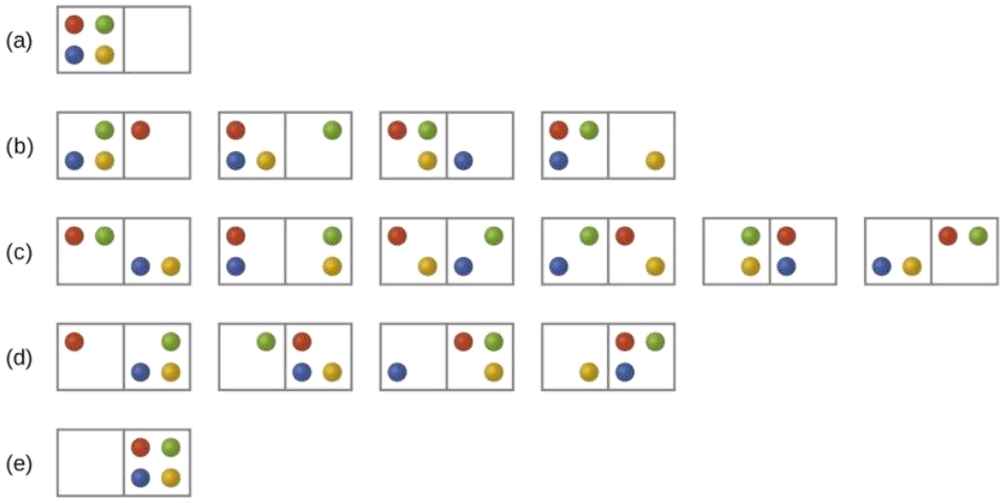


Figure 11.2.2: The sixteen microstates associated with placing four particles in two boxes are shown. The microstates are collected into five distributions—(a), (b), (c), (d), and (e)—based on the numbers of particles in each box.

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

$$\frac{6}{16} = \frac{3}{8}$$

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

$$\frac{1}{16}$$

The probability of finding all particles in only one box (either the left box or right box) is then

$$\left(\frac{1}{16}+\frac{1}{16}\right)=\frac{2}{16}=\frac{1}{8}$$

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.

The previous description of an ideal gas expanding into a vacuum 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. The spontaneous process whereby the gas contained initially in one flask expands to fill both flasks equally therefore yields an increase in entropy for the system.

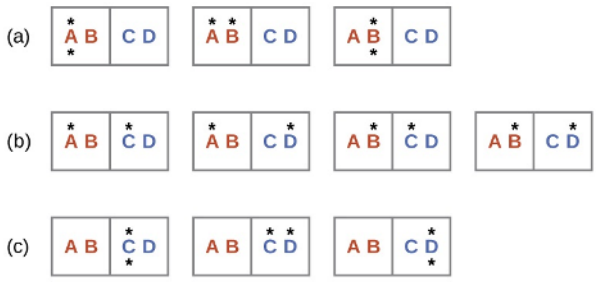
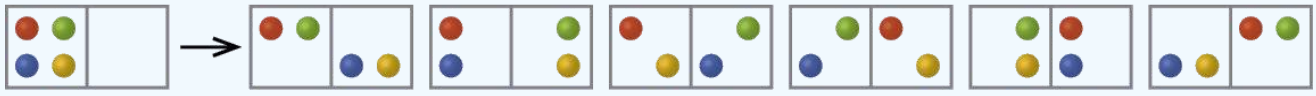


Figure 11.2.3: This shows a microstate model describing the flow of heat from a hot object to a cold object. (a) Before the heat flow occurs, the object comprised of particles A and B contains both units of energy and as represented by a distribution of three microstates. (b) If the heat flow results 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.

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 energy (represented as "*") in Figure 11.2.3. 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. And so, 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 $\frac{4}{10}$. As for the previous example of matter dispersal, extrapolating this treatment to macroscopic collections of particles dramatically increases the probability of the uniform distribution relative to the other distributions. 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.

✔ Example 11.2.1: Determination of ΔS

Consider the system shown here. What is the change in entropy for a process that converts the system from distribution (a) to (c)?



Solution

We are interested in the following change:

The initial number of microstates is one, the final six:

$$\Delta S = k \ln \frac{\Omega_c}{\Omega_a}$$
$$= 1.38 \times 10^{-23}\ J/K \times \ln \frac{6}{1}$$
$$= 2.47 \times 10^{-23}\ J/K$$

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 11.2.1

Consider the system shown in Figure 11.2.3. 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

A disordered system has a greater number of possible microstates than does an ordered system, so it has a higher entropy. This is most clearly seen in the entropy changes that accompany phase transitions, such as solid to liquid or liquid to gas. As you know, a crystalline solid is composed of an ordered array of molecules, ions, or atoms that occupy fixed positions in a lattice, whereas the molecules in a liquid are free to move and tumble within the volume of the liquid; molecules in a gas have even more freedom to move than those in a liquid. Each degree of motion increases the number of available microstates, resulting in a higher entropy. Thus the entropy of a system must increase during melting ($\Delta S_{fus} > 0$). Similarly, when a liquid is converted to a vapor, the greater freedom of motion of the molecules in the gas phase means that $\Delta S_{vap} > 0$. Conversely, the reverse processes (condensing a vapor to form a liquid or freezing a liquid to form a solid) must be accompanied by a decrease in the entropy of the system: $\Delta S < 0$.

Definition: Entropy

Entropy (S) is a thermodynamic property of all substances that is proportional to their degree of disorder. The greater the number of possible microstates for a system, the greater the disorder and the higher the entropy.

Disorder is more probable than order because there are so many more ways of achieving it. Thus coins and cards tend to assume random configurations when tossed or shuffled, and socks and books tend to become more scattered about a teenager's room during the course of daily living. But there are some important differences between these large-scale mechanical, or macro systems, and the collections of sub-microscopic particles that constitute the stuff of chemistry, and which we will refer to here generically as **molecules**. Molecules, unlike macro objects, are capable of accepting, storing, and giving up energy in tiny amounts (quanta), and act as highly efficient carriers and spreaders of thermal energy as they move around. Thus, **in chemical systems**,

1. **We are dealing with huge numbers of particles**. This is important because statistical predictions are always more accurate for larger samples. Thus although for the four tosses there is a good chance (62%) that the H/T ratio will fall outside the range of 0.45 - 0.55, this probability becomes almost zero for 1000 tosses. To express this in a different way, the chances that 1000 gas molecules moving about randomly in a container would at any instant be distributed in a sufficiently non-uniform manner to produce a detectable pressure difference between the two halves of a container will be extremely small. If we increase the number of molecules to a chemically significant number (around 10^{20}, say), then the same probability becomes indistinguishable from zero.
2. **Once the change begins, it proceeds spontaneously.** That is, no external agent (a tosser, shuffler, or teenager) is needed to keep the process going. Gases will spontaneously expand if they are allowed to, and reactions, once started, will proceed toward equilibrium.
3. **Thermal energy is continually being exchanged between the particles of the system, and between the system and the surroundings.** Collisions between molecules result in exchanges of momentum (and thus of kinetic energy) amongst the particles of the system, and (through collisions with the walls of a container, for example) with the surroundings.

4. **Thermal energy spreads rapidly and randomly throughout the various energetically accessible microstates of the system.** The **direction** of spontaneous change is that which results in the maximum possible spreading and sharing of thermal energy.

The importance of these last two points is far greater than you might at first think, but to fully appreciate this, you must recall the various ways in which thermal energy is stored in molecules.

Sign of Entropy Change

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 11.2.4 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, $\Delta S < 0$.

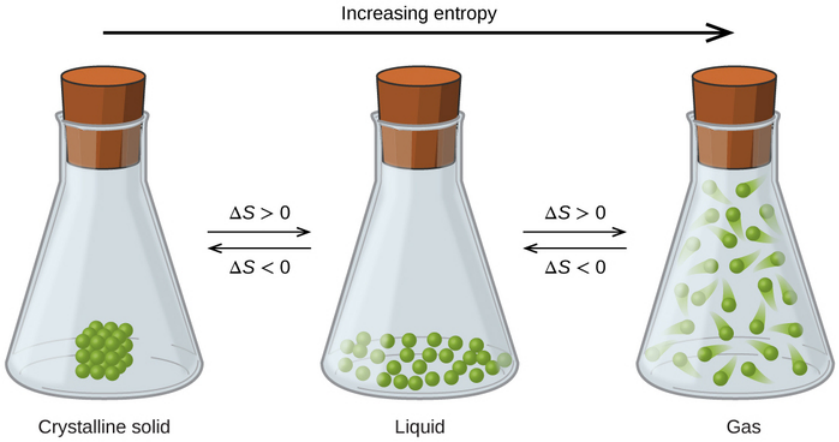


Figure 11.2.4: The entropy of a substance increases ($\Delta S > 0$) as it transforms from a relatively ordered solid, to a less-ordered liquid, and then to a still less-ordered gas. The entropy decreases ($\Delta S < 0$) as the substance transforms from a gas to a liquid and then to a solid.

Now consider the vapor or gas phase. The atoms or molecules occupy a *much* greater volume than in the liquid phase; therefore each atom or molecule can be found in many more locations than in the liquid (or solid) phase. Consequently, for any substance,

$$S_{gas} \gg S_{liquid} > S_{solid} \tag{11.2.6}$$

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 11.2.5).

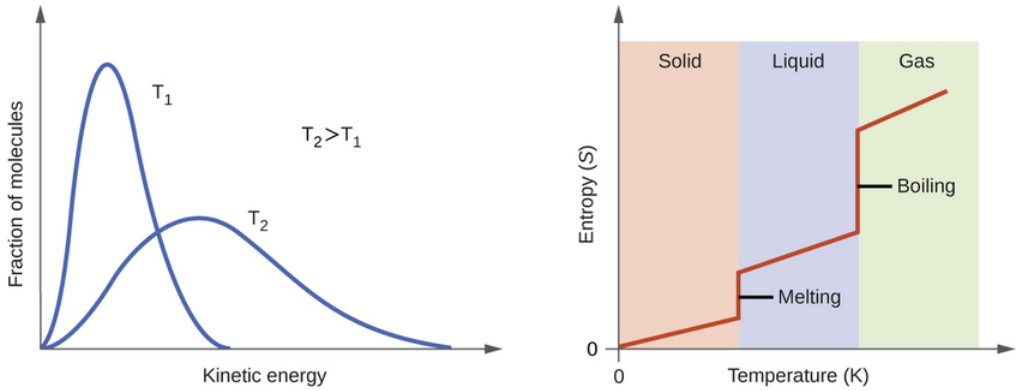


Figure 11.2.5: Entropy increases as the temperature of a substance is raised, which corresponds to the greater spread of kinetic energies. When a substance melts or vaporizes, it experiences a significant increase in entropy.

The entropy of a substance is influenced by 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 (which is a topic beyond the scope of our treatment). For molecules, greater numbers of atoms (regardless of their masses) increase the ways in which the molecules can vibrate and thus the number of possible microstates and the system entropy.

Finally, variations in the types of particles affect 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 11.2.2

Example 11.2.2: 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 $\longrightarrow$ one mole liquid water at 50 °C
b. $\mathrm{Ag^+}(aq) + \mathrm{Cl^-}(aq) \longrightarrow \mathrm{AgCl}(s)$
c. $\mathrm{C_6H_6(l)} + \frac{15}{2}\mathrm{O_2(g)} \longrightarrow 6\,\mathrm{CO_2(g)} + 3\,\mathrm{H_2O(l)}$
d. $\mathrm{NH_3}(s) \longrightarrow \mathrm{NH_3}(l)$

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 11.2.2

Predict the sign of the enthalpy change for the following processes. Give a reason for your prediction.

a. $\mathrm{NaNO_3}(s) \longrightarrow \mathrm{Na^+}(aq) + \mathrm{NO_3^-}(aq)$
b. the freezing of liquid water
c. $\mathrm{CO_2}(s) \longrightarrow \mathrm{CO_2}(g)$
d. $\mathrm{CaCO}(s) \longrightarrow \mathrm{CaO}(s) + \mathrm{CO_2}(g)$

Answer a

Positive; The solid dissolves to give an increase of mobile ions in solution.

Answer b

Negative; The liquid becomes a more ordered solid.

Answer c

Positive; The relatively ordered solid becomes a gas.

Answer d

Positive; There is a net production of one mole of gas.

Summary

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, $S_{solid} < S_{liquid} \ll S_{gas}$ in a given 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 may be reliably predicted.

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11.3: Entropy and Heat - Experimental Basis of the Second Law of Thermodynamics

Learning Objectives

- The Learning Objective of this Module is to understand the relationship between internal energy and entropy.

Thermodynamic Definition of Entropy

Experiments show that the magnitude of ΔS_{vap} is 80–90 J/(mol•K) for a wide variety of liquids with different boiling points. However, liquids that have highly ordered structures due to hydrogen bonding or other intermolecular interactions tend to have significantly higher values of ΔS_{vap}. For instance, ΔS_{vap} for water is 102 J/(mol•K). Another process that is accompanied by entropy changes is the formation of a solution. As illustrated in Figure 11.3.1, the formation of a liquid solution from a crystalline solid (the solute) and a liquid solvent is expected to result in an increase in the number of available microstates of the system and hence its entropy. Indeed, dissolving a substance such as NaCl in water disrupts both the ordered crystal lattice of NaCl and the ordered hydrogen-bonded structure of water, leading to an increase in the entropy of the system. At the same time, however, each dissolved Na^+ ion becomes hydrated by an ordered arrangement of at least six water molecules, and the Cl^- ions also cause the water to adopt a particular local structure. Both of these effects increase the order of the system, leading to a decrease in entropy. The overall entropy change for the formation of a solution therefore depends on the relative magnitudes of these opposing factors. In the case of an NaCl solution, disruption of the crystalline NaCl structure and the hydrogen-bonded interactions in water is quantitatively more important, so $\Delta S_{soln} > 0$.

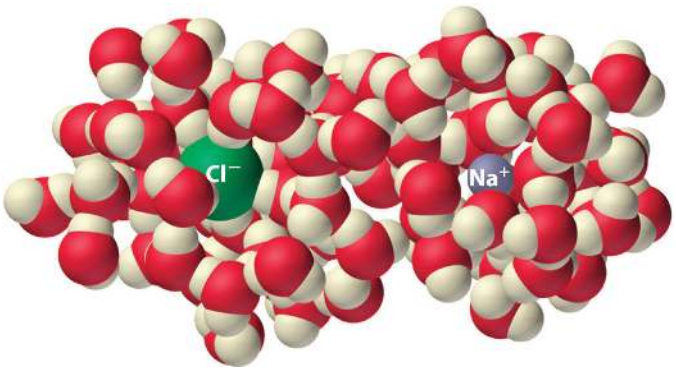


Figure 11.3.1: The Effect of Solution Formation on Entropy

Dissolving NaCl in water results in an increase in the entropy of the system. Each hydrated ion, however, forms an ordered arrangement with water molecules, which decreases the entropy of the system. The magnitude of the increase is greater than the magnitude of the decrease, so the overall entropy change for the formation of an NaCl solution is positive.

Example 11.3.1

Predict which substance in each pair has the higher entropy and justify your answer.

a. 1 mol of NH_3(g) or 1 mol of He(g), both at 25°C
b. 1 mol of Pb(s) at 25°C or 1 mol of Pb(l) at 800°C

Given: amounts of substances and temperature

Asked for: higher entropy

Strategy:

From the number of atoms present and the phase of each substance, predict which has the greater number of available microstates and hence the higher entropy.

Solution:

a. Both substances are gases at 25°C, but one consists of He atoms and the other consists of NH_3 molecules. With four atoms instead of one, the NH_3 molecules have more motions available, leading to a greater number of microstates. Hence we predict that the NH_3 sample will have the higher entropy.

b. The nature of the atomic species is the same in both cases, but the phase is different: one sample is a solid, and one is a liquid. Based on the greater freedom of motion available to atoms in a liquid, we predict that the liquid sample will have the higher entropy.

Exercise 11.3.1

Predict which substance in each pair has the higher entropy and justify your answer.

a. 1 mol of He(g) at 10 K and 1 atm pressure or 1 mol of He(g) at 250°C and 0.2 atm
b. a mixture of 3 mol of $H_2(g)$ and 1 mol of $N_2(g)$ at 25°C and 1 atm or a sample of 2 mol of $NH_3(g)$ at 25°C and 1 atm

Answer a

1 mol of He(g) at 250°C and 0.2 atm (higher temperature and lower pressure indicate greater volume and more microstates)

Answer b

a mixture of 3 mol of $H_2(g)$ and 1 mol of $N_2(g)$ at 25°C and 1 atm (more molecules of gas are present)

Video Solution

Summary

A reversible process is one for which all intermediate states between extremes are equilibrium states; it can change direction at any time. In contrast, an irreversible process occurs in one direction only. The change in entropy of the system or the surroundings is the quantity of heat transferred divided by the temperature. The second law of thermodynamics states that in a reversible process, the entropy of the universe is constant, whereas in an irreversible process, such as the transfer of heat from a hot object to a cold object, the entropy of the universe increases.

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11.4: Entropy Changes in Reversible Processes

Learning Objectives

You are expected to be able to define and explain the significance of terms identified in ***bold***.

- A ***reversible*** *process* is one carried out in infinitesimal steps after which, when undone, both the system and surroundings (that is, the world) remain unchanged (see the example of gas expansion-compression below). Although true reversible change cannot be realized in practice, it can always be approximated.
- As a process is carried out in a more reversible manner, the value of *w* approaches its maximum possible value, and *q* approaches its minimum possible value.
- Although *q* is not a state function, the quotient q_{rev}/T is, and is known as the *entropy*.

A change is said to occur reversibly when it can be carried out in a series of infinitesimal steps, each one of which can be undone by making a similarly minute change to the conditions that bring the change about. For example, the reversible expansion of a gas can be achieved by reducing the external pressure in a series of infinitesimal steps; reversing any step will restore the system and the surroundings to their previous state. Similarly, heat can be transferred reversibly between two bodies by changing the temperature difference between them in infinitesimal steps each of which can be undone by reversing the temperature difference.

The most widely cited example of an **irreversible** change is the free expansion of a gas into a vacuum. Although the system can always be restored to its original state by recompressing the gas, this would require that the surroundings perform work on the gas. Since the gas does no work on the surrounding in a free expansion (the external pressure is zero, so $P\Delta V = 0$,) there will be a permanent change in the surroundings. Another example of irreversible change is the conversion of mechanical work into frictional heat; there is no way, by reversing the motion of a weight along a surface, that the heat released due to friction can be restored to the system.

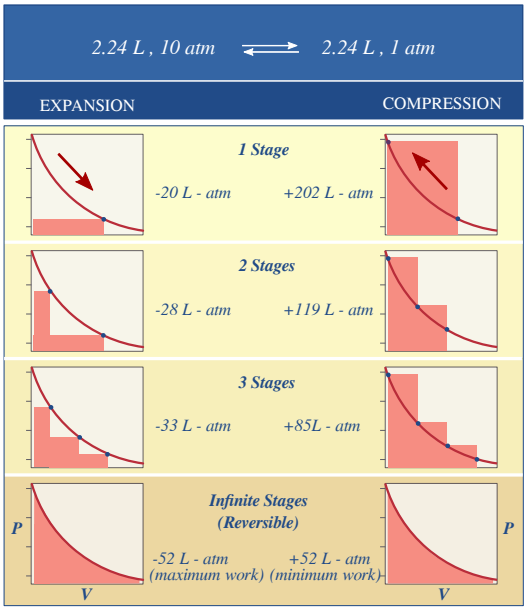


Figure 11.4.1: Reversible vs. Irreversible Expansions and Compressions. (CC BY-NC; Ümit Kaya)

These diagrams show the same expansion and compression ±ΔV carried out in different numbers of steps ranging from a single step at the top to an "infinite" number of steps at the bottom. As the number of steps increases, the processes become less irreversible; that is, the difference between the work done in expansion and that required to re-compress the gas diminishes. In the limit of an ”infinite” number of steps (bottom), these work terms are identical, and both the system and surroundings (the “world”) are unchanged by the expansion-compression cycle. In all other cases the system (the gas) is restored to its initial state, **but the *surroundings* are forever changed.**

Definition: Reversible Changes

A reversible change is one carried out in such as way that, when undone, both the system and surroundings (that is, the world) remain unchanged.

It should go without saying, of course, that any process that proceeds in infinitesimal steps would take infinitely long to occur, so thermodynamic reversibility is an idealization that is never achieved in real processes, except when the system is already at equilibrium, in which case no change will occur anyway! So why is the concept of a reversible process so important?

The answer can be seen by recalling that the change in the internal energy that characterizes any process can be distributed in an infinity of ways between heat flow across the boundaries of the system and work done on or by the system, as expressed by the First Law of thermodynamics

$$\Delta U = q + w. \tag{11.4.1}$$

Each combination of *q* and *w* represents a different pathway between the initial and final states. It can be shown that as a process such as the expansion of a gas is carried out in successively longer series of smaller steps, the absolute value of *q* approaches a minimum, and that of *w* approaches a maximum that is characteristic of the particular process. Thus when a process is carried out reversibly, the *w*-term in Equation 11.4.1 has its greatest possible value, and the *q*-term is at its smallest. These special quantities w_{max} and q_{min} (which we denote as q_{rev} and pronounce "q-reversible") have unique values for any given process and are therefore state functions.

Work and Reversibility

Changes in entropy (ΔS), together with changes in enthalpy (ΔH), enable us to predict in which direction a chemical or physical change will occur spontaneously. Before discussing how to do so, however, we must understand the difference between a reversible process and an irreversible one. In a reversible process, every intermediate state between the extremes is an equilibrium state, regardless of the direction of the change. In contrast, an irreversible process is one in which the intermediate states are not equilibrium states, so change occurs spontaneously in only one direction. As a result, a reversible process can change direction at any time, whereas an irreversible process cannot. When a gas expands reversibly against an external pressure such as a piston, for example, the expansion can be reversed at any time by reversing the motion of the piston; once the gas is compressed, it can be allowed to expand again, and the process can continue indefinitely. In contrast, the expansion of a gas into a vacuum ($P_{ext} = 0$) is irreversible because the external pressure is measurably less than the internal pressure of the gas. No equilibrium states exist, and the gas expands irreversibly. When gas escapes from a microscopic hole in a balloon into a vacuum, for example, the process is irreversible; the direction of airflow cannot change.

Because work done during the expansion of a gas depends on the opposing external pressure ($w = P_{ext}\Delta V$), work done in a reversible process is always equal to or greater than work done in a corresponding irreversible process: $w_{rev} \geq w_{irrev}$. Whether a process is reversible or irreversible, the first law of thermodynamics holds (Equation 11.4.1). Because U is a state function, the magnitude of ΔU does not depend on reversibility and is independent of the path taken. So

$$\Delta U = q_{rev} + w_{rev} \tag{11.4.2}$$

$$= q_{irrev} + w_{irrev} \tag{11.4.3}$$

Work done in a reversible process is always equal to or greater than work done in a corresponding irreversible process:

$$w_{rev} \geq w_{irrev} \tag{11.4.4}$$

In other words, ΔU for a process is the same whether that process is carried out in a reversible manner or an irreversible one. We now return to our earlier definition of entropy, using the magnitude of the heat flow for a reversible process (q_{rev}) to define entropy quantitatively.

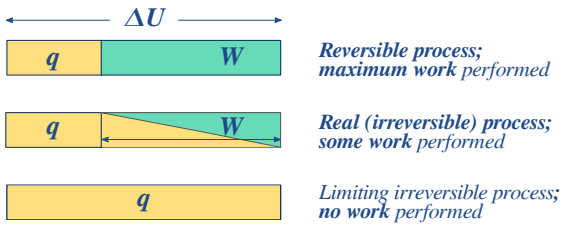


Figure 11.4.2: Note that the reversible condition implies w_{max} and q_{min}. The impossibility of extracting all of the internal energy as work is essentially a statement of the Second Law. (CC BY-NC; Ümit Kaya)

For a process that reversibly exchanges a quantity of heat q_{rev} with the surroundings, the entropy change is defined as

$$\Delta S = \frac{q_{rev}}{T} \tag{11.4.5}$$

This is the basic way of evaluating ΔS for *constant-temperature processes* such as phase changes, or the isothermal expansion of a gas. For processes in which the temperature is not constant such as heating or cooling of a substance, the equation must be integrated over the required temperature range, as discussed below.

Q&A: If no real process can take place reversibly, what use is an expression involving q_{rev}?

This is a rather fine point that you should understand: although transfer of heat between the system and surroundings is impossible to achieve in a truly reversible manner, this idealized pathway is only crucial for the definition of ΔS; by virtue of its being a state function, the same value of ΔS will apply when the system undergoes the same net change via any pathway. For example, the entropy change a gas undergoes when its volume is doubled at constant temperature will be the same regardless of whether the expansion is carried out in 1000 tiny steps (as reversible as patience is likely to allow) or by a single-step (as irreversible a pathway as you can get!) expansion into a vacuum (Figure 11.4.1).

Entropy is an *extensive* quantity; that is, it is proportional to the quantity of matter in a system; thus 100 g of metallic copper has twice the entropy of 50 g at the same temperature. This makes sense because the larger piece of copper contains twice as many quantized energy levels able to contain the thermal energy.

Entropy and "disorder"

Entropy is still described, particularly in older textbooks, as a measure of disorder. In a narrow technical sense this is correct, since the spreading and sharing of thermal energy does have the effect of randomizing the disposition of thermal energy within a system. But to simply equate entropy with “disorder” without further qualification is extremely misleading because it is far too easy to forget that entropy (and thermodynamics in general) applies only to molecular-level systems capable of exchanging thermal energy with the surroundings. Carrying these concepts over to macro systems may yield compelling analogies, but it is no longer science. It is far better to avoid the term “disorder” altogether in discussing entropy.



ΔS_{sys} for an Isothermal Expansion (or Compression)

As a substance becomes more dispersed in space, the thermal energy it carries is also spread over a larger volume, leading to an increase in its entropy. Because entropy, like energy, is an extensive property, a dilute solution of a given substance may well possess a smaller entropy than the same volume of a more concentrated solution, but the entropy *per mole* of solute (the *molar* entropy) will of course always increase as the solution becomes more dilute.

For gaseous substances, the volume and pressure are respectively direct and inverse measures of concentration. For an ideal gas that expands at a constant temperature (meaning that it absorbs heat from the surroundings to compensate for the work it does during the expansion), the increase in entropy is given by

$$\Delta S = R \ln\left(\frac{V_2}{V_1}\right) \tag{11.4.6}$$

Note: If the gas is allowed to cool during the expansion, the relation becomes more complicated and will best be discussed in a more advanced course.

Because the pressure of an ideal gas is *inversely proportional* to its volume, i.e.,

$$P = \frac{nRT}{V} \tag{11.4.7}$$

we can easily alter Equation 11.4.6 to express the entropy change associated with a change in the pressure of an ideal gas:

$$\Delta S = R \ln\left(\frac{P_1}{P_2}\right) \tag{11.4.8}$$

Also the concentration $c = n/V$ for an ideal gas is *proportional* to pressure

$$P = cRT \tag{11.4.9}$$

we can expressing the entropy change directly in concentrations, we have the similar relation

$$\Delta S = R \ln\left(\frac{c_1}{c_2}\right) \tag{11.4.10}$$

Although these equations strictly apply only to perfect gases and cannot be used at all for liquids and solids, it turns out that in a dilute solution, the solute can often be treated as a gas dispersed in the volume of the solution, so the last equation can actually give a fairly accurate value for the entropy of dilution of a solution. We will see later that this has important consequences in determining the equilibrium concentrations in a homogeneous reaction mixture.

The Relationship between Internal Energy and Entropy

Because the quantity of heat transferred (q_{rev}) is directly proportional to the absolute temperature of an object (T) ($q_{rev} \propto T$), the hotter the object, the greater the amount of heat transferred. Moreover, adding heat to a system increases the kinetic energy of the component atoms and molecules and hence their disorder ($\Delta S \propto q_{rev}$). Combining these relationships for any reversible process,

$$q_{\text{rev}} = T\Delta S \tag{11.4.11}$$

and

$$\Delta S = \frac{q_{\text{rev}}}{T} \tag{11.4.12}$$

Because the numerator (q_{rev}) is expressed in units of energy (joules), the units of ΔS are joules/kelvin (J/K). Recognizing that the work done in a reversible process at constant pressure is

$$w_{rev} = -P\Delta V, \tag{11.4.13}$$

we can express Equation 11.4.3 as follows:

$$\Delta U = q_{rev} + w_{rev} \tag{11.4.14}$$

$$= T\Delta S - P\Delta V \tag{11.4.15}$$

Thus the change in the internal energy of the system is related to the change in entropy, the absolute temperature, and the PV work done.

To illustrate the use of Equation 11.4.12 and Equation 11.4.15, we consider two reversible processes before turning to an irreversible process. When a sample of an ideal gas is allowed to expand reversibly at constant temperature, heat must be added to the gas during expansion to keep its T constant (Figure 11.4.5). The internal energy of the gas does not change because the temperature of the gas does not change; that is, $\Delta U = 0$ and $q_{rev} = -w_{rev}$. During expansion, $\Delta V > 0$, so the gas performs work on its surroundings:

$$w_{rev} = -P\Delta V < 0. \tag{11.4.16}$$

According to Equation 11.4.15, this means that q_{rev} must increase during expansion; that is, the gas must absorb heat from the surroundings during expansion, and the surroundings must give up that same amount of heat. The entropy change of the *system* is therefore

$$\Delta S_{sys} = +\frac{q_{rev}}{T} \tag{11.4.17}$$

and the entropy change of the *surroundings* is

$$\Delta S_{surr} = -\frac{q_{rev}}{T}. \tag{11.4.18}$$

The corresponding change in entropy of the universe is then as follows:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \tag{11.4.19}$$

$$= \frac{q_{\text{rev}}}{T} + \left(-\frac{q_{\text{rev}}}{T}\right) \tag{11.4.20}$$

$$= 0 \tag{11.4.21}$$

Thus no change in ΔS_{univ} has occurred.

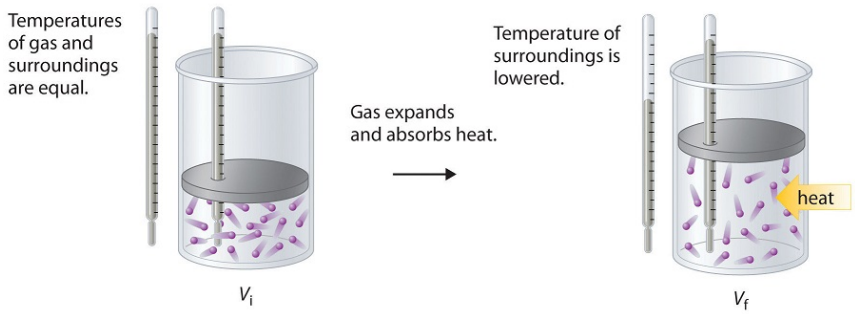


Figure 11.4.5: Expansion of Gas at Constant Temperature. (CC BY-SA-NC; Anonymous by request)

In the initial state (top), the temperatures of a gas and the surroundings are the same. During the reversible expansion of the gas, heat must be added to the gas to maintain a constant temperature. Thus the internal energy of the gas does not change, but work is performed on the surroundings. In the final state (bottom), the temperature of the surroundings is lower because the gas has absorbed heat from the surroundings during expansion.

Now consider the reversible melting of a sample of ice at 0°C and 1 atm. The enthalpy of fusion of ice is 6.01 kJ/mol, which means that 6.01 kJ of heat are absorbed reversibly from the surroundings when 1 mol of ice melts at 0°C, as illustrated in Figure 11.4.6. The surroundings constitute a sample of low-density carbon foam that is thermally conductive, and the system is the ice cube that has been placed on it. The direction of heat flow along the resulting temperature gradient is indicated with an arrow. From Equation 11.4.12, we see that the entropy of fusion of ice can be written as follows:

$$\Delta S_{\text{fus}} = \frac{q_{\text{rev}}}{T} = \frac{\Delta H_{\text{fus}}}{T} \tag{11.4.22}$$

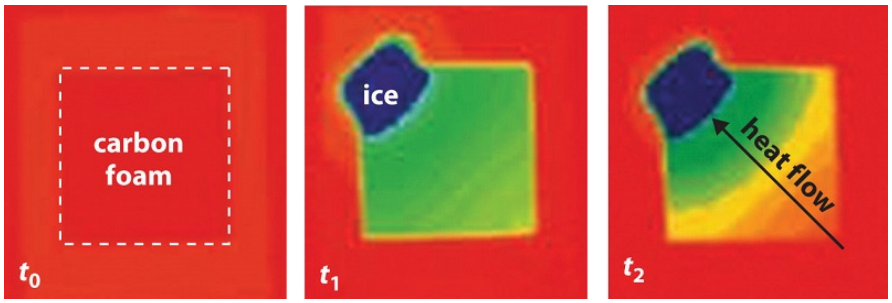


Figure 11.4.6: Thermograms Showing That Heat Is Absorbed from the Surroundings When Ice Melts at 0°C

By convention, a thermogram shows cold regions in blue, warm regions in red, and thermally intermediate regions in green. When an ice cube (the system, dark blue) is placed on the corner of a square sample of low-density carbon foam with very high thermal conductivity, the temperature of the foam is lowered (going from red to green). As the ice melts, a temperature gradient appears, ranging from warm to very cold. An arrow indicates the direction of heat flow from the surroundings (red and green) to the ice cube. The amount of heat lost by the surroundings is the same as the amount gained by the ice, so the entropy of the universe does not change.

In this case,

$$\Delta S_{fus} = \frac{6.01\ kJ/mol}{273\ K} \tag{11.4.23}$$

$$= 22.0\ J/(mol \bullet K) \tag{11.4.24}$$

$$= \Delta S_{sys}. \tag{11.4.25}$$

The amount of heat lost by the surroundings is the same as the amount gained by the ice, so

$$\Delta S_{surr} = \frac{q_{rev}}{T} \tag{11.4.26}$$

$$= \frac{-6.01\ kJ/mol}{273\ K} \tag{11.4.27}$$

$$= -22.0\ J/(mol \bullet K). \tag{11.4.28}$$

Once again, we see that the entropy of the universe does not change:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} \tag{11.4.29}$$

$$= 22.0\ J/(mol \bullet K) - 22.0\ J/(mol \bullet K) \tag{11.4.30}$$

$$= 0 \tag{11.4.31}$$

In these two examples of reversible processes, the entropy of the universe is unchanged. This is true of all reversible processes and constitutes part of the second law of thermodynamics: the entropy of the universe remains constant in a reversible process, whereas the entropy of the universe increases in an irreversible (spontaneous) process.

The Second Law of Thermodynamics

The entropy of the universe **increases** during a spontaneous process. It also **increases** during an observable non-spontaneous process.

As an example of an irreversible process, consider the entropy changes that accompany the spontaneous and irreversible transfer of heat from a hot object to a cold one, as occurs when lava spewed from a volcano flows into cold ocean water. The cold substance, the water, gains heat ($q > 0$), so the change in the entropy of the water can be written as $\Delta S_{cold} = q/T_{cold}$. Similarly, the hot substance, the lava, loses heat ($q < 0$), so its entropy change can be written as $\Delta S_{hot} = -q/T_{hot}$, where T_{cold} and T_{hot} are the temperatures of the cold and hot substances, respectively. The total entropy change of the universe accompanying this process is therefore

$$\Delta S_{\text{univ}} = \Delta S_{\text{cold}} + \Delta S_{\text{hot}} \tag{11.4.32}$$

$$= \frac{q}{T_{\text{cold}}} + \left(-\frac{q}{T_{\text{hot}}}\right) \tag{11.4.33}$$

The numerators on the right side of Equation 11.4.33 are the same in magnitude but opposite in sign. Whether ΔS_{univ} is positive or negative depends on the relative magnitudes of the denominators. By definition, $T_{hot} > T_{cold}$, so $-q/T_{hot}$ must be less than q/T_{cold}, and ΔS_{univ} must be positive. As predicted by the second law of thermodynamics, the entropy of the universe increases during this irreversible process. Any process for which ΔS_{univ} is positive is, by definition, a spontaneous one that will occur as written. Conversely, any process for which ΔS_{univ} approaches zero will not occur spontaneously as written but will occur spontaneously in the reverse direction. We see, therefore, that heat is spontaneously transferred from a hot substance, the lava, to a cold substance, the ocean water. In fact, if the lava is hot enough (e.g., if it is molten), so much heat can be transferred that the water is converted to steam (Figure 11.4.7).



Figure 11.4.7: Spontaneous Transfer of Heat from a Hot Substance to a Cold Substance

When molten lava flows into cold ocean water, so much heat is spontaneously transferred to the water that steam is produced.

Example 11.4.1: Tin Pest

Tin has two allotropes with different structures. Gray tin (α-tin) has a structure similar to that of diamond, whereas white tin (β-tin) is denser, with a unit cell structure that is based on a rectangular prism. At temperatures greater than 13.2°C, white tin is the more stable phase, but below that temperature, it slowly converts reversibly to the less dense, powdery gray phase. This phenomenon was argued to plagued Napoleon's army during his ill-fated invasion of Russia in 1812: the buttons on his soldiers' uniforms were made of tin and disintegrated during the Russian winter, adversely affecting the soldiers' health (and morale). The conversion of white tin to gray tin is exothermic, with $\Delta H = -2.1$ kJ/mol at 13.2°C.

a. What is ΔS for this process?
b. Which is the more highly ordered form of tin—white or gray?

Given: ΔH and temperature

Asked for: ΔS and relative degree of order

Strategy:

Use Equation 11.4.12 to calculate the change in entropy for the reversible phase transition. From the calculated value of ΔS, predict which allotrope has the more highly ordered structure.

Solution

a. We know from Equation 11.4.12 that the entropy change for any reversible process is the heat transferred (in joules) divided by the temperature at which the process occurs. Because the conversion occurs at constant pressure, and ΔH and ΔU are essentially equal for reactions that involve only solids, we can calculate the change in entropy for the reversible phase transition where $q_{rev} = \Delta H$. Substituting the given values for ΔH and temperature in kelvins (in this case, T = 13.2°C = 286.4 K),

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{(-2.1\ \text{kJ/mol})(1000\ \text{J/kJ})}{286.4\ \text{K}} = -7.3\ \text{J/(mol}\cdot\text{K)}$$

b. The fact that ΔS < 0 means that entropy decreases when white tin is converted to gray tin. Thus gray tin must be the more highly ordered structure.

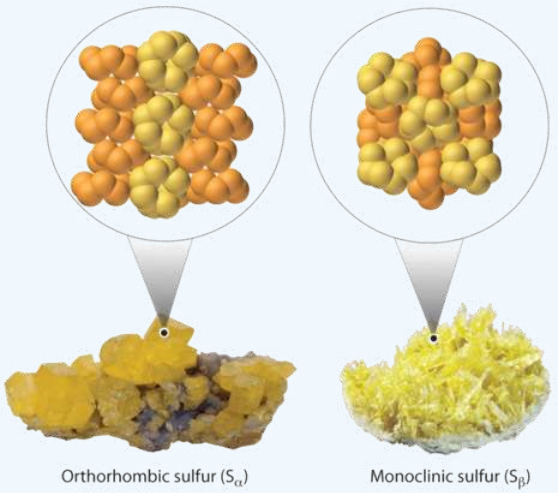


Video 11.4.1: Time lapse tin pest reaction. Beta tin to alpha tin transformation, time lapse video of sample maintained at -40 C. 20 shots per hour.

Note: Whether failing buttons were indeed a contributing factor in the failure of the invasion remains disputed; critics of the theory point out that the tin used would have been quite impure and thus more tolerant of low temperatures. Laboratory tests provide evidence that the time required for unalloyed tin to develop significant tin pest damage at lowered temperatures is about 18 months, which is more than twice the length of Napoleon's Russian campaign. It is clear though that some of the regiments employed in the campaign had tin buttons and that the temperature reached sufficiently low values (at least -40 °C) to facilitate tin pest.

? Exercise 11.4.1: Sulfur

Elemental sulfur exists in two forms: an orthorhombic form (S_α), which is stable below 95.3°C, and a monoclinic form (S_β), which is stable above 95.3°C. The conversion of orthorhombic sulfur to monoclinic sulfur is endothermic, with $\Delta H = 0.401\ kJ/mol$ at 1 atm.



a. What is ΔS for this process?
b. Which is the more highly ordered form of sulfur—S_α or S_β?

Answer a

1.09 J/(mol•K)

Answer b

S_α

Summary

During a spontaneous process, the entropy of the universe increases.

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

A reversible process is one for which all intermediate states between extremes are *equilibrium states*; it can change direction at any time. In contrast, an irreversible process occurs in one direction only. The change in entropy of the system or the surroundings is the quantity of heat transferred divided by the temperature. The second law of thermodynamics states that in a reversible process, the entropy of the universe is constant, whereas in an irreversible process, such as the transfer of heat from a hot object to a cold object, the entropy of the universe increases.

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11.5: Entropy Changes and Spontaneity

Learning Objectives

- State and explain the second and third laws of thermodynamics
- Calculate entropy changes for phase transitions and chemical reactions under standard conditions

Connecting Entropy and Heat to Spontaneity

In the quest to identify a property that may reliably predict the spontaneity of a process, we have identified a very promising candidate: entropy. Processes that involve an increase in entropy *of the system* ($\Delta S_{sys} > 0$) 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:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \tag{11.5.1}$$

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:

$$\Delta S_{\text{sys}} = \frac{-q_{\text{rev}}}{T_{\text{sys}}} \tag{11.5.2}$$

and

$$\Delta S_{\text{surr}} = \frac{q_{\text{rev}}}{T_{\text{surr}}} \tag{11.5.3}$$

The arithmetic signs of q_{rev} denote the loss of heat by the system and the gain of heat by the surroundings. Since $T_{\text{sys}} > T_{\text{surr}}$ in this scenario, the magnitude of the entropy change for the surroundings will be greater than that for the system, and so the sum of ΔS_{sys} and ΔS_{surr} will yield a positive value for ΔS_{univ}. *This process involves an increase in the entropy of the universe.*

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:

$$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T_{\text{sys}}} \tag{11.5.4}$$

and

$$\Delta S_{\text{surr}} = \frac{-q_{\text{rev}}}{T_{\text{surr}}} \tag{11.5.5}$$

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 will yield a negative value for ΔS_{univ}. *This process involves a decrease in the entropy of the universe.*

3. The temperature difference between the objects is infinitesimally small, $T_{sys} \approx T_{surr}$, and so the heat flow is thermodynamically *reversible*. See the previous section's discussion). In this case, the system and surroundings experience entropy changes that are equal in magnitude and therefore sum to yield a value of zero for ΔS_{univ}. *This process involves no change in the entropy of the universe.*

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 11.5.1.

Table 11.5.1: The Second Law of Thermodynamics

$\Delta S_{univ} > 0$	spontaneous

$\Delta S_{univ} < 0$	nonspontaneous (spontaneous in opposite direction)
$\Delta S_{univ} = 0$	reversible (system is at equilibrium)

Definition: The Second Law of Thermodynamics

All spontaneous changes cause an increase in the entropy of the universe, i.e.,

$$\Delta S_{\text{univ}} > 0. \tag{11.5.6}$$

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:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \tag{11.5.7}$$

$$= \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} \tag{11.5.8}$$

We may use this equation to predict the spontaneity of a process as illustrated in Example 11.5.1.

Example 11.5.1: Will Ice Spontaneously Melt?

The entropy change for the process

$$\text{H}_2\text{O}(s) \longrightarrow \text{H}_2\text{O}(l)$$

is 22.1 J/K and requires that the surroundings transfer 6.00 kJ of heat to the system. Is the process spontaneous at −10.00 °C? Is it spontaneous at +10.00 °C?

Solution

We can assess the spontaneity of the process by calculating the entropy change of the universe. If ΔS_{univ} is positive, then the process is spontaneous. At both temperatures, ΔS_{sys} = 22.1 J/K and q_{surr} = −6.00 kJ.

At −10.00 °C (263.15 K), the following is true:

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \\ &= \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} \\ &= 22.1\ \text{J/K} + \frac{-6.00 \times 10^3\ \text{J}}{263.15\ \text{K}} \\ &= -0.7\ J/K\end{aligned}$$

S_{univ} < 0, so melting is nonspontaneous (*not* spontaneous) at −10.0 °C.

At 10.00 °C (283.15 K), the following is true:

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} \\ &= 22.1\ J/K + \frac{-6.00 \times 10^3\ J}{283.15\ K} \\ &= +0.9\ J/K\end{aligned}$$

$\Delta S_{univ} > 0$, so melting *is* spontaneous at 10.00 °C.

? Exercise 11.5.1

Using this information, determine if liquid water will spontaneously freeze at the same temperatures. What can you say about the values of ΔS_{univ}?

Answer

Entropy is a state function, and freezing is the opposite of melting. At −10.00 °C spontaneous, +0.7 J/K; at +10.00 °C nonspontaneous, −0.9 J/K.

Summary

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.

Key Equations

- $\Delta S^\circ = \Delta S^\circ_{298} = \sum \nu S^\circ_{298}(\text{products}) - \sum \nu S^\circ_{298}(\text{reactants})$
- $\Delta S = \dfrac{q_{\text{rev}}}{T}$
- $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$
- $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + \dfrac{q_{\text{surr}}}{T}$

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11.6: The Third Law of Thermodynamics

Learning Objectives

- The *absolute entropy* of a pure substance at a given temperature is the sum of all the entropy it would acquire on warming from absolute zero (where $S = 0$) to the particular temperature.
- Calculate entropy changes for phase transitions and chemical reactions under standard conditions

The atoms, molecules, or ions that compose a chemical system can undergo several types of molecular motion, including translation, rotation, and vibration (Figure 11.6.1). The greater the molecular motion of a system, the greater the number of possible microstates and the higher the entropy. A perfectly ordered system with only a single microstate available to it would have an entropy of zero. The only system that meets this criterion is a perfect crystal at a temperature of absolute zero (0 K), in which each component atom, molecule, or ion is fixed in place within a crystal lattice and exhibits no motion (ignoring quantum *zero point motion*).

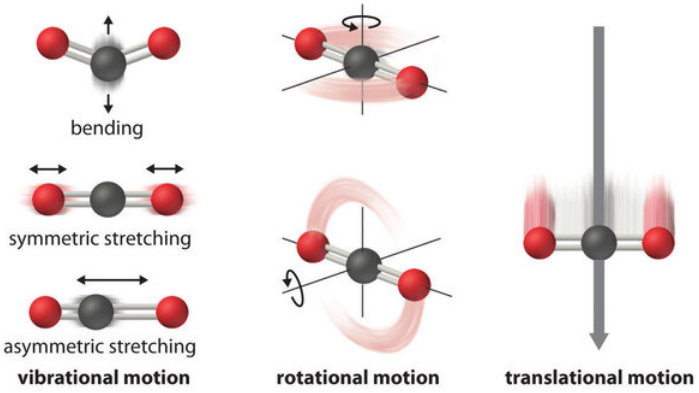


Figure 11.6.1: Molecular Motions. Vibrational, rotational, and translational motions of a carbon dioxide molecule are illustrated here. Only a perfectly ordered, crystalline substance at absolute zero would exhibit no molecular motion (classically; there will always be motion quantum mechanically) and have zero entropy. In practice, this is an unattainable ideal. (CC BY-SA-NC; Anonymous by request)

This system may be described by a single microstate, as its purity, perfect crystallinity and complete lack of motion (at least classically, quantum mechanics argues for constant motion) means there is but one possible location for each identical atom or molecule comprising the crystal ($\Omega = 1$). According to the Boltzmann equation, the entropy of this system is zero.

$$\begin{aligned} S &= k \ln \Omega \\ &= k \ln(1) \\ &= 0 \end{aligned}$$

In practice, absolute zero is an ideal temperature that is unobtainable, and a perfect single crystal is also an ideal that cannot be achieved. Nonetheless, the combination of these two ideals constitutes the basis for the third law of thermodynamics: the entropy of any perfectly ordered, crystalline substance at absolute zero is zero.

Definition: Third Law of Thermodynamics

The entropy of a pure, perfect crystalline substance at 0 K is zero.

The third law of thermodynamics has two important consequences: it defines the sign of the entropy of any substance at temperatures above absolute zero as positive, and it provides a fixed reference point that allows us to measure the absolute entropy of any substance at any temperature. In this section, we examine two different ways to calculate ΔS for a reaction or a physical change. The first, based on the definition of absolute entropy provided by the third law of thermodynamics, uses tabulated values of absolute entropies of substances. The second, based on the fact that entropy is a state function, uses a thermodynamic cycle similar to those discussed previously.

Standard-State Entropies

One way of calculating ΔS for a reaction is to use tabulated values of the standard molar entropy (S^o), which is the entropy of 1 mol of a substance under standard pressure (1 bar). Often the standard molar entropy is given at 298 K and is often demarked as ΔS^o_{298}. The units of S^o are J/(mol•K). Unlike enthalpy or internal energy, it is possible to obtain absolute entropy values by measuring the entropy change that occurs between the reference point of 0 K (corresponding to $S = 0$) and 298 K (Tables T1 and T2).

As shown in Table 11.6.1, for substances with approximately the same molar mass and number of atoms, S^o values fall in the order

$$S^o(\text{gas}) \gg S^o(\text{liquid}) > S^o(\text{solid}). \tag{11.6.1}$$

For instance, S^o for liquid water is 70.0 J/(mol•K), whereas S^o for water vapor is 188.8 J/(mol•K). Likewise, S^o is 260.7 J/(mol•K) for gaseous I_2 and 116.1 J/(mol•K) for solid I_2. This order makes qualitative sense based on the kinds and extents of motion available to atoms and molecules in the three phases (Figure 11.6.1). The correlation between physical state and absolute entropy is illustrated in Figure 11.6.2, which is a generalized plot of the entropy of a substance versus temperature.

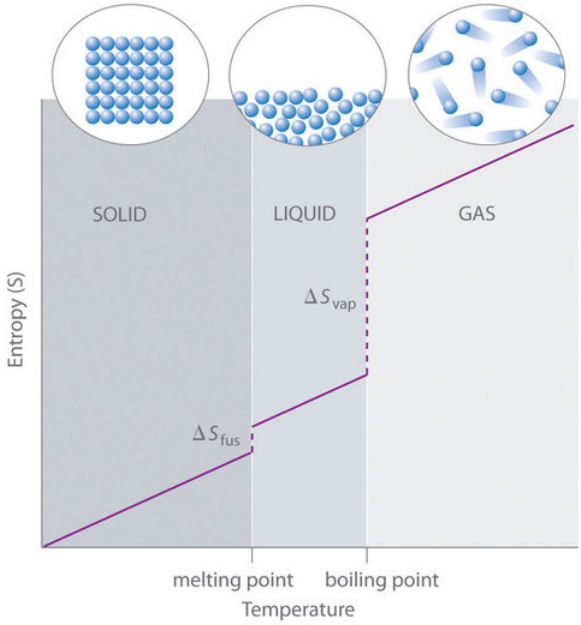


Figure 11.6.2: A Generalized Plot of Entropy versus Temperature for a Single Substance. Absolute entropy increases steadily with increasing temperature until the melting point is reached, where it jumps suddenly as the substance undergoes a phase change from a highly ordered solid to a disordered liquid (ΔS_{fus}). The entropy again increases steadily with increasing temperature until the boiling point is reached, where it jumps suddenly as the liquid undergoes a phase change to a highly disordered gas (ΔS_{vap}). (CC BY-SA-NC; anonymous).

The Third Law Lets us Calculate Absolute Entropies

The *absolute entropy* of a substance at any temperature above 0 K must be determined by calculating the increments of heat q required to bring the substance from 0 K to the temperature of interest, and then summing the ratios q/T. Two kinds of experimental measurements are needed:

1. The enthalpies associated with any **phase changes** the substance may undergo within the temperature range of interest. Melting of a solid and vaporization of a liquid correspond to sizeable increases in the number of microstates available to accept thermal energy, so as these processes occur, energy will flow into a system, filling these new microstates to the extent required to maintain a constant temperature (the freezing or boiling point); these inflows of thermal energy correspond to the heats of fusion and vaporization. The entropy increase associated with transition at temperature T is

$$\frac{\Delta H_{fusion}}{T}. \tag{11.6.2}$$

2. The **heat capacity** C of a phase expresses the quantity of heat required to change the temperature by a small amount ΔT, or more precisely, by an infinitesimal amount dT. Thus the entropy increase brought about by warming a substance over a range of temperatures that does not encompass a phase transition is given by the sum of the quantities $C\frac{dT}{T}$ for each increment of temperature dT. This is of course just the integral

$$S_{0\rightarrow T} = \int_0^T \frac{C_p}{T} dt \tag{11.6.3}$$

Because the heat capacity is itself slightly temperature dependent, the most precise determinations of absolute entropies require that the functional dependence of C on T be used in the integral in Equation 11.6.3, i.e.,:

$$S_{0\rightarrow T} = \int_0^T \frac{C_p(T)}{T} dt. \tag{11.6.4}$$

When this is not known, one can take a series of heat capacity measurements over narrow temperature increments ΔT and measure the area under each section of the curve. The area under each section of the plot represents the entropy change associated with heating the substance through an interval ΔT. To this must be added the enthalpies of melting, vaporization, and of any solid-solid phase changes.

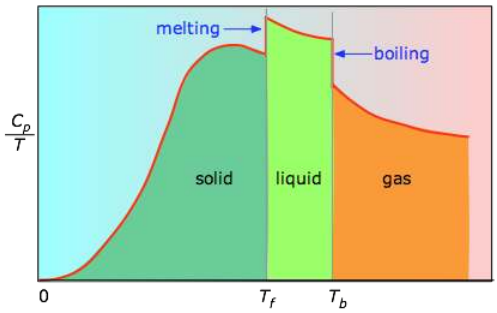


Figure 11.6.3: Heat capacity/temperature as a function of temperature. (CC BY; Stephan Lower)

Values of C_p for temperatures near zero are not measured directly, but can be estimated from quantum theory. The cumulative areas from 0 K to any given temperature (Figure 11.6.3) are then plotted as a function of T, and any phase-change entropies such as

$$S_{vap} = \frac{H_{vap}}{T_b} \tag{11.6.5}$$

are added to obtain the absolute entropy at temperature T. As shown in Figure 11.6.2 above, the entropy of a substance increases with temperature, and it does so for two reasons:

- As the temperature rises, more microstates become accessible, allowing thermal energy to be more widely dispersed. This is reflected in the gradual increase of entropy with temperature.
- The molecules of solids, liquids, and gases have increasingly greater freedom to move around, facilitating the spreading and sharing of thermal energy. Phase changes are therefore accompanied by massive and discontinuous increase in the entropy.

Calculating ΔS_{sys}

We can make careful calorimetric measurements to determine the temperature dependence of a substance's entropy and to derive absolute entropy values under specific conditions. Standard entropies are given the label S^o_{298} for values determined for one mole of substance at a pressure of 1 bar and a temperature of 298 K. The standard entropy change (ΔS^o) for any process may be computed from the standard entropies of its reactant and product species like the following:

$$\Delta S^o = \sum \nu S^o_{298}(\text{products}) - \sum \nu S^o_{298}(\text{reactants}) \tag{11.6.6}$$

Here, ν represents stoichiometric coefficients in the balanced equation representing the process. For example, ΔS^o for the following reaction at room temperature

$$m\text{A} + n\text{B} \longrightarrow x\text{C} + y\text{D} \tag{11.6.7}$$

is computed as the following:

$$\Delta S^o = [xS^o_{298}(\mathrm{C}) + yS^o_{298}(\mathrm{D})] - [mS^o_{298}(\mathrm{A}) + nS^o_{298}(\mathrm{B})] \tag{11.6.8}$$

Table 11.6.1 lists some standard entropies at 298.15 K. You can find additional standard entropies in Tables T1 and T2

Table 11.6.1: Standard Molar Entropy Values of Selected Substances at 25°C

Gases		Liquids		Solids	
Substance	S^o *[J/(mol•K)]*	*Substance*	S^o *[J/(mol•K)]*	*Substance*	S^o *[J/(mol•K)]*
He	126.2	H_2O	70.0	C (diamond)	2.4
H_2	130.7	CH_3OH	126.8	C (graphite)	5.7
Ne	146.3	Br_2	152.2	LiF	35.7
Ar	154.8	CH_3CH_2OH	160.7	SiO_2 (quartz)	41.5
Kr	164.1	C_6H_6	173.4	Ca	41.6
Xe	169.7	CH_3COCl	200.8	Na	51.3
H_2O	188.8	C_6H_{12} (cyclohexane)	204.4	MgF_2	57.2
N_2	191.6	C_8H_{18} (isooctane)	329.3	K	64.7
O_2	205.2			NaCl	72.1
CO_2	213.8			KCl	82.6
I_2	260.7			I_2	116.1

A closer examination of Table 11.6.1 also reveals that substances with similar molecular structures tend to have similar S^o values. Among crystalline materials, those with the lowest entropies tend to be rigid crystals composed of small atoms linked by strong, highly directional bonds, such as diamond ($S^o = 2.4\ J/(mol \bullet K)$). In contrast, graphite, the softer, less rigid allotrope of carbon, has a higher S^o (5.7 J/(mol•K)) due to more ~~disorder~~ (microstates) in the crystal. Soft crystalline substances and those with larger atoms tend to have higher entropies because of increased molecular motion and disorder. Similarly, the absolute entropy of a substance tends to increase with increasing molecular complexity because the number of available microstates increases with molecular complexity. For example, compare the S^o values for $CH_3OH(l)$ and $CH_3CH_2OH(l)$. Finally, substances with strong hydrogen bonds have lower values of S^o, which reflects a more ordered structure.

> *Entropy increases with softer, less rigid solids, solids that contain larger atoms, and solids with complex molecular structures.*

To calculate ΔS^o for a chemical reaction from standard molar entropies, we use the familiar "products minus reactants" rule, in which the absolute entropy of each reactant and product is multiplied by its stoichiometric coefficient in the balanced chemical equation. Example 11.6.1 illustrates this procedure for the combustion of the liquid hydrocarbon isooctane (C_8H_{18}; 2,2,4-trimethylpentane).

Example 11.6.1

Use the data in Table 11.6.1 to calculate ΔS^o for the reaction of liquid isooctane with $O_2(g)$ to give $CO_2(g)$ and $H_2O(g)$ at 298 K.

Given: standard molar entropies, reactants, and products

Asked for: ΔS°

Strategy:

Write the balanced chemical equation for the reaction and identify the appropriate quantities in Table 11.6.1. Subtract the sum of the absolute entropies of the reactants from the sum of the absolute entropies of the products, each multiplied by their appropriate stoichiometric coefficients, to obtain ΔS^o for the reaction.

Solution:

The balanced chemical equation for the complete combustion of isooctane (C_8H_{18}) is as follows:

$$C_8H_{18}(l) + \tfrac{25}{2}O_2(g) \longrightarrow 8\,CO_2(g) + 9\,H_2O(g)$$

We calculate ΔS^o for the reaction using the "products minus reactants" rule, where m and n are the stoichiometric coefficients of each product and each reactant:

$$\begin{aligned}\Delta S^o_{rxn} &= \sum mS^o(\text{products}) - \sum nS^o(\text{reactants})\\ &= [8S^o(CO_2) + 9S^o(H_2O)] - [S^o(C_8H_{18}) + \frac{25}{2}S^o(O_2)]\\ &= \{[8\text{ mol } CO_2 \times 213.8\text{ J/(mol·K)}] + [9\text{ mol } H_2O \times 188.8\text{ J/(mol·K)}]\}\\ &\quad - \left\{[1\text{ mol } C_8H_{18} \times 329.3\text{ J/(mol·K)}] + \left[\frac{25}{2}\text{ mol } O_2 \times 205.2\text{ J/(mol·K)}\right]\right\}\\ &= 515.3\text{ J/K}\end{aligned}$$

ΔS^o is positive, as expected for a combustion reaction in which one large hydrocarbon molecule is converted to many molecules of gaseous products.

? Exercise 11.6.1

Use the data in Table 11.6.1 to calculate ΔS^o for the reaction of $H_2(g)$ with liquid benzene (C_6H_6) to give cyclohexane (C_6H_{12}) at 298 K.

Answer

-361.1 J/K

✔ Example 11.6.2: Determination of ΔS°

Calculate the standard entropy change for the following process at 298 K:

$$H_2O(g) \longrightarrow H_2O(l)$$

Solution

The value of the standard entropy change at room temperature, ΔS^o_{298}, is the difference between the standard entropy of the product, $H_2O(l)$, and the standard entropy of the reactant, $H_2O(g)$.

$$\begin{aligned}\Delta S^o_{298} &= S^o_{298}(H_2O(l)) - S^o_{298}(H_2O(g))\\ &= (70.0\ J\,mol^{-1}K^{-1}) - (188.8\ Jmol^{-1}K^{-1})\\ &= -118.8\ J\,mol^{-1}K^{-1}\end{aligned}$$

The value for ΔS^o_{298} is negative, as expected for this phase transition (condensation), which the previous section discussed.

? Exercise 11.6.2

Calculate the standard entropy change for the following process at 298 K:

$$H_2(g) + C_2H_4(g) \longrightarrow C_2H_6(g)$$

Answer

$-120.6\text{ J mol}^{-1}\text{ K}^{-1}$

Example 11.6.3: Determination of ΔS°

Calculate the standard entropy change for the combustion of methanol, CH_3OH at 298 K:

$$2\,CH_3OH(l) + 3\,O_2(g) \longrightarrow 2\,CO_2(g) + 4\,H_2O(l)$$

Solution

The value of the standard entropy change is equal to the difference between the standard entropies of the products and the entropies of the reactants scaled by their stoichiometric coefficients. The standard entropy of formations are found in Table 11.6.1.

$$\begin{aligned}\Delta S^o &= \Delta S^o_{298} \\ &= \sum \nu S^o_{298}(\text{products}) - \sum \nu S^o_{298}(\text{reactants}) \\ &= 2S^o_{298}(CO_2(g)) + 4S^o_{298}(H_2O(l))] - [2S^o_{298}(CH_3OH(l)) + 3S^o_{298}(O_2(g))] \\ &= [(2 \times 213.8) + (4 \times 70.0)] - [(2 \times 126.8) + (3 \times 205.03)] \\ &= -161.6\ J/mol \cdot K\end{aligned}$$

Exercise 11.6.3

Calculate the standard entropy change for the following reaction at 298 K:

$$Ca(OH)_2(s) \longrightarrow CaO(s) + H_2O(l)$$

Answer

24.7 J/mol•K

Summary

Energy values, as you know, are all relative, and must be defined on a scale that is completely arbitrary; there is no such thing as the absolute energy of a substance, so we can arbitrarily define the enthalpy or internal energy of an element in its most stable form at 298 K and 1 atm pressure as zero. The same is *not* true of the entropy; since entropy is a measure of the "dilution" of thermal energy, it follows that the less thermal energy available to spread through a system (that is, the lower the temperature), the smaller will be its entropy. In other words, as the absolute temperature of a substance approaches zero, so does its entropy. This principle is the basis of the *Third law of thermodynamics*, which states that the entropy of a perfectly-ordered solid at 0 K is zero.

In practice, chemists determine the absolute entropy of a substance by measuring the molar heat capacity (C_p) as a function of temperature and then plotting the quantity C_p/T versus T. The area under the curve between 0 K and any temperature T is the absolute entropy of the substance at T. In contrast, other thermodynamic properties, such as internal energy and enthalpy, can be evaluated in only relative terms, not absolute terms.

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.

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- Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook

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11.7: The Gibbs Free Energy

Learning Objectives

- To understand the relationship between Gibbs free energy and work.

One of the major goals of chemical thermodynamics is to establish criteria for predicting whether a particular reaction or process will occur spontaneously. We have developed one such criterion, the change in entropy of the universe: if $\Delta S_{univ} > 0$ for a process or a reaction, then the process will occur spontaneously as written. Conversely, if $\Delta S_{univ} < 0$, a process cannot occur spontaneously; if $\Delta S_{univ} = 0$, the system is at equilibrium. The sign of ΔS_{univ} is a universally applicable and infallible indicator of the spontaneity of a reaction. Unfortunately, using ΔS_{univ} requires that we calculate ΔS for **both a system and its surroundings**. This is not particularly useful for two reasons: we are normally much more interested in the system than in the surroundings, and it is difficult to make quantitative measurements of the surroundings (i.e., the rest of the universe). A criterion of spontaneity that is based solely on the state functions of a system would be much more convenient and is provided by a new state function: the Gibbs free energy.

Gibbs Energy and Spontaneity

The Gibbs energy (also known as the *Gibbs function*) is defined as

$$G_{sys} = H_{sys} - TS_{sys} \tag{11.7.1}$$

in which S refers to the entropy of the *system*. Since H, T and S are all state functions, so is G. Thus for any change in state, we can expand Equation 11.7.1 to

$$\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys} \tag{11.7.2}$$

How does this simple equation relate to the entropy change of the universe ΔS_{univ} that we know is the sole criterion for spontaneous change from the second law of thermodynamics? Starting with the definition

$$\Delta S_{univ} = \Delta S_{surr} + \Delta S_{sys} \tag{11.7.3}$$

we would first like to get rid of ΔS_{surr}. How can a chemical reaction (a change in the *system*) affect the entropy of the *surroundings*? Because most reactions are either exothermic or endothermic, they are accompanied by heat q_p across the system boundary (we are considering constant pressure processes). The enthalpy change of the reaction ΔH_{sys} is the "flow" of heat into the system from the surroundings under constant pressure, so the heat "withdrawn" from the surroundings will be $-q_p$.

From the thermodynamic definition of entropy, the change of the entropy of the surroundings will be

$$\Delta S_{surr} = -\frac{q_p}{T} = -\frac{\Delta H_{sys}}{T}. \tag{11.7.4}$$

We can therefore rewrite Equation 11.7.3 as

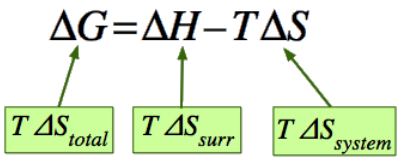
$$\Delta S_{univ} = \frac{-\Delta H_{sys}}{T} + \Delta S_{sys} \tag{11.7.5}$$

Multiplying through by $-T$, we obtain

$$-T\ \Delta S_{univ} = \Delta H_{sys} - T\ \Delta S_{sys} \tag{11.7.6}$$

which expresses the entropy change of the universe in terms of thermodynamic properties of the *system* exclusively.

If $-T\Delta S_{univ}$ is denoted by ΔG, then we have Equation 11.7.2 which defines the *Gibbs energy* change for the process.



The criterion for predicting spontaneity is based on (ΔG), the change in G, at constant temperature and pressure. Although very few chemical reactions actually occur under conditions of constant temperature and pressure, most systems can be brought back to the initial temperature and pressure without significantly affecting the value of thermodynamic state functions such as G. At constant temperature and pressure,

$$\Delta G = \Delta H - T\Delta S \tag{11.7.7}$$

where all thermodynamic quantities are those of the system. Recall that at constant pressure, $\Delta H = q$, whether a process is reversible or irreversible, and

$$T\Delta S = q_{rev}\,. \tag{11.7.8}$$

Using these expressions, we can reduce Equation 11.7.7 to

$$\Delta G = q - q_{rev}\,. \tag{11.7.9}$$

Thus ΔG is the difference between the heat released during a process (via a reversible or an irreversible path) and the heat released for the same process occurring in a reversible manner. Under the special condition in which a process occurs reversibly, $q = q_{rev}$ and $\Delta G = 0$. As we shall soon see, if ΔG is zero, the system is at equilibrium, and there will be no net change.

What about processes for which $\Delta G \neq 0$? To understand how the sign of ΔG for a system determines the direction in which change is spontaneous, we can rewrite the relationship between ΔS and q_{rev}, discussed earlier.

$$\Delta S = \frac{q_{rev}}{T}$$

with the definition of ΔH in terms of q_{rev}

$$q_{rev} = \Delta H$$

to obtain

$$\Delta S_{\text{surr}} = -\frac{\Delta H_{\text{sys}}}{T} \tag{11.7.10}$$

Thus the entropy change of the surroundings is related to the enthalpy change of the system. We have stated that for a spontaneous reaction, $\Delta S_{univ} > 0$, so substituting we obtain

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0\\ &= \Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} > 0\end{aligned}$$

Multiplying both sides of the inequality by $-T$ reverses the sign of the inequality; rearranging,

$$\Delta H_{sys} - T\Delta S_{sys} < 0 \tag{11.7.11}$$

which is equal to ΔG (Equation 11.7.7). We can therefore see that for a spontaneous process, $\Delta G_{sys} < 0$.

The relationship between the entropy change of the surroundings and the heat gained or lost by the system provides the key connection between the thermodynamic properties of the system and the change in entropy of the universe. The relationship shown in Equation 11.7.7 allows us to predict spontaneity by focusing exclusively on the thermodynamic properties and temperature of the system. We predict that highly exothermic processes ($\Delta H \ll 0$) that increase the entropy of a system ($\Delta S_{sys} \gg 0$) would therefore occur spontaneously. An example of such a process is the decomposition of ammonium nitrate fertilizer. Ammonium nitrate was also used to destroy the Murrah Federal Building in Oklahoma City, Oklahoma, in 1995. For a system at constant temperature and pressure, we can summarize the following results:

- If $\Delta G < 0$, the process occurs spontaneously.
- If $\Delta G = 0$, the system is at equilibrium.
- If $\Delta G > 0$, the process is not spontaneous as written but occurs spontaneously in the reverse direction.

To further understand how the various components of ΔG dictate whether a process occurs spontaneously, we now look at a simple and familiar physical change: the conversion of liquid water to water vapor.

Example 11.7.1: Vaporizing Water

At Room Temperature (100 °C)

If the conversion of liquid water to water vapor is carried out at 1 atm and the normal boiling point of 100.00 °C (373.15 K), we can calculate ΔG from the experimentally measured value of ΔH_{vap} (40.657 kJ/mol). For vaporizing 1 mol of water, $\Delta H = 40,657; J$, so the process is highly endothermic. From the definition of ΔS (Equation 11.7.10), we know that for 1 mol of water,

$$\begin{aligned}\Delta S_{\text{vap}} &= \frac{\Delta H_{\text{vap}}}{T_{\text{b}}} \\ &= \frac{40{,}657\ \text{J}}{373.15\ \text{K}} \\ &= 108.96\ \text{J/K}\end{aligned}$$

Hence there is an increase in the disorder of the system. At the normal boiling point of water,

$$\begin{aligned}\Delta G_{100^\circ\text{C}} &= \Delta H_{100^\circ\text{C}} - T\Delta S_{100^\circ\text{C}} \\ &= 40{,}657\ \text{J} - [(373.15\ \text{K})(108.96\ \text{J/K})] \\ &= 0\ \text{J}\end{aligned}$$

The energy required for vaporization offsets the increase in entropy of the system. Thus $\Delta G = 0$, and the liquid and vapor are in equilibrium, as is true of any liquid at its boiling point under standard conditions.

Above Room Temperature (110 °C)

Now suppose we were to superheat 1 mol of liquid water to 110°C. The value of ΔG for the vaporization of 1 mol of water at 110°C, assuming that ΔH and ΔS do not change significantly with temperature, becomes

$$\begin{aligned}\Delta G_{110^\circ\text{C}} &= \Delta H - T\Delta S \\ &= 40{,}657\ \text{J} - [(383.15\ \text{K})(108.96\ \text{J/K})] \\ &= -1{,}091\ \text{J}\end{aligned}$$

Since $\Delta G < 0$, the vaporization of water is predicted to occur spontaneously and irreversibly at 110 °C.

Below Room Temperature (90 °C)

We can also calculate ΔG for the vaporization of 1 mol of water at a temperature below its normal boiling point—for example, 90°C—making the same assumptions:

$$\begin{aligned}\Delta G_{90^\circ\text{C}} &= \Delta H - T\Delta S \\ &= 40{,}657\ \text{J} - [(363.15\ \text{K})(108.96\ \text{J/K})] \\ &= 1{,}088\ \text{J}\end{aligned}$$

Since $\Delta G > 0$, water does not spontaneously convert to water vapor at 90 °C. When using all the digits in the calculator display in carrying out our calculations, $\Delta G_{110^\circ\text{C}} = 1090\ \text{J} = -\Delta G_{90^\circ\text{C}}$, as we would predict.

Equilibrium Temperature

We can also calculate the temperature at which liquid water is in equilibrium with water vapor. Inserting the values of ΔH and ΔS into the definition of ΔG (Equation 11.7.7), setting $\Delta G = 0$, and solving for T,

$$\begin{aligned}0 &= 40,657\ J - T(108.96\ J/K) \\ T &= 373.15\ K\end{aligned}$$

Thus $\Delta G = 0$ at $T = 373.15\ K$ and $1\ atm$, which indicates that liquid water and water vapor are in equilibrium; this temperature is called the normal boiling point of water.

At temperatures greater than 373.15 K, ΔG is negative, and water evaporates spontaneously and irreversibly. Below 373.15 K, ΔG is positive, and water does not evaporate spontaneously. Instead, water vapor at a temperature less than 373.15 K and 1

atm will spontaneously and irreversibly condense to liquid water. Figure 11.7.1 shows how the ΔH and $T\Delta S$ terms vary with temperature for the vaporization of water. When the two lines cross, $\Delta G = 0$, and $\Delta H = T\Delta S$.

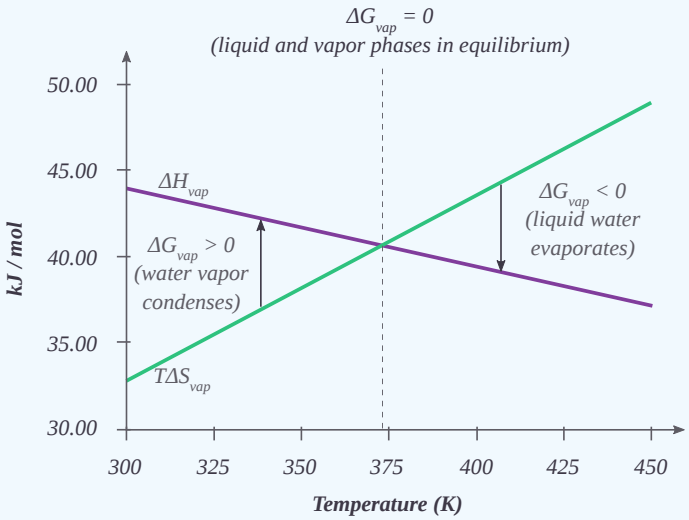


Figure 11.7.1: Temperature Dependence of ΔH and TΔS for the Vaporization of Water. Both ΔH and TΔS are temperature dependent, but the lines have opposite slopes and cross at 373.15 K at 1 atm, where ΔH = TΔS. Because ΔG = ΔH − TΔS, at this temperature ΔG = 0, indicating that the liquid and vapor phases are in equilibrium. The normal boiling point of water is therefore 373.15 K. Above the normal boiling point, the $T\Delta S$ term is greater than ΔH, making ΔG < 0; hence, liquid water evaporates spontaneously. Below the normal boiling point, the ΔH term is greater than $T\Delta S$, making ΔG > 0. Thus liquid water does not evaporate spontaneously, but water vapor spontaneously condenses to liquid. (CC BY-NC; Ümit Kaya)

A similar situation arises in the conversion of liquid egg white to a solid when an egg is boiled. The major component of egg white is a protein called albumin, which is held in a compact, ordered structure by a large number of hydrogen bonds. Breaking them requires an input of energy ($\Delta H > 0$), which converts the albumin to a highly disordered structure in which the molecules aggregate as a disorganized solid ($\Delta S > 0$). At temperatures greater than 373 K, the $T\Delta S$ term dominates, and $\Delta G < 0$, so the conversion of a raw egg to a hard-boiled egg is an irreversible and spontaneous process above 373 K.

Figure 11.7.1

ΔH	ΔS	$-T\Delta S$	ΔG
- (exothermic)	+ (products more disordered)	- (favors spontaneity)	- (spontaneous at all T)
- (exothermic)	- (products less disordered)	+ (opposes spontaneity)	- (spontaneous) at low T + (non-spontaneous) at high T **"Enthalpically-driven process"**
+ (endothermic)	+ (products more disordered)	- (favors spontaneity)	+ (non-spontaneous) at low T - (spontaneous) at high T **"Entropically-driven process"**
+ (endothermic)	- (products less disordered)	+ (opposes spontaneity)	+ (non-spontaneous at all T)

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Enthalpically vs. Entropically Driving Reactions

Some textbooks and teachers say that the free energy, and thus the spontaneity of a reaction, depends on both the enthalpy and entropy changes of a reaction, and they sometimes even refer to reactions as "energy driven" or "entropy driven" depending on whether ΔH or the $T\Delta S$ term dominates. This is technically correct, but misleading because it disguises the important fact that ΔS_{total}, which this equation expresses in an indirect way, is the *only* criterion of spontaneous change.

Consider the following possible states for two different types of molecules with some attractive force:

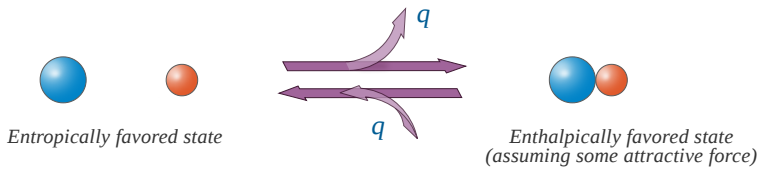


Figure 11.7.2: An enthalpic favored reaction. (CC BY-NC; Ümit Kaya)

There would appear to be greater entropy on the left (state 1) than on the right (state 2). Thus the entropic change for the reaction as written (i.e. going to the right) would be (-) in magnitude, and the energetic contribution to the free energy change would be (+) (i.e. unfavorable) for the reaction as written.

In going to the right, there is an attractive force and the molecules adjacent to each other is a lower energy state (heat energy, *q*, is liberated). To go to the left, we have to overcome this attractive force (input heat energy) and the left direction is unfavorable with regard to heat energy q. The change in enthalpy is (-) in going to the right (q released), and this enthalpy change is negative (-) in going to the right (and (+) in going to the left). This reaction as written, is therefore, *enthalpically favorable* and *entropically unfavorable*. Hence, It is *enthalpically driven.*

From Table 11.7.1, it would appear that we might be able to get the reaction to go to the right at low temperatures (lower temperature would minimize the energetic contribution of the entropic change). Looking at the same process from an opposite direction:

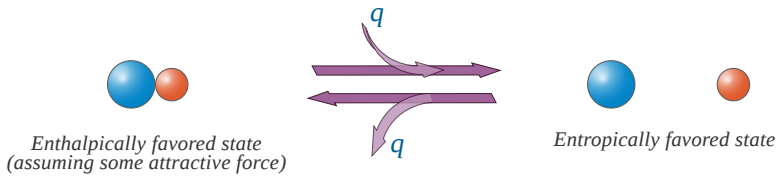


Figure 11.7.3: An entropically favored reaction. (CC BY-NC; Ümit Kaya)

This reaction as written, is *entropically favorable*, and *enthalpically unfavorable;* it is *entropically driven*. From Table 11.7.1, it would appear that we might be able to get the reaction to go to the right at high temperatures (high temperature would increase the energetic contribution of the entropic change).

The Relationship between ΔG and Work

In the previous subsection, we learned that the value of ΔG allows us to predict the spontaneity of a physical or a chemical change. In addition, the magnitude of ΔG for a process provides other important information. The change in Gibbs energy is equal to the maximum amount of work that a system can perform on the surroundings while undergoing a spontaneous change (at constant temperature and pressure):

$$\Delta G = w_{max}. \tag{11.7.12}$$

To see why this is true, let's look again at the relationships among free energy, enthalpy, and entropy expressed in Equation 11.7.7. We can rearrange this equation as follows:

$$\Delta H = \Delta G + T\Delta S \tag{11.7.13}$$

This equation tells us that when energy is released during an exothermic process ($\Delta H < 0$), such as during the combustion of a fuel, some of that energy can be used to do work ($\Delta G < 0$), while some is used to increase the entropy of the universe ($T\Delta S > 0$). Only if the process occurs infinitely slowly in a perfectly reversible manner will the entropy of the universe be unchanged. Because no real system is perfectly reversible, the entropy of the universe increases during all processes that produce energy. As a result, no process that uses stored energy can ever be 100% efficient; that is, ΔH will never equal ΔG because ΔS has a positive value.

One of the major challenges facing engineers is to maximize the efficiency of converting stored energy to useful work or converting one form of energy to another. As indicated in Table 11.7.2, the efficiencies of various energy-converting devices vary widely. For example, an internal combustion engine typically uses only 25%–30% of the energy stored in the hydrocarbon fuel to perform work; the rest of the stored energy is released in an unusable form as heat. In contrast, gas–electric hybrid engines, now used in several models of automobiles, deliver approximately 50% greater fuel efficiency. A large electrical generator is highly efficient (approximately 99%) in converting mechanical to electrical energy, but a typical incandescent light bulb is one of the least efficient devices known (only approximately 5% of the electrical energy is converted to light). In contrast, a mammalian liver cell is a relatively efficient machine and can use fuels such as glucose with an efficiency of 30%–50%.

Table 11.7.2: Approximate Thermodynamic Efficiencies of Various Devices

Device	Energy Conversion	Approximate Efficiency (%)
large electrical generator	mechanical → electrical	99
chemical battery	chemical → electrical	90
home furnace	chemical → heat	65
small electric tool	electrical → mechanical	60
space shuttle engine	chemical → mechanical	50
mammalian liver cell	chemical → chemical	30–50
spinach cell	light → chemical	30
internal combustion engine	chemical → mechanical	25–30
fluorescent light	electrical → light	20
solar cell	light → electricity	10
incandescent light bulb	electricity → light	5
yeast cell	chemical → chemical	2–4

Standard Free-Energy Change

We have seen that there is no way to measure absolute enthalpies, although we can measure changes in enthalpy (ΔH) during a chemical reaction. Because enthalpy is one of the components of Gibbs free energy, we are consequently unable to measure absolute free energies; we can measure only changes in free energy. The standard free-energy change (ΔG°) is the change in free energy when one substance or a set of substances in their standard states is converted to one or more other substances, also in their standard states. The standard free-energy change can be calculated from the definition of free energy, if the standard enthalpy and entropy changes are known, using Equation 11.7.14:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{11.7.14}$$

If ΔS° and ΔH° for a reaction have the same sign, then the sign of ΔG^o depends on the relative magnitudes of the ΔH° and TΔS° terms. It is important to recognize that a positive value of ΔG^o for a reaction does not mean that no products will form if the reactants in their standard states are mixed; it means only that at equilibrium the concentrations of the products will be less than the concentrations of the reactants.

> A positive ΔG^o means that the equilibrium constant is less than 1.

Example 11.7.1

Calculate the standard free-energy change (ΔG°) at 25°C for the reaction

$$\mathrm{H_2(g) + O_2(g) \rightleftharpoons H_2O_2(l)}$$

At 25°C, the standard enthalpy change (ΔH°) is −187.78 kJ/mol, and the absolute entropies of the products and reactants are:

- S°(H_2O_2) = 109.6 J/(mol•K),
- S°(O_2) = 205.2 J/(mol•K), and
- S°(H_2) = 130.7 J/(mol•K).

Is the reaction spontaneous as written?

Given: balanced chemical equation, ΔH° and S° for reactants and products

Asked for: spontaneity of reaction as written

Strategy:

A. Calculate ΔS° from the absolute molar entropy values given.
B. Use Equation 11.7.14, the calculated value of ΔS°, and other data given to calculate ΔG^o for the reaction.
C. Use the value of ΔG^o to determine whether the reaction is spontaneous as written.

Solution

A To calculate ΔG^o for the reaction, we need to know ΔH°, ΔS°, and T. We are given ΔH°, and we know that T = 298.15 K. We can calculate ΔS° from the absolute molar entropy values provided using the "products minus reactants" rule:

$$\begin{aligned}\Delta S^\circ &= S^\circ(\mathrm{H_2O_2}) - [S^\circ(\mathrm{O_2}) + S^\circ(\mathrm{H_2})] \\ &= [1\ \text{mol}\ \mathrm{H_2O_2} \times 109.6\ \mathrm{J/(mol \cdot K)}] \\ &\quad - \{[1\ \text{mol}\ \mathrm{H_2} \times 130.7\ \mathrm{J/(mol \cdot K)}] + [1\ \text{mol}\ \mathrm{O_2} \times 205.2\ \mathrm{J/(mol \cdot K)}]\} \\ &= -226.3\ \mathrm{J/K\ (\text{per mole of}\ H_2O_2)}\end{aligned}$$

As we might expect for a reaction in which 2 mol of gas is converted to 1 mol of a much more ordered liquid, ΔS° is very negative for this reaction.

B Substituting the appropriate quantities into Equation 11.7.14,

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -187.78\ \mathrm{kJ/mol} - (298.15\ \mathrm{K})[-226.3\ \mathrm{J/(mol \cdot K)} \times 1\ \mathrm{kJ/1000\ J}] \\ &= -187.78\ \mathrm{kJ/mol} + 67.47\ \mathrm{kJ/mol} \\ &= -120.31\ \mathrm{kJ/mol}\end{aligned}$$

The negative value of ΔG^o indicates that the reaction is spontaneous as written. Because ΔS° and ΔH° for this reaction have the same sign, the sign of ΔG^o depends on the relative magnitudes of the ΔH° and TΔS° terms. In this particular case, the enthalpy term dominates, indicating that the strength of the bonds formed in the product more than compensates for the unfavorable ΔS° term and for the energy needed to break bonds in the reactants.

Exercise 11.7.1

Calculate the standard free-energy change (ΔG°) at 25°C for the reaction

$$\mathrm{2\,H_2(g) + N_2(g) \rightleftharpoons N_2H_4(l).}$$

At 25°C, the standard enthalpy change (ΔH°) is 50.6 kJ/mol, and the absolute entropies of the products and reactants are S°(N_2H_4) = 121.2 J/(mol•K), S°(N_2) = 191.6 J/(mol•K), and S°(H_2) = 130.7 J/(mol•K). Is the reaction spontaneous as written?

Answer

149.5 kJ/mol; no

Tabulated values of standard free energies of formation allow chemists to calculate the values of ΔG^o for a wide variety of chemical reactions rather than having to measure them in the laboratory. The standard free energy of formation (ΔG_f°)of a compound is the change in free energy that occurs when 1 mol of a substance in its standard state is formed from the component elements in their standard states. By definition, the standard free energy of formation of an element in its standard state is zero at 298.15 K. One mole of Cl_2 gas at 298.15 K, for example, has $\Delta G_f^\circ = 0$. The standard free energy of formation of a compound can be calculated from the standard enthalpy of formation (ΔH°_f) and the standard entropy of formation (ΔS°_f) using the definition of free energy:

$$\Delta G_f^o = \Delta H_f^o - T\Delta S_f^o \tag{11.7.15}$$

Using standard free energies of formation to calculate the standard free energy of a reaction is analogous to calculating standard enthalpy changes from standard enthalpies of formation using the familiar "products minus reactants" rule:

$$\Delta G_{rxn}^o = \sum m\Delta G_f^o(products) - \sum n\Delta G_f^o(reactants) \tag{11.7.16}$$

where m and n are the stoichiometric coefficients of each product and reactant in the balanced chemical equation. A very large negative ΔG^o indicates a strong tendency for products to form spontaneously from reactants; it does not, however, necessarily indicate that the reaction will occur rapidly. To make this determination, we need to evaluate the kinetics of the reaction.

"Products minus Reactants" Rule

The ΔG^o of a reaction can be calculated from tabulated ΔG_f^o values (Table T1) using the "products minus reactants" rule.

Example 11.7.2

Calculate ΔG^o for the reaction of isooctane with oxygen gas to give carbon dioxide and water. Use the following data:

- ΔG°_f(isooctane) = −353.2 kJ/mol,
- $\Delta G^\circ_f(CO_2)$ = −394.4 kJ/mol, and
- $\Delta G^\circ_f(H_2O)$ = −237.1 kJ/mol.

Is the reaction spontaneous as written?

Given: balanced chemical equation and values of ΔG°_f for isooctane, CO_2, and H_2O

Asked for: spontaneity of reaction as written

Strategy:

Use the "products minus reactants" rule to obtain ΔG°_{rxn}, remembering that ΔG°_f for an element in its standard state is zero. From the calculated value, determine whether the reaction is spontaneous as written.

Solution

The balanced chemical equation for the reaction is as follows:

$$C_8H_{18}(l) + \tfrac{25}{2}O_2(g) \longrightarrow 8\,CO_2(g) + 9\,H_2O(l)$$

We are given ΔG°_f values for all the products and reactants except O_2(g). Because oxygen gas is an element in its standard state, $\Delta G^\circ_f(O_2)$ is zero. Using the "products minus reactants" rule,

$$\begin{aligned}\Delta G^\circ &= [8\Delta G_f^\circ(CO_2) + 9\Delta G_f^\circ(H_2O)] - \left[1\Delta G_f^\circ(C_8H_{18}) + \frac{25}{2}\Delta G_f^\circ(O_2)\right] \\ &= [(8\text{ mol})(-394.4\text{ kJ/mol}) + (9\text{ mol})(-237.1\text{ kJ/mol})] \\ &\quad - \left[(1\text{ mol})(-353.2\text{ kJ/mol}) + \left(\frac{25}{2}\text{ mol}\right)(0\text{ kJ/mol})\right] \\ &= -4935.9\text{ kJ (per mol of } C_8H_{18})\end{aligned}$$

Because ΔG^o is a large negative number, there is a strong tendency for the spontaneous formation of products from reactants (though not necessarily at a rapid rate). Also notice that the magnitude of ΔG^o is largely determined by the ΔG°_f of the stable products: water and carbon dioxide.

Exercise 11.7.2

Calculate ΔG^o for the reaction of benzene with hydrogen gas to give cyclohexane using the following data

- ΔG°_f(benzene) = 124.5 kJ/mol
- ΔG°_f (cyclohexane) = 217.3 kJ/mol.

Is the reaction spontaneous as written?

Answer

92.8 kJ; no

Calculated values of ΔG^o are extremely useful in predicting whether a reaction will occur spontaneously if the reactants and products are mixed under standard conditions. We should note, however, that very few reactions are actually carried out under standard conditions, and calculated values of ΔG^o may not tell us whether a given reaction will occur spontaneously under nonstandard conditions. What determines whether a reaction will occur spontaneously is the free-energy change (ΔG) under the actual experimental conditions, which are usually different from ΔG°. If the ΔH and TΔS terms for a reaction have the same sign, for example, then it may be possible to reverse the sign of ΔG by changing the temperature, thereby converting a reaction that is not thermodynamically spontaneous, having $K_{eq} < 1$, to one that is, having a $K_{eq} > 1$, or vice versa. Because ΔH and ΔS usually do not vary greatly with temperature in the absence of a phase change, we can use tabulated values of ΔH° and ΔS° to calculate ΔG^o at various temperatures, as long as no phase change occurs over the temperature range being considered.

In the absence of a phase change, neither ΔH nor ΔS vary greatly with temperature.

Example 11.7.3

Calculate (a) ΔG^o and (b) $\Delta G_{300°C}$ for the reaction $N_2(g)+3H_2(g)\rightleftharpoons 2NH_3(g)$, assuming that ΔH and ΔS do not change between 25°C and 300°C. Use these data:

- $S°(N_2)$ = 191.6 J/(mol•K),
- $S°(H_2)$ = 130.7 J/(mol•K),
- $S°(NH_3)$ = 192.8 J/(mol•K), and
- ΔH°_f (NH_3) = −45.9 kJ/mol.

Given: balanced chemical equation, temperatures, S° values, and ΔH°_f for NH_3

Asked for: ΔG^o and ΔG at 300°C

Strategy:

A. Convert each temperature to kelvins. Then calculate ΔS° for the reaction. Calculate ΔH° for the reaction, recalling that ΔH°_f for any element in its standard state is zero.
B. Substitute the appropriate values into Equation 11.7.14 to obtain ΔG^o for the reaction.
C. Assuming that ΔH and ΔS are independent of temperature, substitute values into Equation 11.7.7 to obtain ΔG for the reaction at 300°C.

Solution

A To calculate ΔG^o for the reaction using Equation 11.7.14, we must know the temperature as well as the values of ΔS° and ΔH°. At standard conditions, the temperature is 25°C, or 298 K. We can calculate ΔS° for the reaction from the absolute molar entropy values given for the reactants and the products using the “products minus reactants” rule:

$$\begin{aligned}\Delta S^\circ_{\text{rxn}} &= 2S^\circ(\text{NH}_3) - [S^\circ(\text{N}_2) + 3S^\circ(\text{H}_2)] \\ &= [2\text{ mol NH}_3 \times 192.8\text{ J/(mol}\cdot\text{K)}] \\ &\quad - \{[1\text{ mol N}_2 \times 191.6\text{ J/(mol}\cdot\text{K)}] + [3\text{ mol H}_2 \times 130.7\text{ J/(mol}\cdot\text{K)}]\} \\ &= -198.1\text{ J/K (per mole of N}_2\text{)}\end{aligned}$$

We can also calculate ΔH° for the reaction using the "products minus reactants" rule. The value of ΔH°_f (NH_3) is given, and ΔH°_f is zero for both N_2 and H_2:

$$\begin{aligned}\Delta H^\circ_{\text{rxn}} &= 2\Delta H^\circ_f(\text{NH}_3) - [\Delta H^\circ_f(\text{N}_2) + 3\Delta H^\circ_f(\text{H}_2)] \\ &= [2 \times (-45.9\text{ kJ/mol})] - [(1 \times 0\text{ kJ/mol}) + (3 \times 0\text{ kJ/mol})] \\ &= -91.8\text{ kJ(per mole of N}_2\text{)}\end{aligned}$$

B Inserting the appropriate values into Equation 11.7.14

$$\begin{aligned}\Delta G^\circ_{\text{rxn}} &= \Delta H^\circ - T\Delta S^\circ \\ &= (-91.8\text{ kJ}) - (298\text{ K})(-198.1\text{ J/K})(1\text{ kJ}/1000\text{ J}) \\ &= -32.7\text{ kJ (per mole of N}_2\text{)}\end{aligned}$$

C To calculate ΔG for this reaction at 300°C, we assume that ΔH and ΔS are independent of temperature (i.e., $\Delta H_{300°C}$ = H° and $\Delta S_{300°C}$ = ΔS°) and insert the appropriate temperature (573 K) into Equation 11.7.7:

$$\begin{aligned}\Delta G_{300^\circ\text{C}} &= \Delta H_{300^\circ\text{C}} - (573\text{ K})(\Delta S_{300^\circ\text{C}}) \\ &= \Delta H^\circ - (573\text{ K})\Delta S^\circ \\ &= (-91.8\text{ kJ}) - (573\text{ K})(-198.1\text{ J/K})(1\text{ kJ}/1000\text{ J}) \\ &= 21.7\text{ kJ (per mole of N}_2\text{)}\end{aligned}$$

In this example, changing the temperature has a major effect on the thermodynamic spontaneity of the reaction. Under standard conditions, the reaction of nitrogen and hydrogen gas to produce ammonia is thermodynamically spontaneous, but in practice, it is too slow to be useful industrially. Increasing the temperature in an attempt to make this reaction occur more rapidly also changes the thermodynamics by causing the −TΔS° term to dominate, and the reaction is no longer spontaneous at high temperatures; that is, its K_{eq} is less than one. This is a classic example of the conflict encountered in real systems between thermodynamics and kinetics, which is often unavoidable.

? Exercise 11.7.3

Calculate

a. ΔG° and
b. $\Delta G_{750^\circ C}$

for the following reaction

$$2\,\text{NO(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2\,\text{NO}_2\text{(g)}$$

which is important in the formation of urban smog. Assume that ΔH and ΔS do not change between 25.0°C and 750°C and use these data:

- S°(NO) = 210.8 J/(mol•K),
- S°(O_2) = 205.2 J/(mol•K),
- S°(NO_2) = 240.1 J/(mol•K),
- ΔH°_f(NO_2) = 33.2 kJ/mol, and
- ΔH°_f (NO) = 91.3 kJ/mol.

Answer a

−72.5 kJ/mol of O_2

Answer b

33.8 kJ/mol of O_2

The effect of temperature on the spontaneity of a reaction, which is an important factor in the design of an experiment or an industrial process, depends on the sign and magnitude of both ΔH° and ΔS°. The temperature at which a given reaction is at equilibrium can be calculated by setting $\Delta G^o = 0$ in Equation 11.7.14, as illustrated in Example 11.7.4.

Example 11.7.4

As you saw in Example 11.7.3, the reaction of nitrogen and hydrogen gas to produce ammonia is one in which ΔH° and ΔS° are both negative. Such reactions are predicted to be thermodynamically spontaneous at low temperatures but nonspontaneous at high temperatures. Use the data in Example 11.7.3 to calculate the temperature at which this reaction changes from spontaneous to nonspontaneous, assuming that ΔH° and ΔS° are independent of temperature.

Given: ΔH° and ΔS°

Asked for: temperature at which reaction changes from spontaneous to nonspontaneous

Strategy:

Set ΔG^o equal to zero in Equation 11.7.14and solve for T, the temperature at which the reaction becomes nonspontaneous.

Solution

In Example 11.7.3, we calculated that ΔH° is −91.8 kJ/mol of N_2 and ΔS° is −198.1 J/K per mole of N_2, corresponding to ΔG^o = −32.7 kJ/mol of N_2 at 25°C. Thus the reaction is indeed spontaneous at low temperatures, as expected based on the signs of ΔH° and ΔS°. The temperature at which the reaction becomes nonspontaneous is found by setting ΔG^o equal to zero and rearranging Equation 11.7.14to solve for T:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 0$$

$$\Delta H^\circ = T\Delta S^\circ$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{(-91.8\ \text{kJ})(1000\ \text{J/kJ})}{-198.1\ \text{J/K}} = 463\ \text{K}$$

This is a case in which a chemical engineer is severely limited by thermodynamics. Any attempt to increase the rate of reaction of nitrogen with hydrogen by increasing the temperature will cause reactants to be favored over products above 463 K.

Exercise 11.7.4

As you found in the exercise in Example 11.7.3, ΔH° and ΔS° are both negative for the reaction of nitric oxide and oxygen to form nitrogen dioxide. Use those data to calculate the temperature at which this reaction changes from spontaneous to nonspontaneous.

Answer

792.6 K

Summary

- The change in Gibbs free energy, which is based solely on changes in state functions, is the criterion for predicting the spontaneity of a reaction.
- Free-energy change

$$\Delta G = \Delta H - T\Delta S$$

- Standard free-energy change

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

We can predict whether a reaction will occur spontaneously by combining the entropy, enthalpy, and temperature of a system in a new state function called Gibbs free energy (G). The change in free energy (ΔG) is the difference between the heat released during a process and the heat released for the same process occurring in a reversible manner. If a system is at equilibrium, ΔG = 0. If the process is spontaneous, ΔG < 0. If the process is not spontaneous as written but is spontaneous in the reverse direction, ΔG > 0. At constant temperature and pressure, ΔG is equal to the maximum amount of work a system can perform on its surroundings while undergoing a spontaneous change. The standard free-energy change (ΔG°) is the change in free energy when one substance or a set of substances in their standard states is converted to one or more other substances, also in their standard states. The standard free energy of formation (ΔG°_f), is the change in free energy that occurs when 1 mol of a substance in its standard state is formed from the component elements in their standard states. Tabulated values of standard free energies of formation are used to calculate ΔG^o for a reaction.

Contributors and Attributions

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11.8: Carnot Cycle, Efficiency, and Entropy

In the early 19th century, steam engines came to play an increasingly important role in industry and transportation. However, a systematic set of theories of the conversion of thermal energy to motive power by steam engines had not yet been developed. Nicolas Léonard Sadi Carnot (1796-1832), a French military engineer, published *Reflections on the Motive Power of Fire* in 1824. The book proposed a generalized theory of heat engines, as well as an idealized model of a thermodynamic system for a heat engine that is now known as the Carnot cycle. Carnot developed the foundation of the second law of thermodynamics, and is often described as the "Father of thermodynamics."

The Carnot Cycle

The Carnot cycle consists of the following four processes:

I. A reversible isothermal gas expansion process. In this process, the ideal gas in the system absorbs q_{in} amount heat from a heat source at a high temperature T_{high} , expands and does work on surroundings.
II. A reversible adiabatic gas expansion process. In this process, the system is thermally insulated. The gas continues to expand and do work on surroundings, which causes the system to cool to a lower temperature, T_{low}.
III. A reversible isothermal gas compression process. In this process, surroundings do work to the gas at T_{low}, and causes a loss of heat, q_{out}.
IV. A reversible adiabatic gas compression process. In this process, the system is thermally insulated. Surroundings continue to do work to the gas, which causes the temperature to rise back to T_{high} .

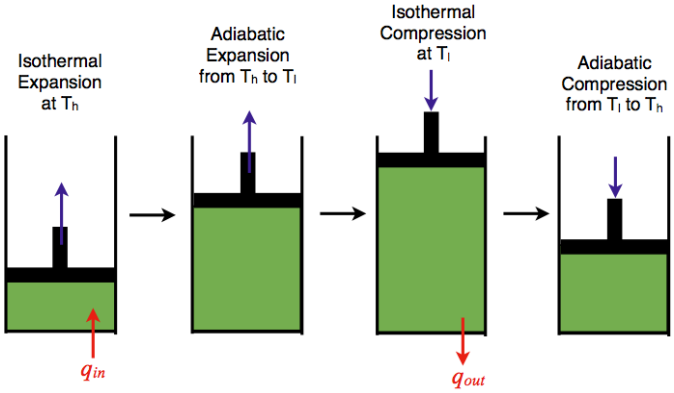


Figure 11.8.1: An ideal gas-piston model of the Carnot cycle. (CC BY 4.0; XiSen Hou via Hope College)

P-V Diagram

The P-V diagram of the Carnot cycle is shown in Figure 11.8.2. In isothermal processes I and III, ΔU=0 because ΔT=0. In adiabatic processes II and IV, q=0. Work, heat, ΔU, and ΔH of each process in the Carnot cycle are summarized in Table 11.8.1.

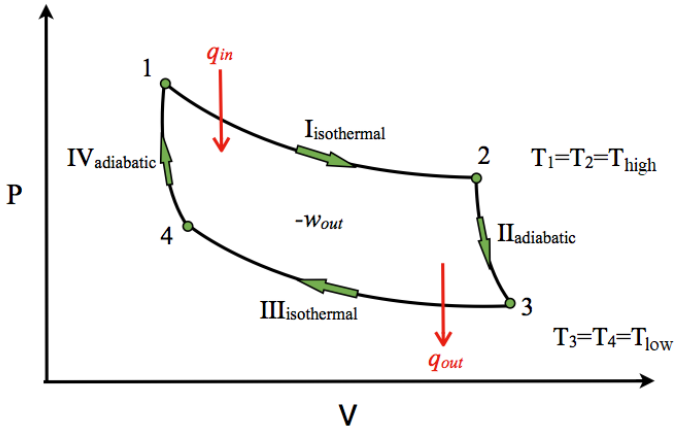


Figure 11.8.2: A P-V diagram of the Carnot Cycle.

Table 11.8.1: Work, heat, ΔU, and ΔH in the P-V diagram of the Carnot Cycle.

Process	w	q	ΔU	ΔH
I	$-nRT_{high}\ln\left(\frac{V_2}{V_1}\right)$	$nRT_{high}\ln\left(\frac{V_2}{V_1}\right)$	0	0
II	$n\bar{C_v}(T_{low}-T_{high})$	0	$n\bar{C_v}(T_{low}-T_{high})$	$n\bar{C_p}(T_{low}-T_{high})$
III	$-nRT_{low}\ln\left(\frac{V_4}{V_3}\right)$	$nRT_{low}\ln\left(\frac{V_4}{V_3}\right)$	0	0
IV	$n\bar{C_v}(T_{high}-T_{low})$	0	$n\bar{C_v}(T_{hight}-T_{low})$	$n\bar{C_p}(T_{high}-T_{low})$
Full Cycle	$-nRT_{high}\ln\left(\frac{V_2}{V_1}\right)-nRT_{low}\ln\left(\frac{V_4}{V_3}\right)+nRT_{low}\ln\left(\frac{V_4}{V_3}\right)0$			0

T-S Diagram

The T-S diagram of the Carnot cycle is shown in Figure 11.8.3 In isothermal processes I and III, ΔT=0. In adiabatic processes II and IV, ΔS=0 because dq=0. ΔT and ΔS of each process in the Carnot cycle are shown in Table 11.8.2

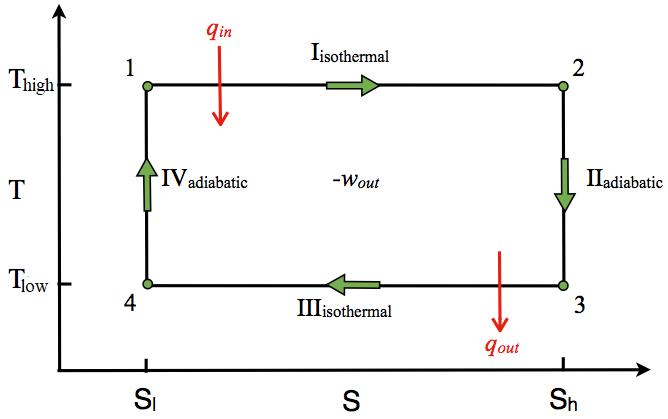


Figure 11.8.3: A T-S diagram of the Carnot Cycle. (CC BY 4.0; XiSen Hou via Hope College)

Table 11.8.1: Work, heat, and ΔU in the T-S diagram of the Carnot Cycle.

Process	ΔT	ΔS
I	0	$-nR\ln\left(\frac{V_2}{V_1}\right)$
II	$T_{low}-T_{high}$	0
III	0	$-nR\ln\left(\frac{V_4}{V_3}\right)$
IV	$T_{high}-T_{low}$	0
Full Cycle	0	0

Efficiency

The Carnot cycle is the most efficient engine possible based on the assumption of the absence of incidental wasteful processes such as friction, and the assumption of no conduction of heat between different parts of the engine at different temperatures. The efficiency of the carnot engine is defined as the ratio of the energy output to the energy input.

$$\text{efficiency} = \frac{\text{net work done by heat engine}}{\text{heat absorbed by heat engine}}$$

$$= \frac{-w_{sys}}{q_{high}}$$

$$= \frac{nRT_{high}\ln\left(\frac{V_2}{V_1}\right) + nRT_{low}\ln\left(\frac{V_4}{V_3}\right)}{nRT_{high}\ln\left(\frac{V_2}{V_1}\right)}$$

Since processes II (2-3) and IV (4-1) are adiabatic,

$$\left(\frac{T_2}{T_3}\right)^{C_V/R} = \frac{V_3}{V_2}$$

and

$$\left(\frac{T_1}{T_4}\right)^{C_V/R} = \frac{V_4}{V_1}$$

And since $T_1 = T_2$ and $T_3 = T_4$,

$$\frac{V_3}{V_4} = \frac{V_2}{V_1}$$

Therefore,

$$\text{efficiency} = \frac{nRT_{high}\ln\left(\frac{V_2}{V_1}\right) - nRT_{low}\ln\left(\frac{V_2}{V_1}\right)}{nRT_{high}\ln\left(\frac{V_2}{V_1}\right)}$$

$$\boxed{\text{efficiency} = \frac{T_{high} - T_{low}}{T_{high}}}$$

Summary

The Carnot cycle has the greatest efficiency possible of an engine (although other cycles have the same efficiency) based on the assumption of the absence of incidental wasteful processes such as friction, and the assumption of no conduction of heat between different parts of the engine at different temperatures.

Problems

1. You are now operating a Carnot engine at 40% efficiency, which exhausts heat into a heat sink at 298 K. If you want to increase the efficiency of the engine to 65%, to what temperature would you have to raise the heat reservoir?
2. A Carnot engine absorbed 1.0 kJ of heat at 300 K, and exhausted 400 J of heat at the end of the cycle. What is the temperature at the end of the cycle?
3. An indoor heater operating on the Carnot cycle is warming the house up at a rate of 30 kJ/s to maintain the indoor temperature at 72 ºF. What is the power operating the heater if the outdoor temperature is 30 ºF?

References

1. Goldstein, M. *J. Chem. Educ.*, **1980**, *57*, 114-116
2. Bader, M. *J. Chem. Educ.*, **1973**, *50*, 834
3. W. F. Luder. *J. Chem. Educ.*, **1944**, *21*, 600-601
4. Salter, C. *J. Chem. Educ.*, **2000**, 77, 1027-1030

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11.E: Spontaneous Processes (Exercises)

These are homework exercises to accompany the Textmap created for "Principles of Modern Chemistry" by Oxtoby et al. Complementary General Chemistry question banks can be found for other Textmaps and can be accessed here.

Q3

Write detailed calculation down for each question involved in gambling,

a. How many “microstates” are there for the cards that come up from five random cards each from a separate deck?
b. What is the probability of getting 5 queens of hearts?
c. What is the probability of getting any specific hand of five cards?

Solution

Microstates are specific configurations in which each particle is distinguishable. The number of ways that they can be arranged to describe the macrostate is the weight of that macrostate and used in the definition of entropy.

a. The number of possible outcomes (microstates) of any repeated independent situation is equal to the number of possibilities in one iteration to the power of the repetitions. So in this case, the answer is 52 to the power of 5.
b. One of these 52^5 possibilities.
c. One of these 52^5 possibilities.

Q5

Is the above reaction spontaneous under 1 atm and room temperature? If so, what are the driving factors?

$$3\,\mathrm{NO(g)} \rightleftharpoons \mathrm{N_2O(g)} + \mathrm{NO_2(g)}$$

Solution

From a superficial overview of the reaction, we would conclude that the enthalpy change would be negative (i.e., $\Delta H < 0$) (why? more bonding in the products than the reactants). We would also expect a negative value of entropy ($\Delta n_{gas} < 0$. It is difficult to argue which would win from just looking at the reaction and we need to do a Hess's law like approach to solve numerically using the Gibbs energies of formation from Table T1:

$$\Delta^o G_{rxn} = \Delta^o G_f\{N_2O\} + \Delta G_f^o\{NO_2\} - 3\Delta G_f^o\{NO\}$$

Q9

For each of the following scenarios predict the system's entropy change whether it is $\Delta S < 0$, $\Delta S = 0$, or $\Delta S > 0$.

a. Increasing the amount of quarters being flipped from 2 to 4.
b. Moving a child from a 30 ft. × 30 ft. room to a 5 ft. × 5 ft. room to play in .
c. Increasing the temperature of a non-ideal polyatomic gas.

Solution

a. Increasing the amount of flipped quarters leads to ($\Delta S > 0$) because it increases the number of microstates available. For example: $2^2 = 4$ so 4 microstates possible with 2 quarters but $2^4 = 16$ so 16 microstates are available with four quarters. 16 > 4 so entropy would increase.
b. If you divided the room in 1 sq. ft cubes as the places where the child may stand/play, there are only 25 squares in which the child could stand so 25 microstates versus 900 squares/microstates in the other room. Therefore $\Delta S < 0$ because there are less microstates available.
c. Increasing the temperature of a non-ideal gas would lead to ($\Delta S > 0$) because the increased temperature would "unfreeze" "frozen" modes in the gas, which would allow it more degrees of freedom and therefore microstates.

Q10

Determine whether the change in entropy for the processes listed down below are positive or negative:

a. condensing of iodine gas into a solid

b. diffusion of an ideal gas

Solution

a. Change in entropy is negative, as gaseous iodine turns solid, the decreased freedom of movement restricts the possible particle locations and hence there is a decrease in the number of microstates.
b. Change of entropy is positive. As diffusion occurs, there is increased freedom of movement and increase in the possible particle locations and an increase in the number of microstates.

Q11

Osmium melts at 3,027 °C and has an enthalpy change of fusion of 31.0 kJ/mol. Calculate the entropy of fusion of osmium.

Solution

Define the system at 1 mole of solid osmium at its melting point of 3027°C (3300 K). Imagine adding 31.0 kJ of heat infinitely slowly in such a way that the temperature remains constant, as the osmium melts. The heat is then equal to the q_{rev} for the melting. Substitute the value of heat supplied and T into the equation that defines the entropy of the change of the entropy of a system. Because the change occurs at a constant temperature, T may be outside the integral sign

$$\Delta S = \int \frac{dq_{rev}}{T} = \frac{1}{T}\int dq_{rev} = \frac{1}{T}q_{rev} = \frac{31.0 \times 10^3\ J\ mol^{-1}}{3300\ K} = 9.39\ J\ K^{-1}\ mol^{-1}$$

Tip. The temperature must be an absolute temperature (in Kelvins, for example).

Q13

Trouton's Rule is used to estimate the molar enthalpy of vaporization. What is iodine's enthalpy of vaporization if its normal boiling point is 184.4^{o}C?

Solution

Trouton's Rule:

$$\Delta H_{vap} = \Delta S_{vap} T_b \tag{11.E.1}$$

$$\Delta S_{vap} \approx 88 \frac{J}{Kmol} \tag{11.E.2}$$

$$T_b = 184.4^oC = 457.55K \tag{11.E.3}$$

$$\Delta H_{vap} = (88 \frac{J}{Kmol})(457.55K) = 40264.4 \frac{J}{mol} = 40.26 \frac{kJ}{mol} \tag{11.E.4}$$

Enthalpy of vaporization of iodine is 40.26 kJ/mol

Q15

If 0.250 mol Argon is expanded reversibly and isothermally at 400 K in its compressible oven from an initial volume of 12.0 L to a final volume of 30.0 L, what will the ΔU, q, w, ΔH, and ΔS for the gas?

Solution

For an isothermal process, ΔU = 0, and consequently, ΔH = 0. However, for the work:

$$w = \int_{v_o}^{v_f} P\, dV$$

Where:

$$P = \frac{nRT}{V}$$

meaning that if we put P into terms of V using PV=nRT, then we can get the work, which comes out look like:

$$w = nRT \ln \frac{V_f}{V_o}$$

$$w = (0.250\ mol) \times (8.314\ \frac{\text{J}}{\text{Kmol}}) \times (400\ \text{K}) \times \ln \frac{30.0\ L}{12.0\ L} = 761.8\ \text{J}$$

$PV = nRT$ is the ideal gas law. it implies that the molecules or atoms of the gas are point masses, they have no volume and undergo only elastic collision.

Therefore, by the first law, the heat, q, must be be the negative of the work. Now, as for ΔS, we know:

$$\Delta S = \frac{-q}{T}$$

which implies that:

$$\Delta S = nR \ln \frac{V_f}{V_o}$$

$$\Delta S = (0.250\ \text{mol}) \times (8.314\ \frac{\text{J}}{\text{Kmol}}) \times \ln \frac{30.0\ \text{L}}{12.0\ \text{L}} = 1.90\ \frac{\text{J}}{\text{K}}$$

Q17

Consider this. Exactly 2 moles of ice undergoes three different processes.

I. heated reversibly at atmospheric pressure from temperature X to 0 °C, then
II. melted reversibly at 0 °C. Finally
III. it was heated reversibly at atmospheric pressure up to an unknown temperature Y.

Find temperature X & Y and identify ΔS_{surr}.

Given:

- ΔH_{fus} = 6007 J.mol^{-1}
- C_p (ice) = 38 J.K^{-1}.mol^{-1}
- C_p (water) = 75 J.K^{-1}.mol^{-1}
- ΔS_{I} = 12.034 J.K^{-1}
- ΔS_{III} = 136 J.K^{-1}

Solution

Since entropy changes are additive (thanks for them being state functions) and we have the entropy changes for Step I and Step III, all we need to do is calculate ΔS_{II}. However, we need to calculate temperatures first.

The equation below can be used to calculate ΔS_{sys} for a temperature change.

$$\Delta S = nC_p \ln\left(\frac{T_2}{T_1}\right) \tag{11.E.5}$$

To solve for unknown temperature, the equation can be arranged in this way.

$$\exp(\frac{\Delta S}{nC_p}) = \frac{T_2}{T_1} \tag{11.E.6}$$

Assuming the C_p stays constant throughout all the temperature change. Initial temperature X and final temperature Y can be found using the formula below.

$$T_x = T_2(\exp(\frac{\Delta S_{\text{I}}}{nC_p}))^{-1} = (273.15K)(\exp(\frac{12.034J.\,K^{-1}}{(2.00mol)(38J.\,K^{-1}.\,mol^{-1})}))^{-1} = 233.15K \tag{11.E.7}$$

$$T_y = T_1(\exp(\frac{\Delta S_{\text{III}}}{nC_p})) = (273.15K)(\exp(\frac{136J.\,K^{-1}}{(2.00mol)(75J.\,K^{-1}.\,mol^{-1})})) = 298.15K \tag{11.E.8}$$

ΔS_{II} must also be determined to obtain the ΔS_{system}.

Since the temperature remains constant in the second step, $\Delta S = q_{rev}$.

$$\Delta S_{\text{II}} = 2\,mol \times \frac{6007\,J/mol}{273.15\,K} = 43.984\,J.\,K^{-1} \tag{11.E.9}$$

Since the entire process is reversible,

$$\Delta \text{S}_{\text{surr}} + \Delta \text{S}_{\text{system}} = 0$$

so

$$\Delta \text{S}_{\text{surr}} = -\Delta \text{S}_{\text{system}}.$$

Now we add the three entropy changes:

$$-\Delta S_{\text{system}} = -(\Delta S_{\text{I}} + \Delta S_{\text{II}} + \Delta S_{\text{III}}) \tag{11.E.10}$$

$$= -(12.034 + 54.98 + 136)J.\,K^{-1} \tag{11.E.11}$$

$$= -80.15\,J.\,K^{-1} \tag{11.E.12}$$

$$= \Delta S_{\text{surr}} \tag{11.E.13}$$

Q18

Suppose 2 moles of water at standard temperature (25°C) and pressure is spontaneously evaporated by allowing it to fall onto a nickel plate maintained at 125°C. Calculate ΔS for the water, ΔS for the nickel plate, and ΔS_{total} if $C_{p(\text{H}_2\text{O})(\text{l})}$= 75.4 J/(K.mol) and $C_{p(\text{H}_2\text{O})(\text{g})}$ = 36.0 J/(K.mol). Take ΔH_{vap} = 40.68 KJ/mol for water and its boiling point of 100°C.

Solution

$$q_1 = \Delta H = mc\Delta T = 2 \times 75.4 \frac{J}{K.\,mol} \times (100 - 25) = 11310\,J \tag{11.E.14}$$

$$q_2 = 40680 \frac{J}{mol} \times 2 = 81.36 \times 10^3\,J \tag{11.E.15}$$

$$q_3 = \Delta H = mc\Delta T = 2 \times 36 \frac{J}{K.\,mol} \times (125 - 100) = 1800\,J \tag{11.E.16}$$

$$q_{total} = 11310 + 81.36 \times 10^3 + 1800 = 94470\,J \tag{11.E.17}$$

$$\Delta S_{\text{H}_2\text{O}} = nC_{p(\text{H}_2\text{O}(\text{l}))} \ln \frac{T_2}{T_1} + nC_p(H_2O(g)) \ln \frac{T_2}{T_1} + n\frac{\Delta H}{T} \tag{11.E.18}$$

$$= (2 \times 75.4 \times \ln \frac{373}{298}) + (2 \times 36 \times \ln \frac{398}{373}) + (2 \times \frac{40680}{373}) = 256.6 \frac{J}{K} \tag{11.E.19}$$

$$\Delta S_{iron} = \frac{-94470J}{398K} = -237.4 \frac{J}{K} \tag{11.E.20}$$

$$\Delta S_{tot} = \Delta S_{\text{H}_2\text{O}} + \Delta S_{\text{iron}} = 19.2 \frac{J}{K} \tag{11.E.21}$$

Q19

A 181.49 g sample of lead at 97.0°C initially is added to a coffee cup calorimeter that contains 150.0 g water which is at 24.7°C. The equilibrium temperature is 29.4°C, assuming that there is no heat lost to the calorimeter or the environment. The molar heat capacity of lead (C_p(Pb)) is 26.4 J K^{-1} mol^{-1} and that of water ($C_p(H_2O)$) is 75.2 J K^{-1} mol^{-1}. What is ΔS for the lead sample, ΔS for the water sample, and ΔS_{total} for this process?

Solution

Since this progress is carried out at a constant pressure, and the temperature change for this progress doesn't include a phase transition, the relationship between the ΔS and the ΔT of a system can be described as:

$$\Delta S = nc_p ln\left(\frac{T_2}{T_1}\right) \tag{11.E.22}$$

Convert the temperatures to Kelvin:

$$T_{equilibrium} = (29.4 + 273.15)K = 302.55\ K \tag{11.E.23}$$

$$T_{initial,\ Pb} = (97.0 + 273.15)K = 370.15\ K \tag{11.E.24}$$

$$T_{initial,\ H_2O} = (24.7 + 273.15)K = 297.85\ K \tag{11.E.25}$$

Calculate the amount of moles of the substance present:

$$n_{Pb} = 181.49\ g\ Pb \times \frac{1\ mol\ Pb}{207.2\ g\ Pb} = 0.8759\ mol\ Pb \tag{11.E.26}$$

$$n_{H_2O} = 150.0\ g\ H_2O \times \frac{1\ mol\ H_2O}{18.02\ g\ H_2O} = 8.324\ mol\ H_2O \tag{11.E.27}$$

The given molar heat capacities:

$$C_{p,\ Pb} = 26.4\frac{J}{K \cdot mol} \tag{11.E.28}$$

$$C_{p,\ H_2O} = 75.2\frac{J}{K \cdot mol} \tag{11.E.29}$$

Substitute the known variables into the equation: $\Delta S = nc_p ln\left(\frac{T_2}{T_1}\right)$

$$\Delta S_{Pb} = nc_{p,Pb} ln\left(\frac{T_{equilibrium}}{T_{inital,\ Pb}}\right) \tag{11.E.30}$$

$$\Delta S_{Pb} = 0.8759\ mol\ Pb \times 26.4\frac{J}{K \cdot mol} \times ln\left(\frac{302.55\ K}{370.15\ K}\right) = -4.66\ \frac{J}{K} \tag{11.E.31}$$

$$\Delta S_{H_2O} = nc_{p,H_2O} ln\left(\frac{T_{equilibrium}}{T_{inital,\ H_2O}}\right) \tag{11.E.32}$$

$$\Delta S_{H_2O} = 8.324\ mol\ H_2O \times 75.2\frac{J}{K \cdot mol} \times ln\left(\frac{302.55\ K}{297.85\ K}\right) = 9.80\ \frac{J}{K} \tag{11.E.33}$$

$$\Delta S_{total} = \Delta S_{Pb} + \Delta S_{H_2O} = (-4.66 + 9.80)\ \frac{J}{K} = 5.14\ \frac{J}{K} \tag{11.E.34}$$

Q20

Copper has a heat capacity of 38.5 J K^{-1} mol^{-1}, approximately independent of temperature between 0°C to 100°C. Calculate the enthalpy and entropy change of 5.00 moles of copper as it is cooled at atmospheric pressure from 100°C to 0°C.

Solution

$$\Delta H = q = nC_p\Delta T \tag{11.E.35}$$

$$= (5.00\ mol)(38.5\ \frac{J}{K.mol})(273\ K - 373\ K)$$

$$\Delta H = -19250\ J$$

$$\Delta S = nC_p ln(\frac{T_2}{T_1}) \tag{11.E.36}$$

$$= (38.5\frac{J}{K.mol})\ln(\frac{273\ K}{373\ K})(5.00\ mol)$$

$$= -60.1\frac{J}{K}$$

Q23

The alkaline earth metals react with oxygen to give the following compounds:

$$2\,\mathrm{Be(g)} + \mathrm{O_2(g)} \longrightarrow 2\,\mathrm{BeO(s)}$$

$$2\,\mathrm{Mg(g)} + \mathrm{O_2(g)} \longrightarrow 2\,\mathrm{MgO(s)}$$

$$2\,\mathrm{Ca(g)} + \mathrm{O_2(g)} \longrightarrow 2\,\mathrm{CaO(s)}$$

Compute ΔS for each reaction, and identify a periodic trend about the entropy.

Solution

All the values you need to solve this problem are in the back of the Oxtoby textbook, so just find the numbers needed and use the formula:

$$\sum S^o_{products} - \sum S^o_{reactants} = \Delta S^o_{rxn}$$

$$2Be_{(g)} + O_{2(g)} \rightarrow 2BeO_{(s)}$$

$$2(14.14) - (2(136.16) + 205.03) = -449.07 \frac{\mathrm{J}}{\mathrm{K.\,mol}}$$

$$2Mg_{(g)} + O_{2(g)} \rightarrow 2MgO_{(s)}$$

$$2(26.92) - (2(148.54) + 205.03) = -448.27 \frac{\mathrm{J}}{\mathrm{K.\,mol}}$$

$$2Ca_{(g)} + O_{2(g)} \rightarrow 2CaO_{(s)}$$

$$2(39.75) - (2(154.77) + 205.03) = -435.07 \frac{\mathrm{J}}{\mathrm{K.\,mol}}$$

The entropy of the reaction decreases as you go up the periodic table.

Q27

Is the entropy change in the reaction positive, negative or zero and why?

$$\mathrm{CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l)}$$

Hint: You don't need to actually calculate the change in entropy to determine whether the change in entropy is positive or negative. Think about it conceptually.

Solution

The answer is negative because the number of gas molecules decreases. Gas molecules have more entropy than liquid molecules since they have more energy in the form of degrees of freedom of motion (translational, rotational, and vibrational). Therefore, fewer gas molecules mean less entropy.

Q33

At $25.0^\circ\mathrm{C}$the reaction below is not spontaneous.

$$\mathrm{2\,H_2O(g) \longrightarrow 2\,H_2(g) + O_2(g)}$$

with ΔG = $+228.59\ \frac{kJ}{mol}$

If the above reaction were coupled with the following nonspontaneous reaction, could it be made to proceed? Why or Why not?

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

with ΔG = $-16.48\ \frac{kJ}{mol}$

Solution

Coupling the nonspontaneous reaction

$$2\,H_2O_{(g)} \rightleftharpoons 2\,H_{2\,(g)} + O_{2\,(g)}$$

with $\Delta G = +228.59\ \frac{kJ}{mol}$

for a spontaneous reaction (ΔG) is negative.

$$3\,H_{2\,(g)} + N_{2\,(g)} \rightleftharpoons 2\,NH_{3\,(g)}$$

with $\Delta G = -16.48\ \frac{kJ}{mol}$

yields

$$2\,H_2O_{(g)} + \cancel{3}\,H_{2\,(g)} + N_{2\,(g)} \rightleftharpoons \cancel{2\,H_{2\,(g)}} + O_{2\,(g)} + 2\,NH_{3\,(g)}$$

with ΔG = $+212.11\ \frac{kJ}{mol}$

Since ΔG is positive, we know the reaction is still not spontaneous after being coupled with a spontaneous reaction

Q35A

A reaction at constant temperature and pressure is spontaneous if $\Delta G < 0$ and nonspontaneous if $\Delta G > 0$. Over what range of temperatures is each of the following processes spontaneous? Assume that all gases are at a pressure of 1 atm. (Hint: Use Tables T1 to calculate ΔH and ΔS (assumed independent of temperature and equal to ΔH° and ΔS°, respectively, and then use the definition of ΔG).

a. Photosynthesis, a reaction of how plants produce food for themselves and animals, and convert carbon dioxide into water:

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

b. The combustion reaction of propane, found in gas grills and some fireplaces:

$$C_3H_8(g) + 5\,O_2(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O(l)$$

c. Methane burning in O_2 gas.

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l)$$

Solution

a. First calculate ΔH° and $\Delta S^\circ$of the reaction $6\,CO_2(g) + 6\,H_2O(l) + \text{light} \longrightarrow C_6H_{12}O_6(s) + 6\,O_2(g)$ from the data in Tables T1.

$$\Delta H^\circ = -1273.3 + (6 \times 0) - (6 \times -393.5) - (6 \times -285.8) = 2802.5\ \frac{kJ}{mol}$$

$$\Delta S^\circ = 212.1 + (6 \times 205.2) - (6 \times 213.8) - (6 \times 70) = -259.5\ \frac{J}{mol.\,K}$$

Since the problem asks for the temperature range in which the reaction is spontaneous. The changeover from spontaneity to non-spontaneity occurs at $\Delta G^\circ = 0$. To find the temperature the makes $\Delta G^\circ = 0$, the relationship of $\Delta G^\circ = \Delta H^\circ - T\ \Delta S^\circ$ will be used. Remember to convert ΔS° to $kJ\ mol^{-1}$ (or ΔH° to $J\ mol^{-1}$) so that the units cancel out properly.

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{2802.5\ \frac{kJ}{mol}}{0.2595\ \frac{kJ}{mol.\,K}} = 10799.6\ K$$

Because ΔH° and ΔS° are both positive, the reaction is spontaneous at temperatures above 10799.6 K.

Reviewer Note: The solution is incorrect here. Because $\Delta H^\circ > 0$ and $\Delta S^\circ < 0$, the reaction is never spontaneous.

b. Perform similar calculations for the reaction $C_3H_8(g) + 5\,O_2(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O(l)$

$$\Delta H^\circ = (3 \times -393.5) + (4 \times -285.83) + 103.8 - (5 \times 0) = -2220.02\ \frac{kJ}{mol}$$

$$\Delta S^\circ = (3 \times 28) + (4 \times 70) - 270.3 - (5 \times 205.2) = -374.9\ \frac{J}{mol.\,K}$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{2220.02\ \frac{kJ}{mol}}{0.3749\ \frac{kJ}{mol.\,K}} = 5922\ K$$

Since ΔH° and ΔS° are both negative, the reaction is spontaneous below 5922 K.

c. The reaction $CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l)$

$$\Delta H^\circ = (-393.5) + (2 \times -285.8) + 74.6 - (2 \times 0) = -890.5\ \frac{kJ}{mol}$$

$$\Delta S^\circ = (28) + (2 \times 70) - 186.3 - (2 \times 205.2) = -242.9\ \frac{J}{mol.\,K}$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{-890.5\ \frac{kJ}{mol}}{-0.2429\ \frac{kJ}{mol.\,K}} = 3666\ K$$

Since ΔH° and ΔS° are both negative, the reaction is spontaneous below 3666 K.

Q35B

Over what temperatures are these reactions spontaneous (under constant pressure and temperature)? You may need to use Table 1.

a. $S(s, \text{rhombic}) + Zn(s) \rightarrow ZnS(s, \text{sphalerite})$
b. $2\,Cu(s) + Cl_2 \rightarrow 2\,CuCl(s)$
c. $4\,Al(s) + 3\,O_2(g) \rightarrow 2\,Al_2O_3(s)$

Answer

By calculating ΔH_{rxn} and ΔS_{rxn} un der standard conditions and at 25°C, we can calculate the range of temperature in which ΔG is positive and therefore spontaneous. To calculate ΔH_{rxn} and ΔS_{rxn}, we use Hess's Law , in which:

$$\Delta H_{rxn} = \sum nH_{products} - \sum nH_{reactants}$$

$$\Delta S_{rxn} = \sum nS_{products} - \sum nS_{reactants}$$

a)

$$\Delta \mathrm{H_{rxn}} = -206.0 - (0 + 0) = -206.0 \frac{\mathrm{kJ}}{\mathrm{mol}}$$

$$\Delta \mathrm{S_{rxn}} = 57.7 - (41.6 + 32.1) = -16 \frac{\mathrm{J}}{\mathrm{K.\,mol}}$$

$$\Delta \mathrm{G_{rxn}} = -206.0 - \mathrm{T}(-0.016)$$

From here, we can set T = 0 because we know that ΔG must be < 0 to be a spontaneous reaction.

T<12875K

b)

$$\Delta \mathrm{H_{rxn}} = (2 \times -137.2) - (0 + 0) = -274.4 \frac{\mathrm{kJ}}{\mathrm{mol}}$$

$$\Delta S_{rxn} = (2 \times 86.2) - ((2 \times 33.2) + 223.1) = -117.1 \frac{J}{K.\,mol}$$

$$\Delta G_{rxn} = -274.4 - T(-0.1171)$$

T < 2343.3K

c)

$$\Delta H_{rxn} = (2(-1675.7)) - (0 + 0) = -3351.4 \frac{kJ}{mol}$$

$$\Delta S_{rxn} = (2(50.92) - (4(28.3) + (3(205.2)) = -626.96 \frac{J}{K.\,mol}$$

$$\Delta G_{rxn} = -3351.4 - T(-0.62696)$$

T < 5345.5K

Q37

Determine if the following reaction is spontaneous at 25°C by evaluating $\Delta H°_{rxn}$, $\Delta S°_{rxn}$ and $\Delta G°_{rxn}$.

$$N_2H_4(l) + O_2(g) \longrightarrow N_2(g) + 2\,H_2O(l)$$

Solution

- $\Delta H^\circ_{rxn} = 0 + (2 \times -285.8) - 0 - 50.6 = 622.2 \frac{kJ}{mol}$
- $\Delta S^\circ_{rxn} = (2 \times 70.0) + 191.6 - 205.2 - 121.2 = 5.2 \frac{J}{mol.K}$
- $\Delta G^\circ_{rxn} = -622.2 - (25 + 273.15)(0.0052) = -623.8 \frac{kJ}{mol}$

=> Spontaneous ($\Delta G^\circ_{rxn} < 0$)

Q39

A thermodynamic engine operates cyclically and reversibly between two temperatures reservoirs, absorbing heat from the high-temperature bath at 600 K and discarding heat to low-temperature bath at 300 K.

a. What is the thermodynamic efficiency of the engine?
b. How much heat is absorbed from the high-temperature bath if -1800 J of heat is discarded to the low-temperature bath during each cycle?
c. How much work does the engine perform in one cycle of operation?

Solution

(a)

$$\text{Thermodynamic efficiency} = \frac{(T_1 - T_2)}{T_1}$$

$$\frac{(600\ K - 300\ K)}{(600\ K)} \times 100\% = 50\%$$

(b)

$$\frac{1800\ J}{50\%} = 3600\ J$$

(c)

$$-3600\ J \times 50\% = -1800\ J$$

Q41

Acetone (C_3H_6O) is an volatile liquid with a normal boiling point of 56°C and a molar enthalpy of vaporization of 29.1 kJ mol^{-1}. What is the molar entropy of vaporization of acetone under 1 atm of pressure?

Solution

First we need the write the equation relating entropy and enthalpy:

$$\Delta G_{vap} = \Delta H_{vap} - T\Delta S_{vap}$$

As a result of the process of normal boiling being at quilibrium $\Delta G = 0$ so all that needs to be done is T in Kelvin and ΔH_{vap} needs to be plugged in and then we solve for ΔS_{vap}:

$$0 = 29.1\ \frac{\text{kJ}}{\text{mol}} - (329\ \text{K})(\Delta \text{S}_{\text{vap}})$$

$$\Delta \text{S}_{\text{vap}} = 88.45 \frac{\text{J}}{\text{K. mol}}$$

Q53

Under standard conditions and 25°C, you have this reversible process

$$\text{Sn(s, white)} \longrightarrow \text{Sn(s, gray)}$$

a. Is the change in entropy (ΔS) for this reaction positive or negative? Calculate the change in entropy using Table T1.
b. Calculate (ΔS) for the reaction if ΔH for this reaction is -2.1 kJ/mol.

Solution

For part a), we use the formula

$$\Delta S^\circ = \sum nS^\circ(\text{products}) - \sum nS^\circ(\text{reactants})$$

Plugging in the values from Table T1 gives us

$$\Delta S = 44.1 - 55.2 = -7.1 \frac{J}{mol \cdot K}$$

For part b), we use the formula for a reversible process

$$\Delta S = \frac{\Delta H}{T}$$

$$\Delta S = \frac{-2100\ J/mol}{298.15\ K}$$

$$\Delta S = -7.04 \frac{J}{mol \cdot K}$$

Q59

Compute the ΔG_f° for the following reaction the reaction. The ΔG_f° of H_2SO_3 (aq) is -537.81 kJ mol^{-1}, the ΔG_f° of SO_2 (g) is -300.19 kJ mol^{-1}, and the ΔG_f° of H_2O (g) is -120.42 kJ mol^{-1}.

$$\text{H}_2\text{SO}_3\text{(aq)} \longrightarrow \text{H}_2\text{O(g)} + \text{SO}_2\text{(g)}$$

Solution

ΔG° for the reaction is equal to the sum of the G_f° for the products minus the sum of the G_f° for the reactants.

$$\Delta G^\circ = \left(-300.19 \frac{kJ}{mol} + -120.42 \frac{kJ}{mol}\right) - \left(-537.81 \frac{kJ}{mol}\right)$$

$$\Delta G^\circ = 117.2 \frac{kJ}{mol}$$

Q61

Professor Nesral wants to create some water through the combustion of hydrogen. This reaction is depicted as follows:

$$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(g)$$

Is this reaction spontaneous? Prove it by calculating ΔG° at 298.15K. Suppose that Nesral asks his friend in El Azizia, Libya, where the temperature is around $57^\circ C$ (330K), to perform the same reaction. Calculate the Gibbs energy for this value and compare it to ΔG°.

Relevant Information:

Entropy Values (S°; $\frac{J}{mol\,K}$)

- Hydrogen: 130.6
- Water: 188.7
- Oxygen: 205.6

Enthalpy Values(H°; $\frac{kJ}{mol}$)

- ΔH_f° Water: -241.826

Solution

From intuition, the equation shows that 3 moles of gas, 2 moles of H_2 and 1 mole of O_2, are reacting to form 2 moles of H_2O gas. This is a decrease in entropy, which may hint at the reaction being non spontaneous. ΔG° should still be calculated to make sure.

The information provided is the entropic values of the product and reactants, and the enthalpy of water. If the ΔS° is calculated, then the ΔG° can also be found using the following equation:

$\Delta G = \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn}$.

Where ΔH°_{rxn} is the Heat and ΔS°_{rxn} is the entropy of the reaction under standard conditions (constant pressure), and T is temperature. Knowing that ΔS°_{rxn} is a state variable, it can be calculated as the difference between the sum of the entropy values of the products and reactants multiplied by their coefficients (This is known as Hess's Law). In other words,

$$\Delta S^\circ = \sum n_{products} \times S^\circ_{f_{products}} - \sum n_{reactants} \times S^\circ_{f_{reactants}}$$

From this, ΔS°_{rxn} can be calculated as such:

$$\Delta S^\circ = \left(2 \times 188.7 \frac{J}{molK}\right) - \left(\left[2 \times 130.6 \frac{J}{molK}\right] + \left[205.6 \frac{J}{molK}\right]\right)$$

$$= -89.4 \frac{J}{mol.\,K}$$

Since both H_2 and O_2 are in their natural states, the H_f° associated with them equals to zero. Since enthalpy (ΔH°_{rxn}) is also a state variable, it can be calculated with Hess's Law as well.

$$\Delta H^\circ = \left(2 \times -241.826 \frac{kJ}{mol}\right) - \left(\left[0 \frac{kJ}{mol}\right] + \left[0 \frac{kJ}{mol}\right]\right)$$

$$\Delta H^\circ = -483.652 \frac{kJ}{mol}$$

Plugging in these values, as well as the temperature, $298.15K$, will yield ΔG°.

$\Delta G^\circ_{rxn} = \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn}$.

$$\Delta G^\circ_{rxn} = -483.652 \frac{kJ}{mol} - 298.15K \left(-0.0894 \frac{kJ}{mol.\,K}.\right)$$

$$\Delta G^\circ_{rxn} = -456.99739 \frac{kJ}{mol}$$

The ΔG_{rxn} is therefore $-456.99739 \frac{kJ}{mol}$ This very negative value means that the reaction is DEFINITELY spontaneous. It also makes sense on a conceptual level because combustion reaction like these release a lot of heat, which means that the process if enthalpically driven! Calculating the ΔG_{rxn} at a different temperature, as mentioned in the problem, has the same method:

$\Delta G_{rxn} = \Delta H^{\circ}_{rxn} - T\Delta S^{\circ}_{rxn}$.

$\Delta G_{rxn} = -483.652 \frac{kJ}{mol} - 330K \left(-0.0894 \frac{kJ}{mol.K}. \right)$

$\Delta G_{rxn} = -454.15 \frac{kJ}{mol}$

In both situations the ΔG_{rxn} is very negative, but in the hotter climate it is slightly less so. What this shows is that, at a higher temperatures the entropic factors contribute more to the gibbs energy than at standard conditions. This showcases the temperature dependence of entropy. In another reaction that released less energy, this difference may have made the reaction non-spontaneous!

Abstract : Hess's Law to find ΔG_{rxn}.

Q63A

The concentration of sodium in the plasma is approximately 0.14 M. While in the fluid outside of the plasma, sodium concentration is about 0.5 M.

a. In what direction will the sodium ions spontaneously move past the cell wall?
b. The spontaneous process of movement in part a is called "passive transport". Movement in the opposite direction is called "active transport" and requires work to happen. Calculate the amount of free energy required to move 5 moles of Na^+ by active transport (non-spontaneous direction) at 273 K.

Solution

a) The Na^+ ions will spontaneously flow into the plasma because it flows from high to low concentration.

b) $\Delta G = nRT \ln \frac{c_2}{c_1}$ where c_2 is the destination of Na^+ after active transport occurs while c_1 is the original concentration of the Na^+ ions.

$\Delta G = (5 \text{ mole})(8.3145 \frac{J}{K.mol})(273 \text{ K}) \ln \frac{0.5}{0.14}$

$\Delta G = 14447.26 \text{ J}$

Q63B

For a hypothetical nerve cell, the sodium ion concentration is 0.015 M outside the cell and 0.00045 M inside the cell. Active transport involves using proteins and chemical energy stored in ATP to move the ions in a thermodynamically unfavorable direction. Assuming that conditions in the cell allow the hydrolysis of a single ATP molecule to give 2.05×10^{-18} J of usable enegy. How many molecules of ATP would be needed to move 0.005 moles of sodium ions using active transport at standard conditions? You can assume that the sodium ion concentrations remain constant.

Solution

To answer this question, the change of free energy is needed which means the following equation is needed

$$\Delta G = -RTlnQ$$

$$R = 8.314 \ \frac{J}{mol.K} \qquad T = 298K \qquad Q = \frac{[Na^+]_{in}}{[Na^+]_{out}}$$

$$\Delta G = -8.314 \ \frac{J}{mol.K} \times 298K \times ln(\frac{0.00045 \ M}{0.015 \ M})$$

$$\Delta G = -2424 \ \frac{J}{mol} \times ln(0.03) = 8688 \ \frac{J}{mol}$$

Now that we have the the free energy, we can determine the number of ATP molecules needed

$$8688 \ \frac{J}{mol} \times 0.005 \ mol = 43.4 \ J$$

$$\frac{43.4 \ J}{2.05 \times 10^{-18} \ J \ molecule^{-1}} = 2.119 \times 10^{19} \ \text{ ATP molecules}$$

Answer: 2.119×10^{19} ATP molecules

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CHAPTER OVERVIEW

12: Chemical Equilibrium- Thermodynamics and General Considerations

An General Chemistry Libretexts Textmap organized around the textbook

Principles of Modern Chemistry

by Oxtoby, Gillis, and Campion

I II III IV V VI VII VIII IX X XI XII XIII XIV XV XVI
XVII XVIII XIX XX XXI XXII XXIII • **Homework Exercises**

Template:HideTOC

Chemical equilibrium is the state in which both reactants and products are present in concentrations which have no further tendency to change with time. This results when the forward reaction proceeds at the same rate as the reverse reaction. Thus, no net changes in the concentrations of the reactant(s) and product(s) are observed. This is known as dynamic equilibrium.

12.1: The Nature of Chemical Equilibrium
12.2: Reaction Directions (Thermodynamic Explanation) (needs work on Q)
12.3: The Empirical Law of Mass Action
12.4: Thermodynamic Description of the Equilibrium State
12.5: The Law of Mass Action for Related and Simultaneous Equilibria
12.6: Equilibrium Calculations for Gas-Phase and Heterogenous Reactions
12.7: Reaction Directions (Empirical Explanation)
12.8: Distribution of a Single Species between Immiscible Phases - Extraction and Separation
12.E: Chemical Equilibria (Exercises)

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12.1: The Nature of Chemical Equilibrium

Learning Objectives

- To understand what is meant by chemical equilibrium.

In the last chapter, we discussed the principles of chemical kinetics, which deal with the *rate of change*, or how quickly a given chemical reaction occurs. We now turn our attention to the *extent* to which a reaction occurs and how reaction conditions affect the final concentrations of reactants and products. For most of the reactions that we have discussed so far, you may have assumed that once reactants are converted to products, they are likely to remain that way. In fact, however, virtually all chemical reactions are *reversible* to some extent. That is, an opposing reaction occurs in which the products react, to a greater or lesser degree, to re-form the reactants. Eventually, the forward and reverse reaction rates become the same, and the system reaches **chemical equilibrium,** the point at which the composition of the system no longer changes with time.



Figure 12.1.1: Dinitrogen tetroxide is a powerful oxidizer that reacts spontaneously upon contact with various forms of hydrazine, which makes the pair a popular propellant combination for rockets. Nitrogen dioxide at −196 °C, 0 °C, 23 °C, 35 °C, and 50 °C. (NO_2) converts to the colorless dinitrogen tetroxide (N_2O_4) at low temperatures, and reverts to NO_2 at higher temperatures. (CC BY-SA 3.0; Eframgoldberg).

Chemical equilibrium is a dynamic process that consists of a forward reaction, in which reactants are converted to products, and a reverse reaction, in which products are converted to reactants. At equilibrium, the forward and reverse reactions proceed at equal rates. Consider, for example, a simple system that contains only one reactant and one product, the reversible dissociation of dinitrogen tetroxide (N_2O_4) to nitrogen dioxide (NO_2). You may recall that NO_2 is responsible for the brown color we associate with smog. When a sealed tube containing solid N_2O_4 (mp = −9.3°C; bp = 21.2°C) is heated from −78.4°C to 25°C, the red-brown color of NO_2 appears (Figure 12.1.1). The reaction can be followed visually because the product (NO_2) is colored, whereas the reactant (N_2O_4) is colorless:

$$\underset{colorless}{N_2O_4(g)} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \underset{red-brown}{2\,NO_2(g)} \tag{12.1.1}$$

The double arrow indicates that both the forward reaction

$$N_2O_4(g) \overset{k_f}{\longrightarrow} 2\,NO_2(g) \tag{12.1.2}$$

and reverse reaction

$$2\,NO_2(g) \overset{k_r}{\longrightarrow} N_2O_4(g) \tag{12.1.3}$$

occurring simultaneously (i.e, the reaction is reversible). However, this does not necessarily mean the system is equilibrium as the following chapter demonstrates.

Figure 12.1.2 shows how the composition of this system would vary as a function of time at a constant temperature. If the initial concentration of NO_2 were zero, then it increases as the concentration of N_2O_4 decreases. Eventually the composition of the system stops changing with time, and chemical equilibrium is achieved. Conversely, if we start with a sample that contains no N_2O_4 but an initial NO_2 concentration twice the initial concentration of N_2O_4 (Figure 12.1.2*a*), in accordance with the

stoichiometry of the reaction, we reach exactly the same equilibrium composition (Figure 12.1.2*b*). Thus equilibrium can be approached from either direction in a chemical reaction.

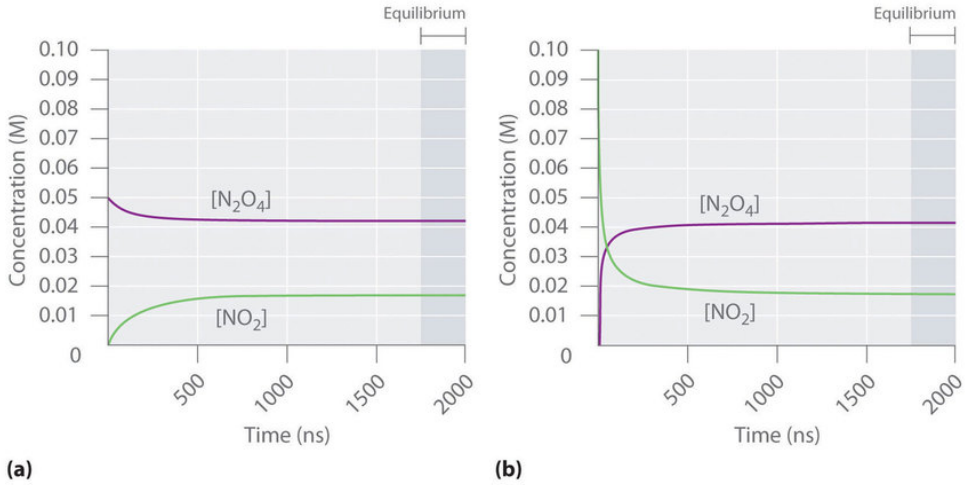


Figure 12.1.2: The Composition of N_2O_4/NO_2 Mixtures as a Function of Time at Room Temperature. (a) Initially, this idealized system contains 0.0500 M gaseous N_2O_4 and no gaseous NO_2. The concentration of N_2O_4 decreases with time as the concentration of NO_2 increases. (b) Initially, this system contains 0.1000 M NO_2 and no N_2O_4. The concentration of NO_2 decreases with time as the concentration of N_2O_4 increases. In both cases, the final concentrations of the substances are the same: [N_2O_4] = 0.0422 M and [NO_2] = 0.0156 M at equilibrium. (CC BY-SA-NC; Anonymous by request)

Figure 12.1.3 shows the forward and reverse reaction rates for a sample that initially contains pure NO_2. Because the initial concentration of N_2O_4 is zero, the forward reaction rate (dissociation of N_2O_4) is initially zero as well. In contrast, the reverse reaction rate (dimerization of NO_2) is initially very high ($2.0 \times 10^6\ M/s$), but it decreases rapidly as the concentration of NO_2 decreases. As the concentration of N_2O_4 increases, the rate of dissociation of N_2O_4 increases—but more slowly than the dimerization of NO_2—because the reaction is only first order in N_2O_4 (rate = $k_f[N_2O_4]$, where k_f is the rate constant for the forward reaction in Equations 12.1.1 and 12.1.2). Eventually, the forward and reverse reaction rates become identical, $k_f = k_r$, and the system has reached chemical equilibrium. If the forward and reverse reactions occur at different rates, then the system is not at equilibrium.

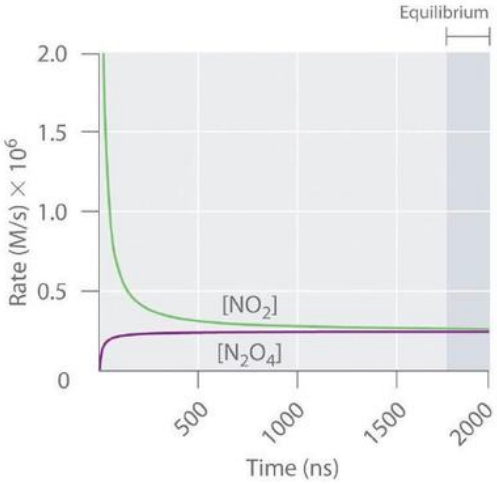


Figure 12.1.3: The Forward and Reverse Reaction Rates as a Function of Time for the $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ System Shown in Part (b) in Figure 12.1.2. (CC BY-SA-NC; Anonymous by request)

The rate of dimerization of NO_2 (reverse reaction) decreases rapidly with time, as expected for a second-order reaction. Because the initial concentration of N_2O_4 is zero, the rate of the dissociation reaction (forward reaction) at $t = 0$ is also zero. As the dimerization reaction proceeds, the N_2O_4 concentration increases, and its rate of dissociation also increases. Eventually the rates of the two reactions are equal: chemical equilibrium has been reached, and the concentrations of N_2O_4 and NO_2 no longer change.

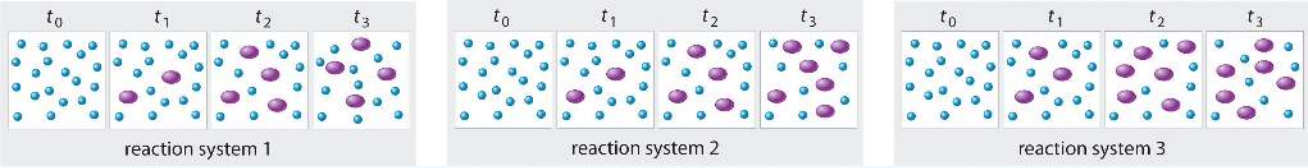
> *At equilibrium, the forward reaction rate is equal to the reverse reaction rate.*

Example 12.1.1

The three reaction systems (1, 2, and 3) depicted in the accompanying illustration can all be described by the equation:

$$2A \rightleftharpoons B$$

where the blue circles are A and the purple ovals are B. Each set of panels shows the changing composition of one of the three reaction mixtures as a function of time. Which system took the longest to reach chemical equilibrium?



In reaction system 1 theree are four purple ovals at t3. In reaction system 2 there are size purple ovals at t3. In reaction system systems there are six ovals at t2 and t3.

Given: three reaction systems

Asked for: relative time to reach chemical equilibrium

Strategy:

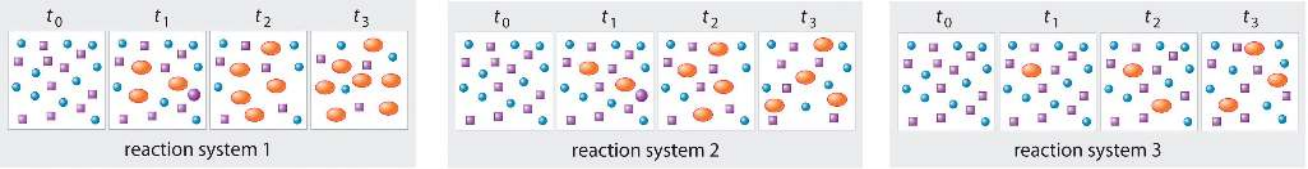
Compare the concentrations of A and B at different times. The system whose composition takes the longest to stabilize took the longest to reach chemical equilibrium.

Solution:

In systems 1 and 3, the concentration of A decreases from t_0 through t_2 but is the same at both t_2 and t_3. Thus systems 1 and 3 are at equilibrium by t_3. In system 2, the concentrations of A and B are still changing between t_2 and t_3, so system 2 may not yet have reached equilibrium by t_3. Thus system 2 took the longest to reach chemical equilibrium.

Exercise 12.1.1

In the following illustration, A is represented by blue circles, B by purple squares, and C by orange ovals; the equation for the reaction is A + B ⇌ C. The sets of panels represent the compositions of three reaction mixtures as a function of time. Which, if any, of the systems shown has reached equilibrium?



In reaction system 1 there are seven orange ovals at t3. In reaction system two there are four orange ovals at t3. In reaction system three there are three orange ovals at t3.

Answer

system 2



A Video Introduction to Dynamic Equilibrium: Introduction to Dynamic Equilibrium(opens in new window) [youtu.be]

Summary

At equilibrium, the forward and reverse reactions of a system proceed at equal rates. Chemical equilibrium is a dynamic process consisting of forward and reverse reactions that proceed at equal rates. At equilibrium, the composition of the system no longer changes with time. The composition of an equilibrium mixture is independent of the direction from which equilibrium is approached.

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12.2: Reaction Directions (Thermodynamic Explanation) (needs work on Q)

Learning Objectives

- To know the relationship between free energy and the equilibrium constant.

We have identified three criteria for whether a given reaction will occur spontaneously:

- $\Delta S_{univ} > 0$ (2nd law of thermodynamics),
- $\Delta G_{sys} < 0$ (Gibbs Energy version), and
- the relative magnitude of the reaction quotient Q versus the equilibrium constant K.

Recall that if $Q < K$, then the reaction proceeds spontaneously to the right as written, resulting in the net conversion of reactants to products. Conversely, if $Q > K$, then the reaction proceeds spontaneously to the left as written, resulting in the net conversion of products to reactants. If $Q = K$, then the system is at equilibrium, and no net reaction occurs. Table 12.2.1 summarizes these criteria and their relative values for spontaneous, nonspontaneous, and equilibrium processes.

Table 12.2.1: Criteria for the Spontaneity of a Process as Written

Spontaneous	Equilibrium	Nonspontaneous*
$\Delta S_{univ} > 0$	$\Delta S_{univ} = 0$	$\Delta S_{univ} < 0$
$\Delta G_{sys} < 0$	$\Delta G_{sys} = 0$	$\Delta G_{sys} > 0$
Q < K	Q = K	Q > K

*Spontaneous in the reverse direction.

Because all three criteria assess the same thing—the spontaneity of the process—it would be most surprising indeed if they were not related. In this section, we explore the relationship between the standard free energy of reaction (ΔG°) and the equilibrium constant (K).

Free Energy and the Equilibrium Constant

Because ΔH° and ΔS° determine the magnitude of ΔG° and because K is a measure of the ratio of the concentrations of products to the concentrations of reactants, we should be able to express K in terms of ΔG° and vice versa. "Free Energy", ΔG is equal to the maximum amount of work a system can perform on its surroundings while undergoing a spontaneous change. For a reversible process that does not involve external work, we can express the change in free energy in terms of volume, pressure, entropy, and temperature, thereby eliminating ΔH from the equation for ΔG. The general relationship can be shown as follow (derivation not shown):

$$\Delta G = V\Delta P - S\Delta T \tag{12.2.1}$$

If a reaction is carried out at constant temperature ($\Delta T = 0$), then Equation 12.2.1 simplifies to

$$\Delta G = V\Delta P \tag{12.2.2}$$

Under normal conditions, the pressure dependence of free energy is not important for solids and liquids because of their small molar volumes. For reactions that involve gases, however, the effect of pressure on free energy is very important.

Assuming ideal gas behavior, we can replace the V in Equation 12.2.2 by nRT/P (where n is the number of moles of gas and R is the ideal gas constant) and express ΔG in terms of the initial and final pressures (P_i and P_f, respectively):

$$\Delta G = \left(\frac{nRT}{P}\right)\Delta P \tag{12.2.3}$$

$$= nRT\frac{\Delta P}{P} = nRT\ln\left(\frac{P_f}{P_i}\right) \tag{12.2.4}$$

If the initial state is the standard state with P_i = 1 atm, then the change in free energy of a substance when going from the standard state to any other state with a pressure P can be written as follows:

$$G - G^\circ = nRT \ln P \tag{12.2.5}$$

This can be rearranged as follows:

$$G = G^\circ + nRT \ln P \tag{12.2.6}$$

As you will soon discover, Equation 12.2.6 allows us to relate ΔG^o and K_p. Any relationship that is true for K_p must also be true for K because K_p and K are simply different ways of expressing the equilibrium constant using different units.

Let's consider the following hypothetical reaction, in which all the reactants and the products are ideal gases and the lowercase letters correspond to the stoichiometric coefficients for the various species:

$$aA + bB \rightleftharpoons cC + dD \tag{12.2.7}$$

Because the free-energy change for a reaction is the difference between the sum of the free energies of the products and the reactants, we can write the following expression for ΔG:

$$\Delta G = \sum_m G_{products} - \sum_n G_{reactants} \tag{12.2.8}$$

$$= (cG_C + dG_D) - (aG_A + bG_B) \tag{12.2.9}$$

Substituting Equation 12.2.6 for each term into Equation 12.2.9,

$$\Delta G = [(cG^o_C + cRT \ln P_C) + (dG^o_D + dRT \ln P_D)] - [(aG^o_A + aRT \ln P_A) + (bG^o_B + bRT \ln P_B)] \tag{12.2.10}$$

Combining terms gives the following relationship between ΔG and the reaction quotient Q:

$$\Delta G = \Delta G^\circ + RT \ln \left(\frac{P_{\mathrm{C}}^c P_{\mathrm{D}}^d}{P_{\mathrm{A}}^a P_{\mathrm{B}}^b} \right) \tag{12.2.11}$$

$$= \Delta G^\circ + RT \ln Q \tag{12.2.12}$$

where ΔG° indicates that all reactants and products are in their standard states. For gases at equilibrium ($Q = K_p$,), and as you've learned in this chapter, $\Delta G = 0$ for a system at equilibrium. Therefore, we can describe the relationship between ΔG^o and K_p for gases as follows:

$$0 = \Delta G^\circ + RT \ln K_p \tag{12.2.13}$$

$$\Delta G^\circ = -RT \ln K_p \tag{12.2.14}$$

If the products and reactants are in their standard states and ΔG° < 0, then K_p > 1, and products are favored over reactants. Conversely, if ΔG° > 0, then K_p < 1, and reactants are favored over products. If ΔG° = 0, then $K_p = 1$, and neither reactants nor products are favored: the system is at equilibrium.

> *For a spontaneous process under standard conditions, K_{eq} and K_p are greater than 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 change 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 12.2.3). If a system is present with reactants and products present in nonequilibrium amounts ($Q \neq K$), the reaction will proceed spontaneously in the direction necessary to establish equilibrium.

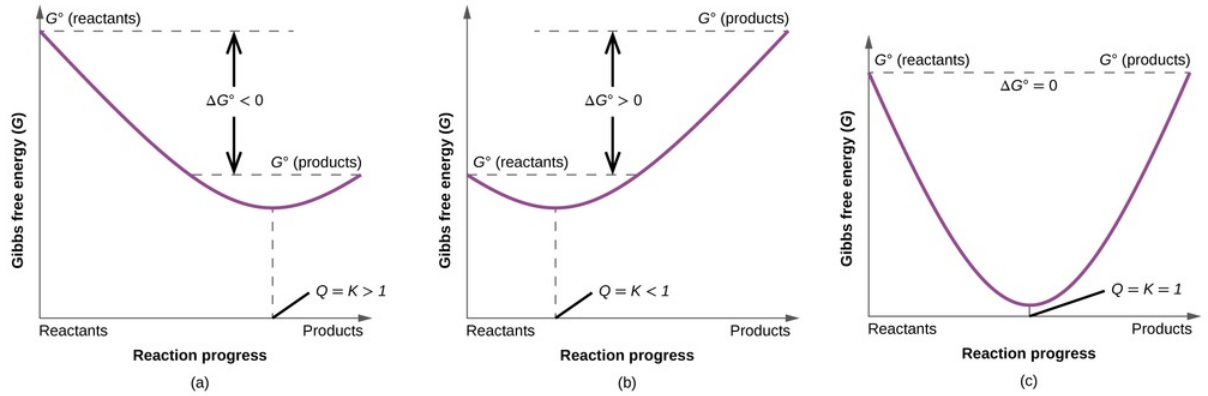


Figure 12.2.1: These plots show the free energy versus reaction progress for systems whose standard free changes are (a) negative, (b) positive, and (c) zero. Nonequilibrium systems will proceed spontaneously in whatever direction is necessary to minimize free energy and establish equilibrium. (CC BY 4.0; OpenStax).

Example 12.2.2

ΔG^o is −32.7 kJ/mol of N_2 for the reaction

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

This calculation was for the reaction under standard conditions—that is, with all gases present at a partial pressure of 1 atm and a temperature of 25°C. Calculate ΔG for the same reaction under the following nonstandard conditions:

- P_{N_2} = 2.00 atm,
- P_{H_2} = 7.00 atm,
- P_{NH_3} = 0.021 atm,
- and T = 100°C.

Does the reaction favor products or reactants?

Given: balanced chemical equation, partial pressure of each species, temperature, and ΔG°

Asked for: whether products or reactants are favored

Strategy:

A. Using the values given and Equation 12.2.12, calculate Q.
B. Substitute the values of ΔG° and Q into Equation 12.2.12to obtain ΔG for the reaction under nonstandard conditions.

Solution:

A The relationship between ΔG° and ΔG under nonstandard conditions is given in Equation 12.2.12 Substituting the partial pressures given, we can calculate Q:

$$Q = \frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3} = \frac{(0.021)^2}{(2.00)(7.00)^3} = 6.4 \times 10^{-7}$$

B Substituting the values of ΔG° and Q into Equation 12.2.12,

$$\begin{aligned}\Delta G &= \Delta G^\circ + RT \ln Q \\ &= -32.7\ \text{kJ} + \left[(8.314\ \text{J/K})(373\ \text{K})\left(\frac{1\ \text{kJ}}{1000\ \text{J}}\right)\ln(6.4 \times 10^{-7})\right] \\ &= -32.7\ \text{kJ} + (-44\ \text{kJ}) \\ &= -77\ \text{kJ/mol of } N_2\end{aligned}$$

Because ΔG < 0 and Q < 1.0, the reaction is spontaneous to the right as written, so products are favored over reactants.

Exercise 12.2.2

Calculate ΔG for the reaction of nitric oxide with oxygen to give nitrogen dioxide under these conditions: T = 50°C, P_{NO} = 0.0100 atm, P_{O_2} = 0.200 atm, and P_{NO_2} = 1.00 × 10^{-4} atm. The value of ΔG° for this reaction is −72.5 kJ/mol of O_2. Are products or reactants favored?

Answer

−92.9 kJ/mol of O_2; the reaction is spontaneous to the right as written, so products are favored.

Example 12.2.3

Calculate K_p for the reaction of H_2 with N_2 to give NH_3 at 25°C. ΔG^o for this reaction is −32.7 kJ/mol of N_2.

Given: balanced chemical equation from Example 12.2.2, ΔG°, and temperature

Asked for: K_p

Strategy:

Substitute values for ΔG° and T (in kelvin) into Equation 12.2.14to calculate K_p, the equilibrium constant for the formation of ammonia.

Solution

In Example 10, we used tabulated values of ΔG°_f to calculate ΔG° for this reaction (−32.7 kJ/mol of N_2). For equilibrium conditions, rearranging Equation 12.2.14,

$$\Delta G^\circ = -RT \ln K_p$$

$$\frac{-\Delta G^\circ}{RT} = \ln K_p$$

Inserting the value of ΔG° and the temperature (25°C = 298 K) into this equation,

$$\ln K_p = -\frac{(-32.7\ \text{kJ})(1000\ \text{J/kJ})}{(8.314\ \text{J/K})(298\ \text{K})} = 13.2$$

$$K_p = 5.4 \times 10^5$$

Thus the equilibrium constant for the formation of ammonia at room temperature is favorable. However, the rate at which the reaction occurs at room temperature is too slow to be useful.

Exercise 12.2.3

Calculate K_p for the reaction of NO with O_2 to give NO_2 at 25°C. ΔG° for this reaction is −70.5 kJ/mol of O_2.

Answer

2.2 × 10^{12}

Although K_p is defined in terms of the partial pressures of the reactants and the products, the equilibrium constant K is defined in terms of the concentrations of the reactants and the products. We described the relationship between the numerical magnitude of \(K_p\) and K previously and showed that they are related:

$$K_p = K(RT)^{\Delta n} \tag{12.2.15}$$

where Δn is the number of moles of gaseous product minus the number of moles of gaseous reactant. For reactions that involve only solutions, liquids, and solids, $\Delta n = 0$, so $K_p = K$. For all reactions that do not involve a change in the number of moles of gas present, the relationship in Equation 12.2.14can be written in a more general form:

$$\Delta G^\circ = -RT \ln K \tag{12.2.16}$$

Only when a reaction results in a net production or consumption of gases is it necessary to correct Equation 12.2.16 for the difference between K_p and K. Although we typically use concentrations or pressures in our equilibrium calculations, recall that equilibrium constants are generally expressed as unitless numbers because of the use of **activities** or **fugacities** in precise thermodynamic work. Systems that contain gases at high pressures or concentrated solutions that deviate substantially from ideal behavior require the use of fugacities or activities, respectively.

Combining Equations 12.2.16 with $\Delta G^o = \Delta H^o - T\Delta S^o$ provides insight into how the components of ΔG° influence the magnitude of the equilibrium constant:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT\ln K \tag{12.2.17}$$

Notice that K becomes larger as ΔS° becomes more positive, indicating that the magnitude of the equilibrium constant is directly influenced by the tendency of a system to move toward maximum disorder. Moreover, K increases as ΔH° decreases. Thus the magnitude of the equilibrium constant is also directly influenced by the tendency of a system to seek the lowest energy state possible.

> *The magnitude of the equilibrium constant is directly influenced by the tendency of a system to move toward maximum disorder and seek the lowest energy state possible.*

Temperature Dependence of the Equilibrium Constant

The fact that ΔG° and K are related provides us with another explanation of why equilibrium constants are temperature dependent. This relationship is shown explicitly in Equation 12.2.17, which can be rearranged as follows:

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{12.2.18}$$

Assuming ΔH° and ΔS° are temperature independent, for an exothermic reaction (ΔH° < 0), the magnitude of K decreases with increasing temperature, whereas for an endothermic reaction (ΔH° > 0), the magnitude of K increases with increasing temperature. The quantitative relationship expressed in Equation 12.2.18agrees with the qualitative predictions made by applying Le Chatelier's principle. Because heat is produced in an exothermic reaction, adding heat (by increasing the temperature) will shift the equilibrium to the left, favoring the reactants and decreasing the magnitude of K. Conversely, because heat is consumed in an endothermic reaction, adding heat will shift the equilibrium to the right, favoring the products and increasing the magnitude of K. Equation 12.2.18 also shows that the magnitude of ΔH° dictates how rapidly K changes as a function of temperature. In contrast, the magnitude and sign of ΔS° affect the magnitude of K but not its temperature dependence.

If we know the value of K at a given temperature and the value of ΔH° for a reaction, we can estimate the value of K at any other temperature, even in the absence of information on ΔS°. Suppose, for example, that K_1 and K_2 are the equilibrium constants for a reaction at temperatures T_1 and T_2, respectively. Applying Equation 12.2.18gives the following relationship at each temperature:

$$\ln K_1 = \frac{-\Delta H^\circ}{RT_1} + \frac{\Delta S^\circ}{R} \tag{12.2.19}$$

$$\ln K_2 = \frac{-\Delta H^\circ}{RT_2} + \frac{\Delta S^\circ}{R} \tag{12.2.20}$$

Subtracting $\ln K_1$ from $\ln K_2$,

$$\ln K_2 - \ln K_1 = \ln\frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{12.2.21}$$

Thus calculating ΔH° from tabulated enthalpies of formation and measuring the equilibrium constant at one temperature (K_1) allow us to calculate the value of the equilibrium constant at any other temperature (K_2), assuming that ΔH° and ΔS° are independent of temperature. Equation 12.2.21is often referred to as the **van 't Hoff equation** after Dutch chemist Jacobus Henricus van 't Hoff in 1884 in his book Études de Dynamique chimique (Studies in dynamic chemistry).

Example 12.2.4

The equilibrium constant for the formation of NH_3 from H_2 and N_2 at 25°C was calculated to be $K_p = 5.4 \times 10^5$ in Example 12.2.2 What is K_p at 500°C? (Use the data from Example 12.2.1)

Given: balanced chemical equation, ΔH°, initial and final T, and K_p at 25°C

Asked for: K_p at 500°C

Strategy:

Convert the initial and final temperatures to kelvin. Then substitute appropriate values into Equation 12.2.21to obtain K_2, the equilibrium constant at the final temperature.

Solution:

The value of ΔH° for the reaction obtained using Hess's law is −91.8 kJ/mol of N_2. If we set T_1 = 25°C = 298 K and T_2 = 500°C = 773 K, then from Equation 12.2.21we obtain the following:

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$= \frac{(-91.8\ \text{kJ})(1000\ \text{J/kJ})}{8.314\ \text{J/K}}\left(\frac{1}{298\ \text{K}} - \frac{1}{773\ \text{K}}\right) = -22.8$$

$$\frac{K_2}{K_1} = 1.3 \times 10^{-10}$$

$$K_2 = (5.4 \times 10^5)(1.3 \times 10^{-10}) = 7.0 \times 10^{-5}$$

Thus at 500°C, the equilibrium strongly favors the reactants over the products.

Exercise 12.2.4

The equilibrium constant for the reaction of NO with O_2 to give NO_2 at 25°C is $K_p = 2.2 \times 1012$. Use the ΔH_f^o values in the exercise in Example 12.2.4to calculate K_p for this reaction at 1000°C.

Answer

5.6×10^{-4}

Summary

For a reversible process that does not involve external work, we can express the change in free energy in terms of volume, pressure, entropy, and temperature. If we assume ideal gas behavior, the ideal gas law allows us to express ΔG in terms of the partial pressures of the reactants and products, which gives us a relationship between ΔG and K_p, the equilibrium constant of a reaction involving gases, or K, the equilibrium constant expressed in terms of concentrations. If ΔG° < 0, then K or K_p > 1, and products are favored over reactants. If ΔG° > 0, then K or K_p < 1, and reactants are favored over products. If ΔG° = 0, then K or K_p = 1, and the system is at equilibrium. We can use the measured equilibrium constant K at one temperature and ΔH° to estimate the equilibrium constant for a reaction at any other temperature.

Contributors and Attributions

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12.3: The Empirical Law of Mass Action

Learning Objectives

- To know the relationship between the equilibrium constant and the rate constants for the forward and reverse reactions.
- To write an equilibrium constant expression for any reaction.
- To understand how different phases affect equilibria.

Because an equilibrium state is achieved when the forward reaction rate equals the reverse reaction rate, under a given set of conditions there must be a relationship between the composition of the system at equilibrium and the kinetics of a reaction (represented by rate constants). We can show this relationship using the decomposition reaction of $\mathrm{N_2O_4}$ to $\mathrm{NO_2}$. Both the forward and reverse reactions for this system consist of a single elementary reaction, so the reaction rates are as follows:

$$\text{forward rate} = k_f[\mathrm{N_2O_4}] \tag{12.3.1}$$

and

$$\text{reverse rate} = k_r[\mathrm{NO_2}]^2 \tag{12.3.2}$$

At equilibrium, the forward rate equals the reverse rate (definition of equilibrium):

$$k_f[\mathrm{N_2O_4}] = k_r[\mathrm{NO_2}]^2 \tag{12.3.3}$$

so

$$\frac{k_f}{k_r} = \frac{[\mathrm{NO_2}]^2}{[\mathrm{N_2O_4}]} \tag{12.3.4}$$

The ratio of the rate constants gives us a new constant, the **equilibrium constant** (K), which is defined as follows:

$$K = \frac{k_f}{k_r} \tag{12.3.5}$$

Hence there is a fundamental relationship between chemical kinetics and chemical equilibrium: under a given set of conditions, the composition of the equilibrium mixture is determined by the magnitudes of the rate constants for the forward and the reverse reactions.

> The equilibrium constant is equal to the rate constant for the forward reaction divided by the rate constant for the reverse reaction.

Table 12.3.1 lists the initial and equilibrium concentrations from five different experiments using the reaction system described by Equation 12.3.1. At equilibrium the magnitude of the quantity $[\mathrm{NO_2}]^2/[\mathrm{N_2O_4}]$ is essentially the same for all five experiments. In fact, no matter what the initial concentrations of $\mathrm{NO_2}$ and $\mathrm{N_2O_4}$ are, at equilibrium the quantity $[\mathrm{NO_2}]^2/[\mathrm{N_2O_4}]$ will always be $6.53 \pm 0.03 \times 10^{-3}$ at 25°C, which corresponds to the ratio of the rate constants for the forward and reverse reactions (Equation 12.3.5). That is, at a given temperature, the equilibrium constant for a reaction always has the same value, even though the specific concentrations of the reactants and products vary depending on their initial concentrations.

Table 12.3.1: Initial and Equilibrium Concentrations for $NO_2 : N_2O_4$ Mixtures at 25°C

	Initial Concentrations		Concentrations at Equilibrium		
Experiment	$[N_2O_4]$ (M)	$[NO_2]$ (M)	$[N_2O_4]$ (M)	$[NO_2]$ (M)	$K = [NO_2]^2/[N_2O_4]$
1	0.0500	0.0000	0.0417	0.0165	6.54×10^{-3}
2	0.0000	0.1000	0.0417	0.0165	6.54×10^{-3}
3	0.0750	0.0000	0.0647	0.0206	6.56×10^{-3}
4	0.0000	0.0750	0.0304	0.0141	6.54×10^{-3}

	Initial Concentrations		Concentrations at Equilibrium		
Experiment	$[N_2O_4]$ (M)	$[NO_2]$ (M)	$[N_2O_4]$ (M)	$[NO_2]$ (M)	$K = [NO_2]^2/[N_2O_4]$
5	0.0250	0.0750	0.0532	0.0186	6.50×10^{-3}

Developing an Equilibrium Constant Expression

In 1864, the Norwegian chemists Cato Guldberg (1836–1902) and Peter Waage (1833–1900) carefully measured the compositions of many reaction systems at equilibrium. They discovered that for any reversible reaction of the general form

$$aA + bB \rightleftharpoons cC + dD \tag{12.3.6}$$

where A and B are reactants, C and D are products, and a, b, c, and d are the stoichiometric coefficients in the balanced chemical equation for the reaction, the ratio of the product of the equilibrium concentrations of the products (raised to their coefficients in the balanced chemical equation) to the product of the equilibrium concentrations of the reactants (raised to their coefficients in the balanced chemical equation) is always a constant under a given set of conditions. This relationship is known as the law of mass action and can be stated as follows:

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{12.3.7}$$

where K is the equilibrium constant for the reaction. Equation 12.3.6 is called the equilibrium equation, and the right side of Equation 12.3.7 is called the equilibrium constant expression. The relationship shown in Equation 12.3.7 is true for any pair of opposing reactions regardless of the mechanism of the reaction or the number of steps in the mechanism.

The equilibrium constant can vary over a wide range of values. The values of K shown in Table 12.3.2, for example, vary by 60 orders of magnitude. Because products are in the numerator of the equilibrium constant expression and reactants are in the denominator, values of K greater than 10^3 indicate a strong tendency for reactants to form products. In this case, chemists say that equilibrium lies to the right as written, favoring the formation of products. An example is the reaction between H_2 and Cl_2 to produce HCl, which has an equilibrium constant of 1.6×10^{33} at 300 K. Because H_2 is a good reductant and Cl_2 is a good oxidant, the reaction proceeds essentially to completion. In contrast, values of K less than 10^{-3} indicate that the ratio of products to reactants at equilibrium is very small. That is, reactants do not tend to form products readily, and the equilibrium lies to the left as written, favoring the formation of reactants.

Table 12.3.2: Equilibrium Constants for Selected Reactions*

Reaction	Temperature (K)	Equilibrium Constant (K)
$S(s) + O_2(g) \rightleftharpoons SO_2(g)$	300	4.4×10^{53}
$2\,H_2(g) + O_2(g) \rightleftharpoons 2\,H_2O(g)$	500	2.4×10^{47}
$H_2(g) + Cl_2(g) \rightleftharpoons 2\,HCl(g)$	300	1.6×10^{33}
$H_2(g) + Br_2(g) \rightleftharpoons 2\,HBr(g)$	300	4.1×10^{18}
$2\,NO(g) + O_2(g) \rightleftharpoons 2\,NO_2(g)$	300	4.2×10^{13}
$3\,H_2(g) + N_2(g) \rightleftharpoons 2\,NH_3(g)$	300	2.7×10^{8}
$H_2(g) + D_2(g) \rightleftharpoons 2\,HD(g)$	100	1.92
$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$	300	2.9×10^{-1}
$I_2(g) \rightleftharpoons 2\,I(g)$	800	4.6×10^{-7}
$Br_2(g) \rightleftharpoons 2\,Br(g)$	1000	4.0×10^{-7}
$Cl_2(g) \rightleftharpoons 2\,Cl(g)$	1000	1.8×10^{-9}
$F_2(g) \rightleftharpoons 2\,F(g)$	500	7.4×10^{-13}

*Equilibrium constants vary with temperature. The K values shown are for systems at the indicated temperatures.

You will also notice in Table 12.3.2 that equilibrium constants have no units, even though Equation 12.3.7 suggests that the units of concentration might not always cancel because the exponents may vary. **In fact, equilibrium constants are calculated using "effective concentrations," or activities, of reactants and products, which are the ratios of the measured concentrations to a standard state of 1 M.** As shown in Equation 12.3.8, the units of concentration cancel, which makes K unitless as well:

$$\frac{[A]_{measured}}{[A]_{standard\ state}} = \frac{\cancel{M}}{\cancel{M}} = \frac{\frac{mol}{\cancel{L}}}{\frac{mol}{\cancel{L}}} \tag{12.3.8}$$

Many reactions have equilibrium constants between 1000 and 0.001 ($10^3 \geq K \geq 10^{-3}$), neither very large nor very small. At equilibrium, these systems tend to contain significant amounts of both products and reactants, indicating that there is not a strong tendency to form either products from reactants or reactants from products. An example of this type of system is the reaction of gaseous hydrogen and deuterium, a component of high-stability fiber-optic light sources used in ocean studies, to form HD:

$$\mathrm{H_2(g) + D_2(g) \rightleftharpoons 2\,HD(g)} \tag{12.3.9}$$

The equilibrium constant expression for this reaction is

$$K = \frac{[HD]^2}{[H_2][D_2]} \tag{12.3.10}$$

with K varying between 1.9 and 4 over a wide temperature range (100–1000 K). Thus an equilibrium mixture of $\mathrm{H_2}$, $\mathrm{D_2}$, and HD contains significant concentrations of both product and reactants.

Figure 12.3.1 summarizes the relationship between the magnitude of K and the relative concentrations of reactants and products at equilibrium for a general reaction, written as reactants \rightleftharpoons products. Because there is a direct relationship between the kinetics of a reaction and the equilibrium concentrations of products and reactants (Equations 12.3.8 and 12.3.7), when $k_f \gg k_r$, K is a **large** number, and the concentration of products at equilibrium predominate. This corresponds to an essentially irreversible reaction. Conversely, when $k_f \ll k_r$, K is a very **small** number, and the reaction produces almost no products as written. Systems for which $k_f \approx k_r$ have significant concentrations of both reactants and products at equilibrium.

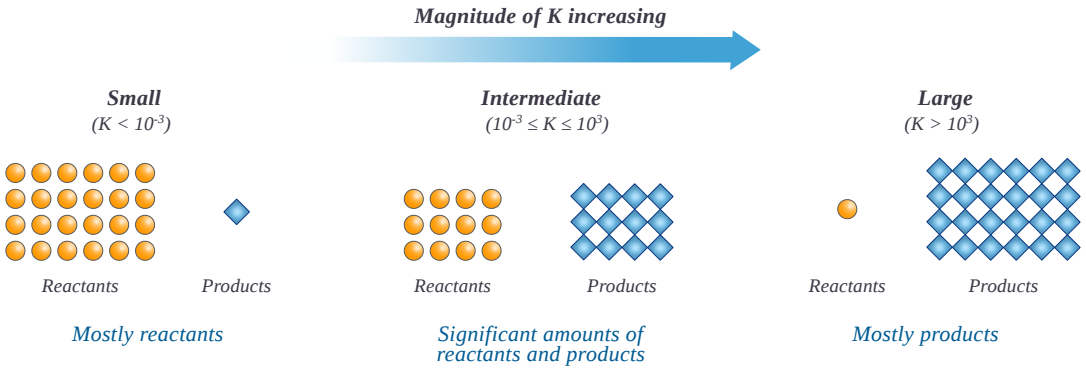


Figure 12.3.1: The Relationship between the Composition of the Mixture at Equilibrium and the Magnitude of the Equilibrium Constant. The larger the K, the farther the reaction proceeds to the right before equilibrium is reached, and the greater the ratio of products to reactants at equilibrium. (CC BY-NC; Ümit Kaya)

A large value of the equilibrium constant K means that products predominate at equilibrium; a small value means that reactants predominate at equilibrium.

Example 12.3.1

Write the equilibrium constant expression for each reaction.

- $\mathrm{N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)}$
- $\mathrm{CO(g) + \frac{1}{2}O_2(g) \rightleftharpoons CO_2(g)}$
- $\mathrm{2\,CO_2(g) \rightleftharpoons 2\,CO(g) + O_2(g)}$

Given: balanced chemical equations

Asked for: equilibrium constant expressions

Strategy:

Refer to Equation 12.3.7. Place the arithmetic product of the concentrations of the products (raised to their stoichiometric coefficients) in the numerator and the product of the concentrations of the reactants (raised to their stoichiometric coefficients) in the denominator.

Solution:

The only product is ammonia, which has a coefficient of 2. For the reactants, N_2 has a coefficient of 1 and $\mathrm{H_2}$ has a coefficient of 3. The equilibrium constant expression is as follows:

$$\frac{[NH_3]^2}{[N_2][H_2]^3}$$

The only product is carbon dioxide, which has a coefficient of 1. The reactants are CO, with a coefficient of 1, and $\mathrm{O_2}$, with a coefficient of $\frac{1}{2}$. Thus the equilibrium constant expression is as follows:

$$\frac{[CO_2]}{[CO][O_2]^{1/2}}$$

This reaction is the reverse of the reaction in part b, with all coefficients multiplied by 2 to remove the fractional coefficient for $\mathrm{O_2}$. The equilibrium constant expression is therefore the inverse of the expression in part b, with all exponents multiplied by 2:

$$\frac{[CO]^2[O_2]}{[CO_2]^2}$$

Exercise 12.3.1

Write the equilibrium constant expression for each reaction.

a. $\mathrm{N_2O(g) \rightleftharpoons N_2(g) + \frac{1}{2}O_2(g)}$
b. $\mathrm{2\,C_8H_{18}(g) + 25\,O_2(g) \rightleftharpoons 16\,CO_2(g) + 18\,H_2O(g)}$
c. $\mathrm{H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)}$

Answer a

$$K = \frac{[N_2][O_2]^{1/2}}{[N_2O]}$$

Answer b

$$K = \frac{[CO_2]^{16}[H_2O]^{18}}{[C_8H_{18}]^2[O_2]^{25}}$$

Answer c

$$K = \frac{[HI]^2}{[H_2][I_2]}$$

Example 12.3.2

Predict which systems at equilibrium will (a) contain essentially only products, (b) contain essentially only reactants, and (c) contain appreciable amounts of both products and reactants.

1. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)} \qquad K_{(700K)} = 54$
2. $2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)} \qquad K_{(1200K)} = 3.1 \times 10^{-18}$
3. $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)} \qquad K_{(613K)} = 97$
4. $2O_{3(g)} \rightleftharpoons 3O_{2(g)} \qquad K_{(298K)} = 5.9 \times 10^{55}$

Given: systems and values of K

Asked for: composition of systems at equilibrium

Strategy:

Use the value of the equilibrium constant to determine whether the equilibrium mixture will contain essentially only products, essentially only reactants, or significant amounts of both.

Solution:

a. Only system 4 has $K >> 10^3$, so at equilibrium it will consist of essentially only products.
b. System 2 has $K << 10^{-3}$, so the reactants have little tendency to form products under the conditions specified; thus, at equilibrium the system will contain essentially only reactants.
c. Both systems 1 and 3 have equilibrium constants in the range $10^3 \geq K \geq 10^{-3}$, indicating that the equilibrium mixtures will contain appreciable amounts of both products and reactants.

Exercise 12.3.2

Hydrogen and nitrogen react to form ammonia according to the following balanced chemical equation:

$$3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

Values of the equilibrium constant at various temperatures were reported as

- $K_{25^\circ C} = 3.3 \times 10^8$,
- $K_{177^\circ C} = 2.6 \times 10^3$, and
- $K_{327^\circ C} = 4.1$.

a. At which temperature would you expect to find the highest proportion of H_2 and N_2 in the equilibrium mixture?
b. Assuming that the reaction rates are fast enough so that equilibrium is reached quickly, at what temperature would you design a commercial reactor to operate to maximize the yield of ammonia?

Answer a

327°C, where K is smallest

Answer b

25°C

Variations in the Form of the Equilibrium Constant Expression

Because equilibrium can be approached from either direction in a chemical reaction, the equilibrium constant expression and thus the magnitude of the equilibrium constant depend on the form in which the chemical reaction is written. For example, if we write the reaction described in Equation 12.3.6 in reverse, we obtain the following:

$$cC + dD \rightleftharpoons aA + bB \tag{12.3.11}$$

The corresponding equilibrium constant K' is as follows:

$$K' = \frac{[A]^a[B]^b}{[C]^c[D]^d} \tag{12.3.12}$$

This expression is the inverse of the expression for the original equilibrium constant, so $K' = 1/K$. That is, when we write a reaction in the reverse direction, the equilibrium constant expression is inverted. For instance, the equilibrium constant for the reaction $N_2O_4 \rightleftharpoons 2NO_2$ is as follows:

$$K = \frac{[NO_2]^2}{[N_2O_4]} \tag{12.3.13}$$

but for the opposite reaction, $2NO_2 \rightleftharpoons N_2O_4$, the equilibrium constant K′ is given by the inverse expression:

$$K' = \frac{[N_2O_4]}{[NO_2]^2} \tag{12.3.14}$$

Consider another example, the formation of water: $2H_{2(g)} + O_{2(g)} \rightleftharpoons 2H_2O_{(g)}$. Because H_2 is a good reductant and O_2 is a good oxidant, this reaction has a very large equilibrium constant ($K = 2.4 \times 10^{47}$ at 500 K). Consequently, the equilibrium constant for the reverse reaction, the decomposition of water to form O_2 and H_2, is very small: $K' = 1/K = 1/(2.4 \times 10^{47}) = 4.2 \times 10^{-48}$. As suggested by the very small equilibrium constant, and fortunately for life as we know it, a substantial amount of energy is indeed needed to dissociate water into H_2 and O_2.

> The equilibrium constant for a reaction written in reverse is the *inverse* of the equilibrium constant for the reaction as written originally.

Writing an equation in different but chemically equivalent forms also causes both the equilibrium constant expression and the magnitude of the equilibrium constant to be different. For example, we could write the equation for the reaction

$$2NO_2 \rightleftharpoons N_2O_4 \tag{12.3.15}$$

as

$$NO_2 \rightleftharpoons \frac{1}{2}N_2O_4 \tag{12.3.16}$$

with the equilibrium constant K″ is as follows:

$$K'' = \frac{[N_2O_4]^{1/2}}{[NO_2]} \tag{12.3.17}$$

The values for K′ (Equation 12.3.14) and K″ are related as follows:

$$K'' = (K')^{1/2} = \sqrt{K'} \tag{12.3.18}$$

In general, if all the coefficients in a balanced chemical equation were subsequently multiplied by n, then the new equilibrium constant is the original equilibrium constant raised to the nth power.

Example 12.3.3: The Haber Process

At 745 K, K is 0.118 for the following reaction:

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

What is the equilibrium constant for each related reaction at 745 K?

a. $\mathrm{2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g)}$
b. $\mathrm{\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)}$

Given: balanced equilibrium equation, K at a given temperature, and equations of related reactions

Asked for: values of K for related reactions

Strategy:

Write the equilibrium constant expression for the given reaction and for each related reaction. From these expressions, calculate K for each reaction.

Solution:

The equilibrium constant expression for the given reaction of $\mathrm{N_2(g)}$ with $\mathrm{H_2(g)}$ to produce $\mathrm{NH_3(g)}$ at 745 K is as follows:

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = 0.118$$

This reaction is the reverse of the one given, so its equilibrium constant expression is as follows:

$$K' = \frac{1}{K} = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{1}{0.118} = 8.47$$

In this reaction, the stoichiometric coefficients of the given reaction are divided by 2, so the equilibrium constant is calculated as follows:

$$K'' = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}} = K^{1/2} = \sqrt{K} = \sqrt{0.118} = 0.344$$

? Exercise

At 527°C, the equilibrium constant for the reaction

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

is 7.9×10^4. Calculate the equilibrium constant for the following reaction at the same temperature:

$$\mathrm{SO_3(g) \rightleftharpoons SO_2(g) + \tfrac{1}{2}O_2(g)}$$

Answer

3.6×10^{-3}

Law of Mass Action for Gas-Phase Reactions

For reactions that involve species in solution, the concentrations used in equilibrium calculations are usually expressed in moles/liter. For gases, however, the concentrations are usually expressed in terms of partial pressures rather than molarity, where the standard state is 1 atm of pressure. The symbol K_p is used to denote equilibrium constants calculated from partial pressures. For the general reaction

$$\mathrm{aA + bB \rightleftharpoons cC + dD}$$

in which all the components are gases, the equilibrium constant expression can be written as the ratio of the partial pressures of the products and reactants (each raised to its coefficient in the chemical equation):

$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b} \tag{12.3.19}$$

Thus K_p for the decomposition of N_2O_4 (Equation 12.3.1) is as follows:

$$K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}} \tag{12.3.20}$$

Like K, K_p is a unitless quantity because the quantity that is actually used to calculate it is an “effective pressure,” the ratio of the measured pressure to a standard state of 1 bar (approximately 1 atm), which produces a unitless quantity. The “effective pressure” is called the **fugacity**, just as activity is the effective concentration.

Because partial pressures are usually expressed in atmospheres or mmHg, the molar concentration of a gas and its partial pressure do not have the same numerical value. Consequently, the numerical values of K and K_p are usually different. They are, however, related by the ideal gas constant (R) and the absolute temperature (T):

$$K_p = K(RT)^{\Delta n} \tag{12.3.21}$$

where K is the equilibrium constant expressed in units of concentration and Δn is the difference between the numbers of moles of gaseous products and gaseous reactants ($n_p - n_r$). The temperature is expressed as the absolute temperature in Kelvin. According to Equation 12.3.21, $K_p = K$ only if the moles of gaseous products and gaseous reactants are the same (i.e., $\Delta n = 0$). For the decomposition of N_2O_4, there are 2 mol of gaseous product and 1 mol of gaseous reactant, so $\Delta n = 1$. Thus, for this reaction,

$$K_p = K(RT)^1 = KRT \tag{12.3.22}$$

Example 12.3.4: The Haber Process (again)

The equilibrium constant for the reaction of nitrogen and hydrogen to give ammonia is 0.118 at 745 K. The balanced equilibrium equation is as follows:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

What is K_p for this reaction at the same temperature?

Given: equilibrium equation, equilibrium constant, and temperature

Asked for: K_p

Strategy:

Use the coefficients in the balanced chemical equation to calculate Δn. Then use Equation 12.3.21to calculate K from K_p.

Solution:

This reaction has 2 mol of gaseous product and 4 mol of gaseous reactants, so $\Delta n = (2 - 4) = -2$. We know K, and $T = 745\ K$. Thus, from Equation 12.3.18, we have the following:

$$K_p = K(RT)^{-2} = \frac{K}{(RT)^2} = \frac{0.118}{\{[0.08206(L \cdot atm)/(mol \cdot K)][745\ K]\}^2} = 3.16 \times 10^{-5}$$

Because K_p is a unitless quantity, the answer is $K_p = 3.16 \times 10^{-5}$.

Exercise 12.3.4:

Calculate K_p for the reaction

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

at 527°C, if $K = 7.9 \times 10^4$ at this temperature.

Answer

$K_p = 1.2 \times 10^3$

Law of Mass Action for Reactions Involving Pure Substances and Multiple Phases

When the products and reactants of a reaction at equilibrium in a single phase (e.g., liquid, gas or solids of different lattices), the system is a **homogeneous equilibrium**. In such situations, the concentrations of the reactants and products can vary over a wide range. In contrast, a system where the reactants and products are in two or more phase is called a **heterogeneous equilibrium** (e.g, the reaction of a gas with a solid or liquid or two different solid lattices in co-existing).

Because the molar concentrations of pure liquids and solids normally do not vary greatly with temperature, their concentrations are treated as constants, which allows us to simplify equilibrium constant expressions that involve pure solids or liquids.The reference states for pure solids and liquids are those forms stable at 1 bar (approximately 1 atm), which are assigned an activity of 1. (Recall that the density of water, and thus its volume, changes by only a few percentage points between 0 °C and 100 °C.)

Consider the following reaction, which is used in the final firing of some types of pottery to produce brilliant metallic glazes:

$$\mathrm{CO_2(g) + C(s) \rightleftharpoons 2\,CO(g)} \tag{12.3.23}$$

The glaze is created when metal oxides are reduced to metals by the product, carbon monoxide. The equilibrium constant expression for this reaction is as follows:

$$K = \frac{[CO]^2}{[CO_2][C]} \tag{12.3.24}$$

Because graphite is a solid, however, its molar concentration, determined from its density and molar mass, is essentially constant and has the following value:

$$[C] = \frac{2.26\ \cancel{g}/\ \cancel{cm^3}}{12.01\ \cancel{g}/mol} \times 1000\ \ \cancel{cm^3}/L = 188\ mol/L = 188\ M \tag{12.3.25}$$

We can rearrange Equation 12.3.25 so that the constant terms are on one side:

$$K[C] = K(188) = \frac{[CO]^2}{[CO_2]} \tag{12.3.26}$$

Incorporating the constant value of $[C]$ into the equilibrium equation for the reaction in Equation 12.3.26,

$$K' = \frac{[CO]^2}{[CO_2]} \tag{12.3.27}$$

The equilibrium constant for this reaction can also be written in terms of the partial pressures of the gases:

$$K_p = \frac{(P_{CO})^2}{P_{CO_2}} \tag{12.3.28}$$

Incorporating all the constant values into K' or K_p allows us to focus on the substances whose concentrations change during the reaction.

Although the concentrations of pure liquids or solids are not written explicitly in the equilibrium constant expression, these substances must be present in the reaction mixture for chemical equilibrium to occur. Whatever the concentrations of CO and CO_2, the system described in Equation 12.3.23 will reach chemical equilibrium only if a stoichiometric amount of solid carbon or excess solid carbon has been added so that some is still present once the system has reached equilibrium. As shown in Figure 12.3.2, it does not matter whether 1 g or 100 g of solid carbon is present; in either case, the composition of the gaseous components of the system will be the same at equilibrium.

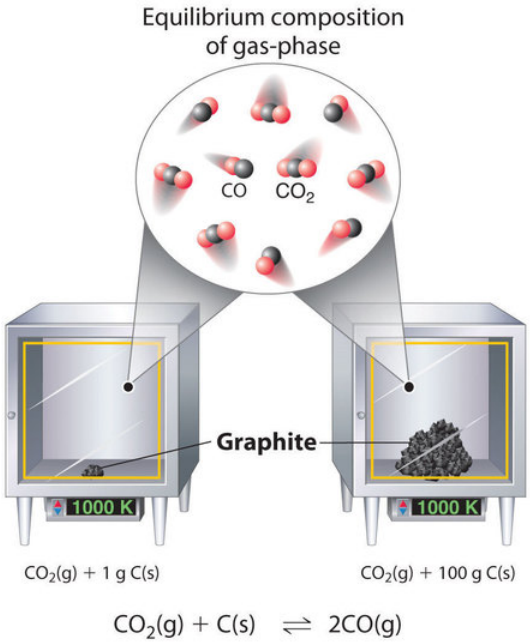


Figure 12.3.2: Effect of the Amount of Solid Present on Equilibrium in a Heterogeneous Solid–Gas System. In the system, the equilibrium composition of the gas phase at a given temperature, 1000 K in this case, is the same whether a small amount of solid carbon (left) or a large amount (right) is present.

Example 12.3.1

Write each expression for K, incorporating all constants, and K_p for the following equilibrium reactions.

a. $PCl_{3(l)} + Cl_{2(g)} \rightleftharpoons PCl_{5(s)}$
b. $Fe_3O_{4(s)} + 4H_{2(g)} \rightleftharpoons 3Fe_{(s)} + 4H_2O_{(g)}$

Given: balanced equilibrium equations

Asked for: expressions for K and K_p

Strategy:

Find K by writing each equilibrium constant expression as the ratio of the concentrations of the products and reactants, each raised to its coefficient in the chemical equation. Then express K_p as the ratio of the partial pressures of the products and reactants, each also raised to its coefficient in the chemical equation.

Solution

This reaction contains a pure solid (PCl_5) and a pure liquid (PCl_3). Their concentrations do not appear in the equilibrium constant expression because they do not change significantly. So

$$K = \frac{1}{[Cl_2]}$$

and

$$K_p = \frac{1}{P_{Cl_2}}$$

This reaction contains two pure solids (Fe_3O_4 and Fe), which do not appear in the equilibrium constant expressions. The two gases do, however, appear in the expressions:

$$K = \frac{[H_2O]^4}{[H_2]^4}$$

and

$$K_p = \frac{(P_{H_2O})^4}{(P_{H_2})^4}$$

Exercise 12.3.1

Write the expressions for K and K_p for the following reactions.

a. $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$
b. $\underset{glucose}{C_6H_{12}O_{6(s)}} + 6O_{2(g)} \rightleftharpoons 6CO_{2(g)} + 6H_2O_{(g)}$

Answer a

$K = [CO_2]$ and $K_p = P_{CO_2}$

Answer b

$$K = \frac{[CO_2]^6[H_2O]^6}{[O_2]^6} \text{ and } K_p = \frac{(P_{CO_2})^6(P_{H_2O})^6}{(P_{O_2})^6}$$

For reactions carried out in solution, the concentration of the solvent is omitted from the equilibrium constant expression even when the solvent appears in the balanced chemical equation for the reaction. The concentration of the solvent is also typically much greater than the concentration of the reactants or products (recall that pure water is about 55.5 M, and pure ethanol is about 17 M). Consequently, the solvent concentration is essentially constant during chemical reactions, and the solvent is therefore treated as a pure liquid. The equilibrium constant expression for a reaction contains only those species whose concentrations could change significantly during the reaction.

> The concentrations of pure solids, pure liquids, and solvents are omitted from equilibrium constant expressions because they do not change significantly during reactions when enough is present to reach equilibrium.

Summary

- The law of mass action describes a system at equilibrium in terms of the concentrations of the products and the reactants.
- For a system involving one or more gases, either the molar concentrations of the gases or their partial pressures can be used.
- Definition of equilibrium constant in terms of forward and reverse rate constants:

$$K = \frac{k_f}{k_r}$$

- Equilibrium constant expression (law of mass action):

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

- Equilibrium constant expression for reactions involving gases using partial pressures:

$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$$

- Relationship between K_p and K:

$$K_p = K(RT)^{\Delta n}$$

The ratio of the rate constants for the forward and reverse reactions at equilibrium is the equilibrium constant (K), a unitless quantity. The composition of the equilibrium mixture is therefore determined by the magnitudes of the forward and reverse rate constants at equilibrium. Under a given set of conditions, a reaction will always have the same K. For a system at equilibrium, the law of mass action relates K to the ratio of the equilibrium concentrations of the products to the concentrations of the reactants raised to their respective powers to match the coefficients in the equilibrium equation. The ratio is called the equilibrium constant

expression. When a reaction is written in the reverse direction, K and the equilibrium constant expression are inverted. For gases, the equilibrium constant expression can be written as the ratio of the partial pressures of the products to the partial pressures of the reactants, each raised to a power matching its coefficient in the chemical equation. An equilibrium constant calculated from partial pressures (K_p) is related to K by the ideal gas constant (R), the temperature (T), and the change in the number of moles of gas during the reaction. An equilibrated system that contains products and reactants in a single phase is a homogeneous equilibrium; a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium.

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12.4: Thermodynamic Description of the Equilibrium State

Learning Objectives

- Gibbs Energy is a state function defined as $G = H - TS$.
- The practical utility of the Gibbs function is that ΔG for any process is negative if it leads to an increase in the entropy of the world. Thus spontaneous change at a given temperature and pressure can only occur when it would lead to a decrease in G.
- The sign of the standard free energy change ΔG^o of a chemical reaction determines whether the reaction will tend to proceed in the forward or reverse direction.
- Similarly, the relative signs of ΔH^o and ΔH^o determine whether the spontaneity of a chemical reaction will be affected by the temperature, and if so, in what way.
- The existence of sharp melting and boiling points reflects the differing temperature dependancies of the free energies of the solid, liquid, and vapor phases of a pure substance, which are in turn reflect their differing entropies.

Previously, we saw that it is the **sum** of the entropy changes of the system and surroundings that determines whether a process will occur spontaneously. In chemical thermodynamics we prefer to focus our attention on the system rather than the surroundings, and would like to avoid having to calculate the entropy change of the surroundings explicitly.

In this unit we introduce a new thermodynamic function, the *free energy*, which turns out to be the single most useful criterion for predicting the direction of a chemical reaction and the composition of the system at equilibrium. However, the term "free energy", although still widely used, is rather misleading, so we will often refer to it as "Gibbs energy." The free energy enables us to do this for changes that occur at a constant temperature and pressure (the *Gibbs energy*) or constant temperature and volume (the *Helmholtz energy*.)

Free energy: the Gibbs function

The Gibbs energy (also known as the *Gibbs function* or *Gibbs Potential*) is defined as

$$G = H - TS \tag{12.4.1}$$

in which S refers to the entropy of the *system*. Since H, T and S are all state functions, so is G. Thus for any change in state (under constant temperature), we can write the extremely important relation

$$\Delta G = \Delta H - T\Delta S \tag{12.4.2}$$

How does this simple equation encompass the entropy change of the world ΔS_{total}, which we already know is the sole criterion for spontaneous change from the second law of thermodynamics? Starting with the definition

$$\Delta S_{total} = \Delta S_{surr} + \Delta S_{sys} \tag{12.4.3}$$

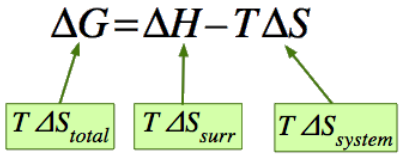
we would first like to get rid of ΔS_{surr}. How can a chemical reaction (a change in the *system*) affect the entropy of the *surroundings*? Because most reactions are either exothermic or endothermic, they are accompanied by a flow of heat q_p across the system boundary. The enthalpy change of the reaction ΔH is defined as the flow of heat into the system from the surroundings when the reaction is carried out at constant pressure, so the heat withdrawn from the surroundings will be $-q_p$ which will cause the entropy of the surroundings to change by $-q_p/T = -\Delta H/T$. We can therefore rewrite Equation 12.4.3 as

$$\Delta S_{total} = \frac{-\Delta H}{T} + \Delta S_{sys} \tag{12.4.4}$$

Multiplying each side by $-T$, we obtain

$$-T\Delta S_{total} = \Delta H - T\Delta S_{sys} \tag{12.4.5}$$

which expresses the entropy change of the world in terms of thermodynamic properties of the *system* exclusively. If $-T\Delta S_{total}$ is denoted by ΔG, then we have Equation 12.4.2 which defines the *Gibbs energy* change for the process.



From the foregoing, you should convince yourself that G will decrease in any process occurring at constant temperature and pressure which is accompanied by an overall increase in the entropy. The constant temperature is a consequence of the temperature and the enthalpy appearing in the preceding Equation 12.4.5. Since most chemical and phase changes of interest to chemists take place under such conditions, the Gibbs energy is the most useful of all the thermodynamic properties of a substance, and (as we shall see in the lesson that follows this one) it is closely linked to the equilibrium constant.

Some textbooks and teachers say that the free energy, and thus the spontaneity of a reaction, depends on both the enthalpy and entropy changes of a reaction, and they sometimes even refer to reactions as "energy driven" or "entropy driven" depending on whether ΔH or the $T\Delta S$ term dominates. This is technically correct, but misleading because it disguises the important fact that ΔS_{total}, which this equation expresses in an indirect way, is the *only* criterion of spontaneous change.

Helmholtz Energy is also a "Free Energy"

We will deal only with the Gibbs energy in this course. The Helmholtz free energy is of interest mainly to chemical engineers (whose industrial-scale processes are often confined to tanks and reactors of fixed volume) and some geochemists whose interest is centered on the chemistry that occurs deep within the earth's surface.

Gibbs Energy and Chemical Change

Remember that ΔG is meaningful only for changes in which the *temperature and pressure remain constant*. These are the conditions under which most reactions are carried out in the laboratory; the system is usually open to the atmosphere (constant pressure) and we begin and end the process at room temperature (after any heat we have added or which is liberated by the reaction has dissipated.) The importance of the Gibbs function can hardly be over-stated: it serves as the single master variable that determines whether a given chemical change is thermodynamically possible. Thus if the free energy of the reactants is greater than that of the products, the entropy of the world will increase when the reaction takes place as written, and so the reaction will tend to take place spontaneously. Conversely, if the free energy of the products exceeds that of the reactants, then the reaction will not take place in the direction written, but it will tend to proceed in the reverse direction.

> *ΔG serves as the single master variable that determines whether a given chemical change is thermodynamically possible. Moreover, it determines the direction and extent of chemical change.*

In a spontaneous change, Gibbs energy always decreases and never increases. This of course reflects the fact that the entropy of the world behaves in the exact opposite way (owing to the negative sign in the $T\Delta S$ term).

$$\mathrm{H_2O(l) \rightarrow H_2O(s)} \tag{12.4.6}$$

water below its freezing point undergoes a decrease in its entropy, but the heat released into the surroundings more than compensates for this, so the entropy of the world increases, the free energy of the H_2O diminishes, and the process proceeds spontaneously.

> *In a spontaneous change, Gibbs energy **always** decreases and never increases.*

An important consequence of the one-way downward path of the free energy is that once it reaches its minimum possible value, all net change comes to a halt. This, of course, represents the state of chemical equilibrium. These relations are nicely summarized as follows:

- $\Delta G < 0$: reaction can spontaneously proceed to the right:

$$A \rightarrow B$$

- $\Delta G > 0$: reaction can spontaneously proceed to the left:

$$A \leftarrow B$$

- $\Delta G = 0$: the reaction is at **equilibrium** and both $[A]$ and $[B]$ will not change:

$$A \rightleftharpoons B.$$

No need to find the value of ΔG for a Specific Reaction!

This might seem strange, given the key importance ΔG in determining whether or not a reaction will take place in a given direction. It turns out, however, that it is almost never necessary to explicitly evaluate ΔG. As we will show in the lesson that follows this one, it is far more convenient to work with the equilibrium constant of a reaction, within which ΔG is "hidden". This is just as well, because for most reactions (those that take place in solutions or gas mixtures) the value of ΔG depends on the **proportions** of the various reaction components in the mixture; it is not a simple sum of the "products minus reactants" type, as is the case with ΔH.

Recalling the condition for spontaneous change

$$\Delta G = \Delta H - T\Delta S < 0 \tag{12.4.7}$$

it is apparent that the temperature dependence of ΔG depends almost entirely on the entropy change associated with the process. (We say "almost" because the values of ΔH and ΔS are themselves slightly temperature dependent; both gradually increase with temperature). In particular, notice that in the above equation **the sign of the entropy change determines whether the reaction becomes more or less spontaneous as the temperature is raised.** For any given reaction, the sign of ΔH can also be positive or negative. This means that there are four possibilities for the influence that temperature can have on the spontaneity of a process:

Case 1: ΔH < 0 and ΔS > 0

Both enthalpic ΔH and entropic $-T\Delta S$ terms will be negative, so ΔG will be negative regardless of the temperature. An exothermic reaction whose entropy increases will be spontaneous at all temperatures.

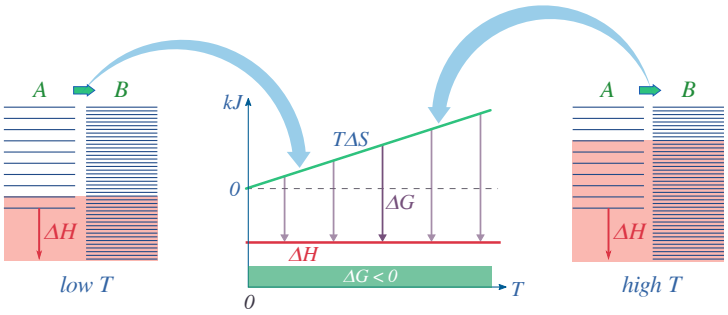


Figure 12.4.1: A hypothetical A ⟶ B reaction that is favored enthalpically and entropically (spontaneous at all temperatures). (CC BY 4.0; Ümit Kaya via LibreTexts)

Case 2: ΔH < 0 and ΔS < 0

If the reaction is sufficiently exothermic it can force ΔG negative only at temperatures below which $|T\Delta S| < |\Delta H|$. This means that there is a temperature $T = \Delta H / \Delta S$ at which the reaction is at equilibrium; the reaction will only proceed spontaneously below this temperature. The freezing of a liquid or the condensation of a gas are the most common examples of this condition.

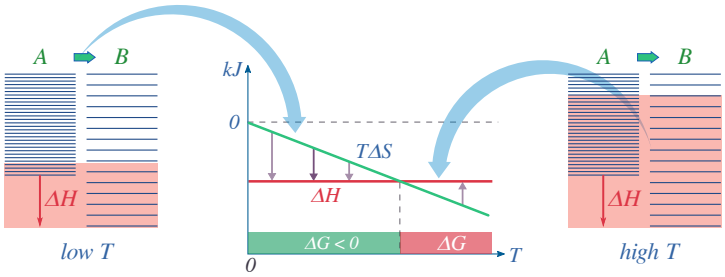


Figure 12.4.2: A hypothetical A ⟶ B reaction that is favored enthalpically and is not favored entropically (spontaneous at low temperatures). (CC BY 4.0; Ümit Kaya via LibreTexts)

Case 3: $\Delta H > 0$ and $\Delta S > 0$

This is the reverse of the previous case; the entropy increase must overcome the handicap of an endothermic process so that $T\Delta S > \Delta H$. Since the effect of the temperature is to "magnify" the influence of a positive ΔS, the process will be spontaneous at temperatures above $T = \Delta H / \Delta S$. (Think of melting and boiling.)

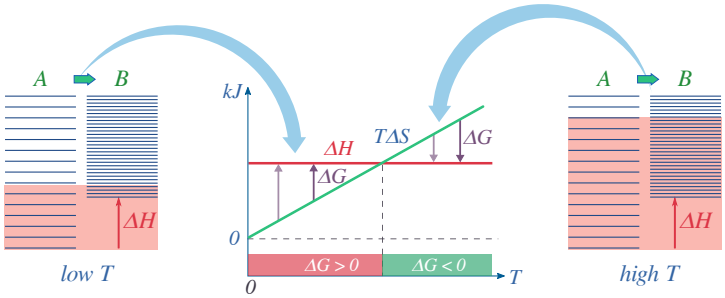


Figure 12.4.3: A hypothetical A ⟶ B reaction that is not favored enthalpically and is favored entropically (spontaneous at high temperatures). (CC BY 4.0; Ümit Kaya via LibreTexts)

Case 4: $\Delta H > 0$ and $\Delta S < 0$

With both ΔH and ΔS working against it, this kind of process will not proceed spontaneously at any temperature. Substance A always has a greater number of accessible energy states, and is therefore always the preferred form.

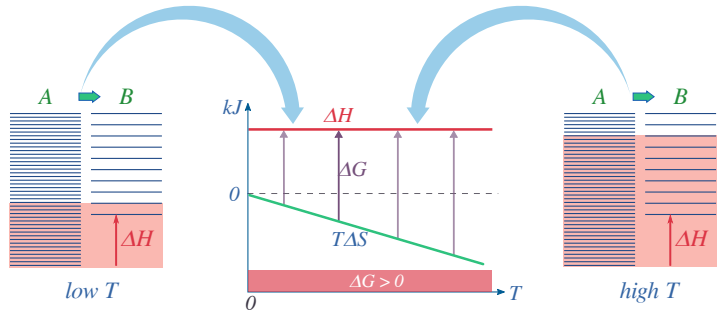


Figure 12.4.4: A hypothetical A ⟶ B reaction that is not favored enthalpically and is not is favored entropically (not spontaneous at temperatures). (CC BY 4.0; Ümit Kaya via LibreTexts)

The plots above are the important ones; do not try to memorize them, but make sure you understand and can explain or reproduce them for a given set of ΔH and ΔS.

- Their most important differentiating features are the position of the ΔH line (above or below the is $T\Delta S$ line), and the slope of the latter, which of course depends on the sign of ΔS.
- The reaction A → B will occur spontaneously only when ΔG is negative (blue arrows pointing down.)
- $T\Delta S$ plots are not quite straight lines as shown here. Similarly, the lines representing ΔH are even more curved.

The other two plots on each diagram are only for the chemistry-committed.

- Each pair of energy-level diagrams depicts the relative spacing of the microscopic energy levels in the reactants and products as reflected by the value of $\Delta S°$. (The greater the entropy, the more closely-spaced are the quantized microstates.)
- The red shading indicates the range of energy levels that are accessible to the system at each temperature. The spontaneous direction of the reaction will always be in the direction in which the red shading overlaps the greater number of energy levels, resulting in the maximum dispersal of thermal energy.
- Note that the vertical offsets correspond to $\Delta H°$ for the reaction.
- Never forget that it is the ability of thermal energy to spread into as many of these states as possible that determines the tendency of the process to take place. None of this is to scale, of course!

The Standard Gibbs Energy

You have already been introduced to the terms such as ΔU^o and ΔH^o in which the ^{o} sign indicates that all components (reactants and products) are in their *standard states*. This concept of standard states is especially important in the case of the free energy, so let's take a few moments to review it. More exact definitions of the conventional standard states can be found in most physical chemistry textbooks. In specialized fields such as biochemistry and oceanography, alternative definitions may apply. For example, the "standard pH" of zero (corresponding to $[H^+] = 1\ M$) is impractical in biochemistry, so pH = 7 is commonly employed. For most practical purposes, the following definitions are good enough:

- **gases:** 1 atmosphere partial pressure
- **pure liquids:** the liquid under a total (hydrostatic) pressure of 1 atm.
- **solutes:** an effective concentration of 1 mol L^{-1} (1 mol dm^{-3}). ("Effective" concentrations approach real concentrations as the latter approach zero; for practical purposes, these can be considered identical at real concentrations smaller than about 10^{-4} molar.)
- **solids:** the pure solid under 1 atm pressure

Reminder on Standard States

- There is actually no "standard temperature", but because most thermodynamics tables list values for 298.15 K (25° C), this temperature is usually implied.
- These same definitions apply to standard enthalpies and internal energies.
- Do not confuse these thermodynamic standard states with the "standard temperature and pressure" (STP) widely employed in gas law calculations.

To make use of Gibbs energies to predict chemical changes, we need to know the free energies of the individual components of the reaction. For this purpose we can combine the standard enthalpy of formation and the standard entropy of a substance to get its **standard free energy of formation**

$$\Delta G^o_f = \Delta H^o_f - T\Delta S^o_f \tag{12.4.8}$$

Recall that the symbol ° refers to the *standard state* of a substance measured under the conditions of 1 atm pressure or an effective concentration of 1 mol L^{-1} and a temperature of 298 K. Then determine the standard Gibbs energy of the reaction according to

$$\Delta G^o = \sum \Delta G^o_f\ (\text{products}) - \sum \Delta G^o_f\ (\text{reactants}) \tag{12.4.9}$$

As with standard heats of formation, the standard free energy of a substance represents the free energy change associated with the formation of the substance from the elements in their most stable forms as they exist under the standard conditions of 1 atm pressure and 298 K. Standard Gibbs free energies of formation are normally found directly from tables. Once the values for all the reactants and products are known, the standard Gibbs energy change for the reaction is found by Equation 12.4.8. Most tables of thermodynamic values list ΔG^o_f values for common substances (e.g., Table T2), which can, of course, always be found from values of $\Delta H_f°$ and $\Delta S_f°$.

Example 12.4.1

Find the standard Gibbs energy change for the reaction

$$\mathrm{CaCO_3(s) \rightarrow CaO(s) + CO_2(g)}$$

The $\Delta G_f^{o\,\circ}$ values for the three components of this reaction system are $\mathrm{CaCO_3(s)}$: –1128 kJ mol^{-1}, CaO*(s)*: –603.5 kJ mol^{-1}, CO_2*(g)*: –137.2 kJ mol^{-1}.

Solution

Substituting into Equation 12.4.8, we have

$$\Delta G^o = (-603.5 - 137.2) - (-1128) kJ\,mol^{-1} = +130.9\ kJ\,mol^{-1}$$

This indicates that the process is not spontaneous under standard conditions (i.e., solid calcium carbone will not form solid calcium oxide and CO_2 at 1 atm partial pressure at 25° C).

Comment: This reaction is carried out on a huge scale to manufacture cement, so it is obvious that the process can be spontaneous under different conditions.

The practical importance of the Gibbs energy is that it allows us to make predictions based on the properties ($\Delta G°$ values) of the reactants and products themselves, eliminating the need to experiment. But bear in mind that while thermodynamics always correctly predicts whether a given process *can* take place (is spontaneous in the thermodynamic sense), it is unable to tell us if it *will* take place at an observable rate.

> *When thermodynamics says "no", it means exactly that. When it says "yes", it means "maybe".*

Example 12.4.2

The reaction

$$\mathrm{\tfrac{1}{2}O_2(g) + H_2(g) \rightarrow H_2O(l)}$$

is used in fuel cells to produce an electrical current. The reaction can also be carried out by direct combustion.

Thermodynamic data: molar entropies in J mol^{-1} K^{-1}: O_2(g) 205.0; H_2(g)130.6; H_2O(l) 70.0; H_2O(l) $\Delta H°_f$ = –285.9 kJ mol^{-1}.

Use this information to find

a. The amount of heat released when the reaction takes place by direct combustion;
b. The amount of electrical work the same reaction can perform when carried out in a fuel cell at 298 K under reversible conditions;
c. The amount of heat released under the same conditions.

Solution

First, we need to find ΔH^o and ΔS^o for the process. Recalling that the standard enthalpy of formation of the elements is zero,

$$\begin{aligned}\Delta H^o &= \Delta H_f^p(\text{products}) - \Delta H_f^\circ(\text{reactants}) \\ &= -285.9\ kJ\,mol^{-1} - 0 \\ &= -285.9\ kJ\,mol^{-1}\end{aligned}$$

Similarly,

$$\begin{aligned}\Delta S^o &= S_f^o(\text{products}) - S_f^o(\text{reactants}) \\ &= (70.0) - (½ \times 205.0 + 130.6) \\ &= -163\ J\,K^{-1}mol^{-1}\end{aligned}$$

a. When the hydrogen and oxygen are combined directly, the heat released will be $\Delta H^o = -285.9\ kJ\,mol^{-1}$.

b. The maximum electrical work the fuel cell can perform is given by

$$\begin{aligned}\Delta G^o &= \Delta H^o - T\Delta S^o \\ &= -285.9\ kJ\,mol^{-1} - (298\ K)(-163\ JK^{-1}mol^{-1}). \\ &= -237.2\ kJ\,mol^{-1}.\end{aligned}$$

c. The heat released in the fuel cell reaction is the difference between the enthalpy change (the total energy available) and the reversible work that was expended:

$$\begin{aligned}\Delta H^o - \Delta G^o &= T\Delta S^o \\ &= (298\ K)(-163\ JK^{-1}mol^{-1}) \\ &= -48,800\ J\,mol^{-1} \\ &= -48.8\ kJ\,mol^{-1}.\end{aligned}$$

The foregoing example illustrates an important advantage of fuel cells. Although direct combustion of a mole of hydrogen gas yields more energy than is produced by the same net reaction within the fuel cell, the latter, in the form of electrical energy, can be utilized at nearly 100-percent energy efficiency by a motor or some other electrical device. If the thermal energy released by direct combustion were supplied to a heat engine, second-law considerations would require that at least half of this energy be "wasted" to the surroundings.

ΔG vs. ΔG°: what's the difference?

ΔG° refer to *single, specific chemical changes* in which all components (reactants and products) are in their *standard states*.

The ΔG_f^o of a substance, like ΔH_f^o, refers to the reaction in which that substance is formed from the elements as they exist in their most stable forms at 1 atm pressure and (usually) 298 K. Both of these terms are by definition zero for the elements in their standard states. There are only a few common cases in which this might create some ambiguity:

Table 12.4.1: Standard Gibbs Energies of Select Substances

Stable Form	ΔG_f^o (kJ mol^{-1})	Unstable Form	ΔG_f^o (kJ mol^{-1})
$O_2(g)$	0	$O_3(g)$	163.2
C(graphite)	0	C(diamond)	2.9
S(rhombic)	0	S(monoclinic)	0.1
P(white)	0	$P_4(g)$	24.4

Ions in aqueous solution are a special case; their standard free energies are relative to the hydrated hydrogen ion $H^+(aq)$ which is assigned $\Delta G_f^o = 0$.

ΔG is very different from ΔG°. The distinction is nicely illustrated in Figure 12.4.5 in which ΔG is plotted on a vertical axis for two hypothetical reactions having opposite signs of ΔG°. The horizontal axis schematically expresses the relative concentrations of reactants and products at any point of the process. Note that the origin corresponds to the composition at which half of the reactants have been converted into products.

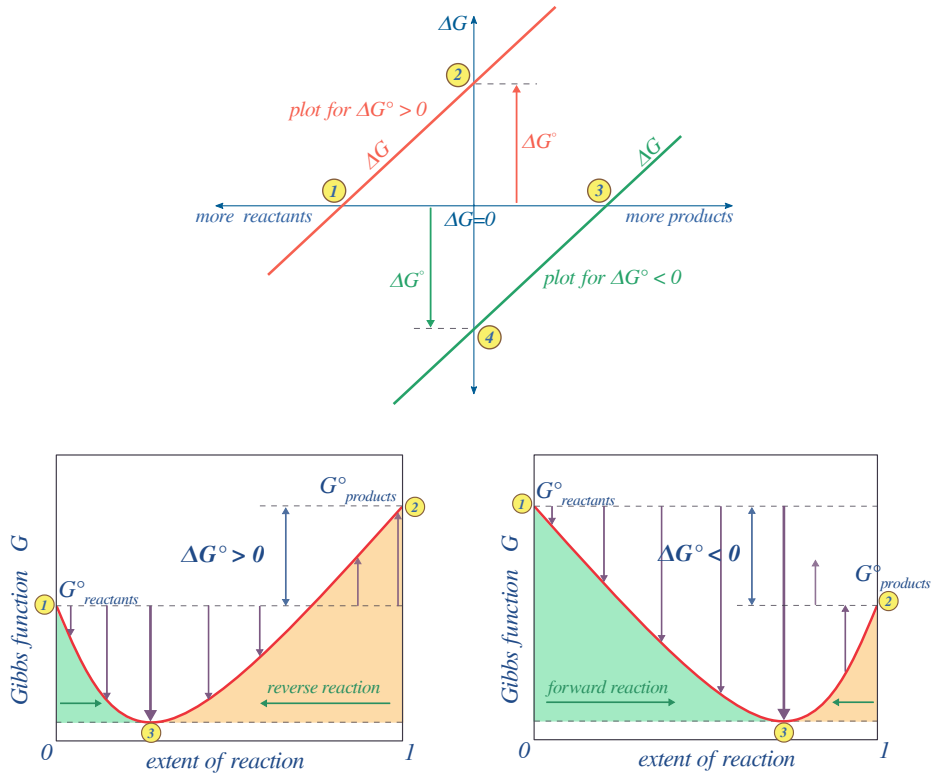


Figure 12.4.5: (CC BY 4.0; Ümit Kaya via LibreTexts)

Take careful note of the following:

- for the $\Delta G° > 0$ reaction. Notice that there are an infinite number of these values, depending on the progress of the reaction. In contrast there is only a single value ② of $\Delta G°$, corresponding to the composition at which $\Delta G = 0$ (①).
- At this point, some products have been formed, but the composition is still dominated by reactants.
- If we begin at a composition to the left of ①, ΔG will be negative and the composition will move to the right. Similarly if we begin with a composition to the right of ①, ΔG will be positive and the composition will move to the left.
- The plot on the right is for the $\Delta G° < 0$ reaction, for which $\Delta G°$ is shown at ④. At its equilibrium point ③, there are more products than reactants. If we start at a composition to the right of ③, the composition will tend to move to the left. If the initial composition is to the left of ③, the reaction will tend to proceed to the right.
- What would happen if $\Delta G°$ were 0? The equilibrium point of such a reaction would be at the origin, corresponding to half the reactants being converted to products.

The important principle you should understand from this is that a negative $\Delta G°$ does not mean that the reactants will be completely transformed into products. By the same token, a positive $\Delta G°$ does not mean that no products are formed at all.

It should now be clear from the discussion above that a given reaction carried out under standard conditions is characterized by a *single value* of $\Delta G°$.

The reason for the Gibbs energy minimum at equilibrium relates to the increase in entropy when products and reactants coexist in the same phase. As seen in the plot, even a minute amount of "contamination" of products by reactants reduces the free energy below that of the pure products. In contrast, composition of a chemical reaction system undergoes continual change until the equilibrium state is reached. So the a single reaction can have an infinite number of ΔG values, reflecting the infinite possible compositions between the extremes of pure reactants (zero extent of reaction) and pure products (unity extent of reaction).

In the example of a reaction A → B, depicted in the above diagram, the standard free energy of the products ② is smaller than that of the reactants ①, so the reaction will take place spontaneously. This does not mean that each mole of pure A will be converted into one mole of pure B. For reactions in which products and reactants occupy a single phase (gas or solution), the meaning of "spontaneous" is that the equilibrium composition ③ will correspond to an extent of reaction greater than 0.5 but smaller than unity.Note, however, that for $\Delta G°$ values in excess of about ±50 kJ mol^{-1}, the equilibrium composition will be negligibly different

from zero or unity extent-of-reaction. The physical meaning of ΔG is that it tells us how far the free energy of the system has changed from $G°$ of the pure reactants ①. As the reaction proceeds to the right, the composition changes, and ΔG begins to fall. When the composition reaches ③, ΔG reaches its minimum value and further reaction would cause it to rise. But because free energy can only decrease but never increase, this does not happen. The composition of the system remains permanently at its equilibrium value.

A *G vs.* extent-of-reaction diagram for a non-spontaneous reaction can be interpreted in a similar way; the equilibrium composition ③ will correspond to an extent of reaction greater than zero but less than 0.5. In this case, the minimum at ③ reflects the increase in entropy when the reactants are "contaminated" by a small quantity of products.

If all this detail about ΔG seems a bit overwhelming, do not worry: it all gets hidden in the equilibrium constant and reaction quotient that we discuss in the next lesson!

Interpretation of Standard Gibbs energy changes

Although it is ΔG rather than ΔG^o that serves as a criterion for spontaneous change at constant temperature and pressure, ΔG^o values are so readily available that they are often used to get a rough idea of whether a given chemical change is possible. This is practical to do in some cases, but not in others:

Example

It generally works for reactions such as

$$4\,NH_3(g) + 5\,O_2(g) \rightarrow 4\,NO(g) + 6\,H_2O(g)$$

with $\Delta G^o = -1,010\ kJ$.

(industrially important for the manufacture of nitric acid) because ΔG^o is so negative that the reaction will be spontaneous and virtually complete under just about any reasonable set of conditions.

Example

The following reaction expresses the fact that the water molecule is thermodynamically stable:

$$2\,H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l)$$

with $\Delta G^o = -237.2\ kJ$.

Note that this refers to *liquid* water (the standard state of H_2O at 25°). If you think about it, a negative standard Gibbs energy of formation (of which this is an example) can in fact be considered a definition of molecular stability.

Example

Similarly, dissociation of dihydrogen into its atoms is highly unlikely under standard conditions:

$$H_2O(g) \rightarrow 2\,H(g) + O(g)$$

with $\Delta G^o = +406.6\ kJ$.

Again, an analogous situation would apply to any stable molecule.

Example

Now consider the dissociation of dinitrogen tetroxide

$$N_2O_4(g) \rightarrow 2\,NO_2(g)$$

with $\Delta G^o = +2.8 kJ$.

in which the positive value of $\Delta G°$ tells us that N_2O_4 at 1 atm pressure will not change into two moles of NO_2 at the same pressure, but owing to the small absolute value of $\Delta G°$, we can expect the spontaneity of the process to be quite sensitive to

both the temperature (as shown in the table below) and to the pressure in exactly the way the Le Chatelier principle predicts.

Example

For reactions involving dissolved ions, one has to be quite careful. Thus for the dissociation of the weak hydrofluoric acid

$$\mathrm{HF(aq) \rightarrow H^+(aq) + F^-(aq)}$$

with $\Delta G^o = -317\ kJ$.

it is clear that a 1 mol/L solution of HF will not dissociate into 1M ions, but this fact is not very useful because if the HF is added to water, the initial concentration of the fluoride ion will be zero (and that of H^+ very close to zero), and the Le Chatelier principle again predicts that *some* dissociation will be spontaneous.

Example

It is common knowledge that dissociation of water into hydrogen- and hydroxyl ions occurs only very sparingly:

$$\mathrm{H_2O(l) \rightarrow H^+(aq) + OH^-(aq)}$$

with $\Delta G^o = 79.9\ kJ$.

which correctly predicts that the water will not form 1M (effective concentration) of the ions, but this is hardly news if you already know that the product of these ion concentrations can never exceed 10^{-14} at 298K.

Example

Finally, consider this most familiar of all phase change processes, the vaporization of liquid water:

$$\mathrm{H_2O(l) \rightarrow H_2O(g)}$$

with $\Delta G^o = 8.58\ kJ$.

Conversion of liquid water to its vapor at 1 atm partial pressure does not take place at 25° C, at which temperature the equilibrium partial pressure of the vapor (the "vapor pressure") is only 0.031 atm (23.8 torr.) Gaseous H_2O at a pressure of 1 atm can only exist at 100° C. Of course, water left in an open container at room temperature will spontaneously evaporate if the partial pressure of water vapor in the air is less than 0.031 atm, corresponding to a relative humidity of under 100%

Finding the Equilibrium Temperature

A reaction is in its equilibrium state when

$$\Delta G = \Delta H - T\Delta S = 0 \tag{12.4.10}$$

The temperature at which this occurs is given by

$$T = \frac{\Delta H}{\Delta S} \tag{12.4.11}$$

If we approximate ΔH by ΔH^o and ΔS by ΔS^o, so Equation 12.4.10would be

$$\Delta G \approx \Delta H^o - T\Delta S^o = 0 \tag{12.4.12}$$

We can then estimate the normal boiling point of a liquid. From the following thermodynamic data for water:

$H_2O(l)$	→	$H_2O(g)$	
−285.9		−241.8	$\Delta H°$ = +44.1 kJ
69.9		188.7	$\Delta S°$ = +118.7 J K^{-1}

Caution!

Because ΔH° values are normally expressed in kilojoules while ΔS° is given in joules, a very common student error is to overlook the need to express both in the same units.

We find that liquid water is in equilibrium with water vapor at a partial pressure of 1 atm when the temperature is

$$T = \frac{44,100\ J}{118.7\ J\,K^{-1}} = 371.5\ K \tag{12.4.13}$$

But "*the normal boiling point of water is 373 K*", you say? Very true. The reason we are off here is that both ΔH° and ΔS° have their own temperature dependencies; we are using the "standard" 25° values without correcting them to 100° C. Nevertheless, if you think about it, the fact that we can estimate the boiling point of a liquid from a table of thermodynamic data should be rather impressive! Of course, the farther one gets from 298 K, the more unreliable will be the result. Thus for the dissociation of dihydrogen into its atoms,

$$\begin{array}{lll} H_2(g) & \rightarrow & 2\ H(g) \\ 0 & & 2 \times (218.0) \qquad \Delta H^\circ = +436.0\ kJ \\ 130.6 & & 2 \times (114.6) \qquad \Delta S^\circ = +98.6\ J\ K^{-1} \end{array}$$

$$T = \frac{436,000\ J}{98.6\ JK^{-1}} = 4,420\ K \tag{12.4.14}$$

All one can say here is that H_2 will break down at something over 3000 K or so. (You may already know that *all* molecules will dissociate into their atoms at high temperatures.) We tend to think of high temperatures as somehow "forcing" molecules to dissociate into their atoms, but this is wrong. In order to get the H–H bond to vibrate so violently through purely thermal excitation that the atoms would fly apart, a temperature more like 30,000 K would be required. The proper interpretation is at the temperature corresponding to $\Delta H/T\Delta S$, the molecule *spontaneously* absorbs energy from the surroundings sufficient to overcome the H-H bond strength.

Predicting the Effects of Temperature

The $T\Delta S$ term interacts with the ΔH term in ΔG to determine whether the reaction can take place at a given temperature. This can be more clearly understood by examining plots of $T\Delta S^o$ and ΔH^o as functions of the temperature for some actual reactions. Of course these parameters refer to standard states that generally do not correspond to the temperatures, pressures, or concentrations that might be of interest in an actual case. Nevertheless, these quantities are easily found and they can usefully predict the way that temperature affects these systems.

Case 1: Exothermic reaction, ΔS° > 0

$$\mathrm{C(graphite) + O_2(g) \rightarrow CO_2(g)}$$

- $\Delta H^o = -393\ kJ$
- $\Delta G^o = -394\ kJ$ at $298\ K$

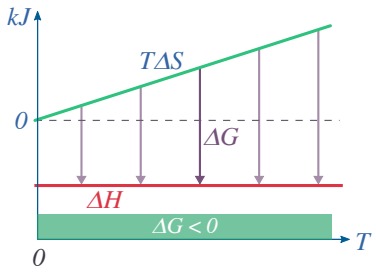


Figure 12.4.6: (CC BY 4.0; Ümit Kaya via LibreTexts)

This *combustion reaction*, like most such reactions, is **spontaneous at all temperatures**. The positive entropy change is due mainly to the greater mass of CO_2 molecules compared to those of O_2.

Case 2: Exothermic reaction, ΔS° < 0

$$3\,H_2 + N_2 \rightarrow 2\,NH_3(g)$$

- $\Delta H^o = -46.2\ kJ$
- $\Delta G^o = -16.4\ kJ$ at $298\ K$

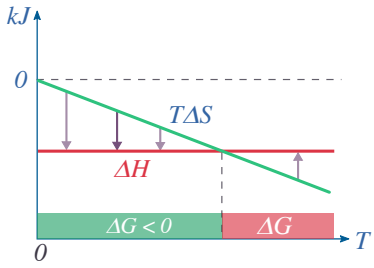


Figure 12.4.7: (CC BY 4.0; Ümit Kaya via LibreTexts)

The decrease in moles of gas in the **Haber ammonia synthesis** drives the entropy change negative, making the reaction **spontaneous only at low temperatures**. Thus higher T, which speeds up the reaction, also reduces its extent.

Case 3: Endothermic reaction, ΔS° > 0

$$N_2O_4(g) \rightarrow 2\,NO_2(g)$$

- $\Delta H^o = 55.3\ kJ$
- $\Delta G^o = +2.8\ kJ$ at $298\ K$

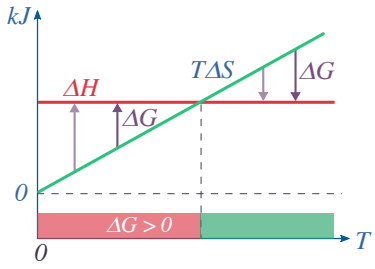


Figure 12.4.8: (CC BY 4.0; Ümit Kaya via LibreTexts)

Dissociation reactions are typically endothermic with positive entropy change, and are therefore **spontaneous at high temperatures**. Ultimately, all molecules decompose to their atoms at sufficiently high temperatures.

Case 4: Endothermic Reaction, ΔS° < 0

$$\tfrac{1}{2}N_2(g) + O_2(g) \rightarrow NO_2(g)$$

- $\Delta H^\circ = 33.2\ kJ$
- $\Delta S^o = -249\ J\,K^{-1}$
- $\Delta G^o = +51.3\ kJ$ at $298\ K$

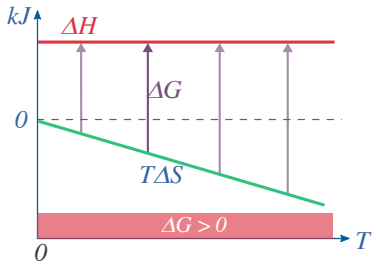


Figure 12.4.9: (CC BY 4.0; Ümit Kaya via LibreTexts)

This reaction is **not spontaneous at any temperature**, meaning that *its reverse is always spontaneous*. But because the reverse reaction is kinetically inhibited, NO_2 can exist indefinitely at ordinary temperatures even though it is thermodynamically unstable.

Concluding remarks on Gibbs Energy

The appellation “free energy” for G has led to so much confusion that many scientists now refer to it simply as the *Gibbs energy*. The “free” part of the older name reflects the steam-engine origins of thermodynamics with its interest in converting heat into work: ΔG is the maximum amount of energy, which can be “freed” from the system to perform useful work. By "useful", we mean work other than that which is associated with the expansion of the system. This is most commonly in the form of electrical work (moving electric charge through a potential difference), but other forms of work (osmotic work, increase in surface area) are also possible.

A much more serious difficulty with the Gibbs function, particularly in the context of chemistry, is that although G has the *units* of energy (joules, or in its intensive form, J mol^{-1}), it lacks one of the most important attributes of energy in that it is not *conserved*. Thus, although the free energy always falls when a gas expands or a chemical reaction takes place spontaneously, there need be no compensating *increase* in energy anywhere else. Referring to G as an energy also reinforces the false but widespread notion that a fall in energy must accompany any change. But if we accept that energy is conserved, it is apparent that the only necessary condition for change (whether the dropping of a weight, expansion of a gas, or a chemical reaction) is the *redistribution* of energy. The quantity \(–ΔG\) associated with a process represents the quantity of energy that is “shared and spread”, which as we have already explained is the meaning of the increase in the entropy. The quotient $-\Delta G/T$ is in fact identical with ΔS_{total}, the entropy change of the world, whose increase is the primary criterion for any kind of change.

G differs from the thermodynamic quantities H and S in another significant way: it has no physical reality as a property of matter, whereas H and S can be related to the quantity and distribution of energy in a collection of molecules. The free energy is simply a useful construct that serves as a criterion for change and makes calculations easier.

What Gibbs Energy is not...

- Gibbs Energy is not free energy
- Gibbs Energy is not energy
- Gibbs Energy is not even "real"

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12.5: The Law of Mass Action for Related and Simultaneous Equilibria

Learning Objectives

- To know the relationship between the equilibrium constant and the rate constants for the forward and reverse reactions.
- To write an equilibrium constant expression for any reaction.

Relationship among Equilibrium Expressions

Chemists frequently need to know the equilibrium constant for a reaction that has not been previously studied. In such cases, the desired reaction can often be written as the sum of other reactions for which the equilibrium constants are known. The equilibrium constant for the unknown reaction can then be calculated from the tabulated values for the other reactions.

To illustrate this procedure, let's consider the reaction of N_2 with O_2 to give NO_2. This reaction is an important source of the NO_2 that gives urban smog its typical brown color. The reaction normally occurs in two distinct steps. In the first reaction (1), N_2 reacts with O_2 at the high temperatures inside an internal combustion engine to give NO. The released NO then reacts with additional O_2 to give NO_2 (2). The equilibrium constant for each reaction at 100°C is also given.

1. $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)} \qquad K_1 = 2.0 \times 10^{-25}$
2. $2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)} \qquad K_2 = 6.4 \times 10^{9}$

Summing reactions (1) and (2) gives the overall reaction of N_2 with O_2:

3. $N_{2(g)} + 2O_{2(g)} \rightleftharpoons 2NO_{2(g)} \qquad K_3 = ?$

The equilibrium constant expressions for the reactions are as follows:

$$K_1 = \frac{[NO]^2}{[N_2][O_2]} \qquad K_2 = \frac{[NO_2]^2}{[NO]^2[O_2]} \qquad K_3 = \frac{[NO_2]^2}{[N_2][O_2]^2} \tag{12.5.1}$$

What is the relationship between K_1, K_2, and K_3, all at 100°C? The expression for K_1 has $[NO]^2$ in the numerator, the expression for K_2 has $[NO]^2$ in the denominator, and $[NO]^2$ does not appear in the expression for K_3. Multiplying K_1 by K_2 and canceling the $[NO]^2$ terms,

$$K_1K_2 = \frac{\cancel{[NO]^2}}{[N_2][O_2]} \times \frac{[NO_2]^2}{\cancel{[NO]^2}[O_2]} = \frac{[NO_2]^2}{[N_2][O_2]^2} = K_3 \tag{12.5.2}$$

Thus the product of the equilibrium constant expressions for K_1 and K_2 is the same as the equilibrium constant expression for K_3:

$$K_3 = K_1K_2 = (2.0 \times 10^{-25})(6.4 \times 10^{9}) = 1.3 \times 10^{-15} \tag{12.5.3}$$

The equilibrium constant for a reaction that is the sum of two or more reactions is equal to the product of the equilibrium constants for the individual reactions. In contrast, recall that according to Hess's Law, ΔH for the sum of two or more reactions is the sum of the ΔH values for the individual reactions.

Note

To determine K for a reaction that is the sum of two or more reactions, add the reactions but multiply the equilibrium constants.

Example 12.5.6

The following reactions occur at 1200°C:

1. $CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)} \qquad K_1 = 9.17 \times 10^{-2}$
2. $CH_{4(g)} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + 4H_{2(g)} \qquad K_2 = 3.3 \times 10^{4}$

Calculate the equilibrium constant for the following reaction at the same temperature.

3. $CO_{(g)} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + H_2O_{(g)} + H_{2(g)} \qquad K_3 = ?$

Given: two balanced equilibrium equations, values of K, and an equilibrium equation for the overall reaction

Asked for: equilibrium constant for the overall reaction

Strategy:

Arrange the equations so that their sum produces the overall equation. If an equation had to be reversed, invert the value of K for that equation. Calculate K for the overall equation by multiplying the equilibrium constants for the individual equations.

Solution:

The key to solving this problem is to recognize that reaction 3 is the sum of reactions 1 and 2:

$$CO_{(g)} + \cancel{3H_{2(g)}} \rightleftharpoons \cancel{CH_{4(g)}} + H_2O_{(g)} \tag{12.5.4}$$

$$\cancel{CH_{4(g)}} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + \cancel{3H_{2(g)}} + H_{2(g)} \tag{12.5.5}$$

$$CO_{(g)} + 3H_{2(g)} \rightleftharpoons CS_{2(g)} + H_2O_{(g)} + H_{2(g)} \tag{12.5.6}$$

The values for K_1 and K_2 are given, so it is straightforward to calculate K_3:

$$K_3 = K_1K_2 = (9.17 \times 10^{-2})(3.3 \times 10^4) = 3.03 \times 10^3 \tag{12.5.7}$$

? Exercise 12.5.6

In the first of two steps in the industrial synthesis of sulfuric acid, elemental sulfur reacts with oxygen to produce sulfur dioxide. In the second step, sulfur dioxide reacts with additional oxygen to form sulfur trioxide. The reaction for each step is shown, as is the value of the corresponding equilibrium constant at 25°C. Calculate the equilibrium constant for the overall reaction at this same temperature.

1. $\frac{1}{8}S_{8(s)} + O_{2(g)} \rightleftharpoons SO_{2(g)}$ $\quad K_1 = 4.4 \times 10^{53}$
2. $SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)}$ $\quad K_2 = 2.6 \times 10^{12}$
3. $\frac{1}{8}S_{8(s)} + \frac{3}{2}O_{2(g)} \rightleftharpoons SO_{3(g)}$ $\quad K_3 = ?$

Answer

$K_3 = 1.1 \times 10^{66}$

Summary

An equilibrium system that contains products and reactants in a single phase is a homogeneous equilibrium; a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium. When a reaction can be expressed as the sum of two or more reactions, its equilibrium constant is equal to the product of the equilibrium constants for the individual reactions.

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12.6: Equilibrium Calculations for Gas-Phase and Heterogenous Reactions

Learning Objectives

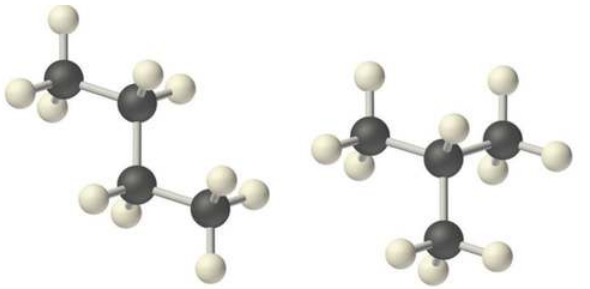
- To solve quantitative problems involving chemical equilibriums.

There are two fundamental kinds of equilibrium problems:

1. those in which we are given the concentrations of the reactants and the products at equilibrium (or, more often, information that allows us to calculate these concentrations), and we are asked to calculate the equilibrium constant for the reaction; and
2. those in which we are given the equilibrium constant and the initial concentrations of reactants, and we are asked to calculate the concentration of one or more substances at equilibrium. In this section, we describe methods for solving both kinds of problems.

Calculating an Equilibrium Constant from Equilibrium Concentrations

The equilibrium constant for the decomposition of $CaCO_{3(s)}$ to $CaO_{(s)}$ and $CO_{2(g)}$ is $K = [CO_2]$. At 800°C, the concentration of CO_2 in equilibrium with solid $CaCO_3$ and CaO is $2.5 \times 10^{-3}\ M$. Thus K at 800°C is 2.5×10^{-3} (remember that equilibrium constants are unitless). A more complex example of this type of problem is the conversion of n-butane, an additive used to increase the volatility of gasoline, into isobutane (2-methylpropane).



This reaction can be written as follows:

$$\mathrm{n\text{-}butane}_{(g)} \rightleftharpoons \mathrm{isobutane}_{(g)} \tag{12.6.1}$$

and the equilibrium constant $K = [\mathrm{isobutane}]/[\mathrm{n\text{-}butane}]$. At equilibrium, a mixture of n-butane and isobutane at room temperature was found to contain 0.041 M isobutane and 0.016 M n-butane. Substituting these concentrations into the equilibrium constant expression,

$$\begin{aligned} K &= \frac{[\mathrm{isobutane}]}{[\texttt{\textbackslash texT}n-butane]} \\ &= \frac{0.041\ M}{0.016\ M} \\ &= 2.6 \end{aligned}$$

Thus the equilibrium constant for the reaction as written is 2.6.

Example 12.6.1

The reaction between gaseous sulfur dioxide and oxygen is a key step in the industrial synthesis of sulfuric acid:

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

A mixture of SO_2 and O_2 was maintained at 800 K until the system reached equilibrium. The equilibrium mixture contained

- $5.0 \times 10^{-2}\ M\ SO_3$,

- $3.5 \times 10^{-3}\ M\ O_2$, and
- $3.0 \times 10^{-3}\ M\ SO_2$.

Calculate K and K_p at this temperature.

Given: balanced equilibrium equation and composition of equilibrium mixture

Asked for: equilibrium constant

Strategy

Write the equilibrium constant expression for the reaction. Then substitute the appropriate equilibrium concentrations into this equation to obtain K.

Solution

Substituting the appropriate equilibrium concentrations into the equilibrium constant expression,

$$K = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(5.0 \times 10^{-2})^2}{(3.0 \times 10^{-3})^2(3.5 \times 10^{-3})} = 7.9 \times 10^4$$

To solve for K_p, we need to identify Δn where $\Delta n = 2 - 3 = -1$ and then

$$K_p = K(RT)^{\Delta n}$$

$$K_p = 7.9 \times 10^4[(0.08206\ L \cdot atm/mol \cdot K)(800K)]^{-1}$$

$$K_p = 1.2 \times 10^3$$

? Exercise 12.6.1

Hydrogen gas and iodine react to form hydrogen iodide via the reaction

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

A mixture of H_2 and I_2 was maintained at 740 K until the system reached equilibrium. The equilibrium mixture contained

- $1.37 \times 10^{-2}\ M\ HI$,
- $6.47 \times 10^{-3}\ M\ H_2$, and
- $5.94 \times 10^{-4}\ M\ I_2$.

Calculate K and K_p for this reaction.

Answer (K)

$K = 48.8$

Answer (K_p)

$K_p = 48.8$

Chemists are not often given the concentrations of all the substances, and they are not likely to measure the equilibrium concentrations of all the relevant substances for a particular system. In such cases, we can obtain the equilibrium concentrations from the initial concentrations of the reactants and the balanced chemical equation for the reaction, as long as the equilibrium concentration of one of the substances is known. Example 12.6.2shows one way to do this.

✓ Example 12.6.2

A 1.00 mol sample of $NOCl$ was placed in a 2.00 L reactor and heated to 227°C until the system reached equilibrium. The contents of the reactor were then analyzed and found to contain 0.056 mol of Cl_2. Calculate K at this temperature. The equation for the decomposition of $NOCl$ to NO and Cl_2 is as follows:

$$\mathrm{2\,NOCl(g) \rightleftharpoons 2\,NO(g) + Cl_2(g)}$$

Given: balanced equilibrium equation, amount of reactant, volume, and amount of one product at equilibrium

Asked for: K

Strategy:

A. Write the equilibrium constant expression for the reaction. Construct a table showing the initial concentrations, the changes in concentrations, and the final concentrations (as initial concentrations plus changes in concentrations).
B. Calculate all possible initial concentrations from the data given and insert them in the table.
C. Use the coefficients in the balanced chemical equation to obtain the changes in concentration of all other substances in the reaction. Insert those concentration changes in the table.
D. Obtain the final concentrations by summing the columns. Calculate the equilibrium constant for the reaction.

Solution

A The first step in any such problem is to balance the chemical equation for the reaction (if it is not already balanced) and use it to derive the equilibrium constant expression. In this case, the equation is already balanced, and the equilibrium constant expression is as follows:

$$K = \frac{[NO]^2[Cl_2]}{[NOCl]^2}$$

To obtain the concentrations of $NOCl$, NO, and Cl_2 at equilibrium, we construct a table showing what is known and what needs to be calculated. We begin by writing the balanced chemical equation at the top of the table, followed by three lines corresponding to the initial concentrations, the changes in concentrations required to get from the initial to the final state, and the final concentrations.

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	$[NOCl]$	$[NO]$	$[Cl_2]$
Initial			
Change			
Final			

B Initially, the system contains 1.00 mol of $NOCl$ in a 2.00 L container. Thus $[NOCl]_i = 1.00\ mol/2.00\ L = 0.500\ M$ The initial concentrations of NO and Cl_2 are 0 M because initially no products are present. Moreover, we are told that at equilibrium the system contains 0.056 mol of Cl_2 in a 2.00 L container, so $[Cl_2]_f = 0.056\ mol/2.00\ L = 0.028\ M$ We insert these values into the following table:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	$[NOCl]$	$[NO]$	$[Cl_2]$
Initial	0.500	0	0
Change			
Final			0.028

C We use the stoichiometric relationships given in the balanced chemical equation to find the change in the concentration of Cl_2, the substance for which initial and final concentrations are known:

$$\Delta[Cl_2] = 0.028\ M_{(final)} - 0.00\ M_{(initial)}] = +0.028\ M$$

According to the coefficients in the balanced chemical equation, 2 mol of NO are produced for every 1 mol of Cl_2, so the change in the NO concentration is as follows:

$$\Delta[NO] = \left(\frac{0.028\ \cancel{mol\ Cl_2}}{L}\right)\left(\frac{2\ mol\ NO}{1\ \cancel{mol\ Cl_2}}\right) = 0.056\ M$$

Similarly, 2 mol of $NOCl$ are consumed for every 1 mol of Cl_2 produced, so the change in the $NOCl$ concentration is as follows:

$$\Delta[NOCl] = \left(\frac{0.028\ \cancel{mol\ Cl_2}}{L}\right)\left(\frac{-2\ mol\ NOCl}{1\ \cancel{mol\ Cl_2}}\right) = -0.056\ M$$

We insert these values into our table:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	$[NOCl]$	$[NO]$	$[Cl_2]$
Initial	0.500	0	0
Change	−0.056	+0.056	+0.028
Final			0.028

D We sum the numbers in the $[NOCl]$ and $[NO]$ columns to obtain the final concentrations of NO and $NOCl$:

$$[NO]_f = 0.000\ M + 0.056\ M = 0.056\ M$$

$$[NOCl]_f = 0.500\ M + (-0.056\ M) = 0.444M$$

We can now complete the table:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	$[NOCl]$	$[NO]$	$[Cl_2]$
initial	0.500	0	0
change	−0.056	+0.056	+0.028
final	0.444	0.056	0.028

We can now calculate the equilibrium constant for the reaction:

$$K = \frac{[NO]^2[Cl_2]}{[NOCl]^2} = \frac{(0.056)^2(0.028)}{(0.444)^2} = 4.5 \times 10^{-4}$$

? Exercise 12.6.2

The German chemist Fritz Haber (1868–1934; Nobel Prize in Chemistry 1918) was able to synthesize ammonia (NH_3) by reacting $0.1248\ M\ H_2$ and $0.0416\ M\ N_2$ at about 500°C. At equilibrium, the mixture contained 0.00272 M NH_3. What is K for the reaction

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

at this temperature? What is K_p?

Answer (K)

$K = 0.105$

Answer (K_p)

$K_p = 2.61 \times 10^{-5}$

Calculating Equilibrium Concentrations from the Equilibrium Constant

To describe how to calculate equilibrium concentrations from an equilibrium constant, we first consider a system that contains only a single product and a single reactant, the conversion of n-butane to isobutane (Equation 12.6.1), for which K = 2.6 at 25°C. If we begin with a 1.00 M sample of n-butane, we can determine the concentration of n-butane and isobutane at equilibrium by constructing a table showing what is known and what needs to be calculated, just as we did in Example 12.6.2

$$\text{n-butane}(g) \rightleftharpoons \text{isobutane}(g) \tag{12.6.2}$$

ICE	$[\text{n-butane}_{(g)}]$	$[\text{isobutane}_{(g)}]$
Initial		
Change		
Final		

The initial concentrations of the reactant and product are both known: [n-butane]i = 1.00 M and [isobutane]i = 0 M. We need to calculate the equilibrium concentrations of both n-butane and isobutane. Because it is generally difficult to calculate final concentrations directly, we focus on the change in the concentrations of the substances between the initial and the final (equilibrium) conditions. If, for example, we define the change in the concentration of isobutane (Δ[isobutane]) as +x, then the change in the concentration of n-butane is Δ[n-butane] = −x. This is because the balanced chemical equation for the reaction tells us that 1 mol of n-butane is consumed for every 1 mol of isobutane produced. We can then express the final concentrations in terms of the initial concentrations and the changes they have undergone.

$$\text{n-butane}_{(g)} \rightleftharpoons \text{isobutane}_{(g)} \tag{12.6.3}$$

ICE	$[\text{n-butane}_{(g)}]$	$[\text{isobutane}_{(g)}]$
Initial	1.00	0
Change	−x	+x
Final	(1.00 − x)	(0 + x) = x

Substituting the expressions for the final concentrations of n-butane and isobutane from the table into the equilibrium equation,

$$K = \frac{[\text{isobutane}]}{[\text{n-butane}]} = \frac{x}{1.00 - x} = 2.6 \tag{12.6.4}$$

Rearranging and solving for x,

$$\begin{aligned} x &= 2.6(1.00 - x) = 2.6 - 2.6x \\ x + 2.6x &= 2.6 \\ x &= 0.72 \end{aligned}$$

We obtain the final concentrations by substituting this x value into the expressions for the final concentrations of n-butane and isobutane listed in the table:

$$[\text{n-butane}]_f = (1.00 - x)M = (1.00 - 0.72)M = 0.28\ M \tag{12.6.5}$$

$$[\text{isobutane}]_f = (0.00 + x)M = (0.00 + 0.72)M = 0.72\ M \tag{12.6.6}$$

We can check the results by substituting them back into the equilibrium constant expression to see whether they give the same K that we used in the calculation:

$$K = \frac{[\text{isobutane}]}{[\text{n-butane}]} = \left(\frac{0.72\ \cancel{M}}{0.28\ \cancel{M}}\right) = 2.6 \tag{12.6.7}$$

This is the same K we were given, so we can be confident of our results.

Example 12.6.3 illustrates a common type of equilibrium problem that you are likely to encounter.

Example 12.6.3

The water–gas shift reaction is important in several chemical processes, such as the production of H_2 for fuel cells. Thisreaction can be written as follows:

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$

$K = 0.106$ at 700 K. If a mixture of gases that initially contains 0.0150 M H_2 and 0.0150 M CO_2 is allowed to equilibrate at 700 K, what are the final concentrations of all substances present?

Given: balanced equilibrium equation, K, and initial concentrations

Asked for: final concentrations

Strategy:

A. Construct a table showing what is known and what needs to be calculated. Define x as the change in the concentration of one substance. Then use the reaction stoichiometry to express the changes in the concentrations of the other substances in terms of x. From the values in the table, calculate the final concentrations.
B. Write the equilibrium equation for the reaction. Substitute appropriate values from the ICE table to obtain x.
C. Calculate the final concentrations of all species present. Check your answers by substituting these values into the equilibrium constant expression to obtain K.

Solution

A The initial concentrations of the reactants are $[H_2]_i = [CO_2]_i = 0.0150\ M$. Just as before, we will focus on the change in the concentrations of the various substances between the initial and final states. If we define the change in the concentration of H_2O as x, then $\Delta[H_2O] = +x$. We can use the stoichiometry of the reaction to express the changes in the concentrations of the other substances in terms of x. For example, 1 mol of CO is produced for every 1 mol of H_2O, so the change in the CO concentration can be expressed as $\Delta[CO] = +x$. Similarly, for every 1 mol of H_2O produced, 1 mol each of H_2 and CO_2 are consumed, so the change in the concentration of the reactants is $\Delta[H_2] = \Delta[CO_2] = -x$. We enter the values in the following table and calculate the final concentrations.

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$

ICE	$[H_2]$	$[CO_2]$	$[H_2O]$	$[CO]$
Initial	0.0150	0.0150	0	0
Change	−x	−x	+x	+x
Final	(0.0150 − x)	(0.0150 − x)	x	x

B We can now use the equilibrium equation and the given K to solve for x:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(x)(x)}{(0.0150-x)(0.0150-x)} = \frac{x^2}{(0.0150-x)^2} = 0.106$$

We could solve this equation with the quadratic formula, but it is far easier to solve for x by recognizing that the left side of the equation is a perfect square; that is,

$$\frac{x^2}{(0.0150-x)^2} = \left(\frac{x}{0.0150-x}\right)^2 = 0.106$$

Taking the square root of the middle and right terms,

$$\frac{x^2}{(0.0150-x)^2} = (0.106)^{1/2} = 0.326$$

$$x = (0.326)(0.0150) - 0.326x$$

$$1.326x = 0.00489$$

$$x = 0.00369 = 3.69 \times 10^{-3}$$

C The final concentrations of all species in the reaction mixture are as follows:

- $[H_2]_f = [H_2]_i + \Delta[H_2] = (0.0150 - 0.00369)\ M = 0.0113\ M$
- $[CO_2]_f = [CO_2]_i + \Delta[CO_2] = (0.0150 - 0.00369)\ M = 0.0113\ M$
- $[H_2O]_f = [H_2O]_i + \Delta[H_2O] = (0 + 0.00369)\ M = 0.00369\ M$
- $[CO]_f = [CO]_i + \Delta[CO] = (0 + 0.00369)\ M = 0.00369\ M$

We can check our work by inserting the calculated values back into the equilibrium constant expression:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(0.00369)^2}{(0.0113)^2} = 0.107$$

To two significant figures, this K is the same as the value given in the problem, so our answer is confirmed.

? Exercise 12.6.3

Hydrogen gas reacts with iodine vapor to give hydrogen iodide according to the following chemical equation:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

$K = 54$ at 425°C. If 0.172 M H_2 and I_2 are injected into a reactor and maintained at 425°C until the system equilibrates, what is the final concentration of each substance in the reaction mixture?

Answer

$[HI]_f = 0.270\ M\ [H_2]_f = [I_2]_f = 0.037\ M$

In Example 12.6.3, the initial concentrations of the reactants were the same, which gave us an equation that was a perfect square and simplified our calculations. Often, however, the initial concentrations of the reactants are not the same, and/or one or more of the products may be present when the reaction starts. Under these conditions, there is usually no way to simplify the problem, and we must determine the equilibrium concentrations with other means. Such a case is described in Example 12.6.4

✓ Example 12.6.4

In the water–gas shift reaction shown in Example 12.6.3, a sample containing 0.632 M CO_2 and 0.570 M H_2 is allowed to equilibrate at 700 K. At this temperature, $K = 0.106$. What is the composition of the reaction mixture at equilibrium?

Given: balanced equilibrium equation, concentrations of reactants, and K

Asked for: composition of reaction mixture at equilibrium

Strategy:

A. Write the equilibrium equation. Construct a table showing the initial concentrations of all substances in the mixture. Complete the table showing the changes in the concentrations (x) and the final concentrations.
B. Write the equilibrium constant expression for the reaction. Substitute the known K value and the final concentrations to solve for x.
C. Calculate the final concentration of each substance in the reaction mixture. Check your answers by substituting these values into the equilibrium constant expression to obtain K.

Solution

A $[CO_2]_i = 0.632\ M$ and $[H_2]_i = 0.570\ M$. Again, x is defined as the change in the concentration of H_2O: $\Delta[H_2O] = +x$. Because 1 mol of CO is produced for every 1 mol of H_2O, the change in the concentration of CO is the same as the change in the concentration of H2O, so Δ[CO] = +x. Similarly, because 1 mol each of H_2 and CO_2 are consumed for every 1 mol of H_2O produced, $\Delta[H_2] = \Delta[CO_2] = -x$. The final concentrations are the sums of the initial concentrations and the changes in concentrations at equilibrium.

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$

ICE	$H_{2(g)}$	$CO_{2(g)}$	$H_2O_{(g)}$	$CO_{(g)}$
Initial	0.570	0.632	0	0
Change	−x	−x	+x	+x
Final	(0.570 − x)	(0.632 − x)	x	x

B We can now use the equilibrium equation and the known K value to solve for x:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{x^2}{(0.570 - x)(0.632 - x)} = 0.106$$

In contrast to Example 12.6.3, however, there is no obvious way to simplify this expression. Thus we must expand the expression and multiply both sides by the denominator:

$$x^2 = 0.106(0.360 - 1.20x + x^2)$$

Collecting terms on one side of the equation,

$$0.894x^2 + 0.127x - 0.0382 = 0$$

This equation can be solved using the quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.127 \pm \sqrt{(0.127)^2 - 4(0.894)(-0.0382)}}{2(0.894)}$$

$$x = 0.148 \text{ and } -0.290$$

Only the answer with the positive value has any physical significance, so $\Delta[H_2O] = \Delta[CO] = +0.148M$, and $\Delta[H_2] = \Delta[CO_2] = -0.148\ M$.

C The final concentrations of all species in the reaction mixture are as follows:

- $[H_2]_f [= [H_2]_i + \Delta[H_2] = 0.570\ M - 0.148\ M = 0.422M$
- $[CO_2]_f = [CO_2]_i + \Delta[CO_2] = 0.632\ M - 0.148\ M = 0.484M$
- $[H_2O]_f = [H_2O]_i + \Delta[H_2O] = 0\ M + 0.148\ M = 0.148\ M$
- $[CO]_f = [CO]_i + \Delta[CO] = 0M + 0.148\ M = 0.148M$

We can check our work by substituting these values into the equilibrium constant expression:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(0.148)^2}{(0.422)(0.484)} = 0.107$$

Because K is essentially the same as the value given in the problem, our calculations are confirmed.

? Exercise 12.6.4

The exercise in Example 12.6.1 showed the reaction of hydrogen and iodine vapor to form hydrogen iodide, for which $K = 54$ at 425°C. If a sample containing 0.200 M H_2 and 0.0450 M I_2 is allowed to equilibrate at 425°C, what is the final concentration of each substance in the reaction mixture?

Answer

$[H_I]_f = 0.0882\ M$

$[H_2]_f = 0.156\ M$

$[I_2]_f = 9.2 \times 10^{-4} M$

In many situations it is not necessary to solve a quadratic (or higher-order) equation. Most of these cases involve reactions for which the equilibrium constant is either very small ($K \leq 10^{-3}$) or very large ($K \geq 10^{3}$), which means that the change in the concentration (defined as x) is essentially negligible compared with the initial concentration of a substance. Knowing this simplifies the calculations dramatically, as illustrated in Example 12.6.5.

Example 12.6.5

Atmospheric nitrogen and oxygen react to form nitric oxide:

$$\mathrm{N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)} \tag{12.6.8}$$

with $K_p = 2.0 \times 10^{-31}$ at 25°C.

What is the partial pressure of NO in equilibrium with N_2 and O_2 in the atmosphere (at 1 atm) $P_{N_2} = 0.78\ atm$ and $P_{O_2} = 0.21\ atm$?

Given: balanced equilibrium equation and values of K_p, P_{O_2}, and P_{N_2}

Asked for: partial pressure of NO

Strategy:

A. Construct a table and enter the initial partial pressures, the changes in the partial pressures that occur during the course of the reaction, and the final partial pressures of all substances.
B. Write the equilibrium equation for the reaction. Then substitute values from the table to solve for the change in concentration (x).
C. Calculate the partial pressure of NO. Check your answer by substituting values into the equilibrium equation and solving for K.

Solution

A Because we are given Kp and partial pressures are reported in atmospheres, we will use partial pressures. The initial partial pressure of O_2 is 0.21 atm and that of N_2 is 0.78 atm. If we define the change in the partial pressure of NO as 2x, then the change in the partial pressure of O_2 and of N_2 is −x because 1 mol each of N_2 and of O_2 is consumed for every 2 mol of NO produced. Each substance has a final partial pressure equal to the sum of the initial pressure and the change in that pressure at equilibrium.

$$\mathrm{N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)} \tag{12.6.9}$$

ICE	P_{N_2}	P_{O_2}	P_{NO}
Initial	0.78	0.21	0
Change	−x	−x	+2x
Final	(0.78 − x)	(0.21 − x)	2x

B Substituting these values into the equation for the equilibrium constant,

$$K_p = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})} = \frac{(2x)^2}{(0.78 - x)(0.21 - x)} = 2.0 \times 10^{-31}$$

In principle, we could multiply out the terms in the denominator, rearrange, and solve the resulting quadratic equation. In practice, it is far easier to recognize that an equilibrium constant of this magnitude means that the extent of the reaction will be very small; therefore, the x value will be negligible compared with the initial concentrations. If this assumption is correct, then to two significant figures, (0.78 − x) = 0.78 and (0.21 − x) = 0.21. Substituting these expressions into our original equation,

$$\frac{(2x)^2}{(0.78)(0.21)} = 2.0 \times 10^{-31}$$

$$\frac{4x^2}{0.16} = 2.0 \times 10^{-31}$$

$$x^2 = \frac{0.33 \times 10^{-31}}{4}$$

$$x^{=} 9.1 \times 10^{-17}$$

C Substituting this value of x into our expressions for the final partial pressures of the substances,

- $P_{NO} = 2x\ atm = 1.8 \times 10^{-16}\ atm$
- $P_{N_2} = (0.78 - x)\ atm = 0.78\ atm$
- $P_{O_2} = (0.21 - x)\ atm = 0.21\ atm$

From these calculations, we see that our initial assumption regarding x was correct: given two significant figures, 2.0×10^{-16} is certainly negligible compared with 0.78 and 0.21. When can we make such an assumption? As a general rule, if x is less than about 5% of the total, or $10^{-3} > K > 10^{3}$, then the assumption is justified. Otherwise, we must use the quadratic formula or some other approach. The results we have obtained agree with the general observation that toxic NO, an ingredient of smog, does not form from atmospheric concentrations of N_2 and O_2 to a substantial degree at 25°C. We can verify our results by substituting them into the original equilibrium equation:

$$K_p = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})} = \frac{(1.8 \times 10^{-16})^2}{(0.78)(0.21)} = 2.0 \times 10^{-31}$$

The final K_p agrees with the value given at the beginning of this example.

? Exercise 12.6.5

Under certain conditions, oxygen will react to form ozone, as shown in the following equation:

$$3O_{2(g)} \rightleftharpoons 2O_{3(g)}$$

with $K_p = 2.5 \times 10^{-59}$ at 25°C. What ozone partial pressure is in equilibrium with oxygen in the atmosphere ($P_{O_2} = 0.21\ atm$)?

Answer

$4.8 \times 10^{-31}\ atm$

Another type of problem that can be simplified by assuming that changes in concentration are negligible is one in which the equilibrium constant is very large (K ≥ 10^3). A large equilibrium constant implies that the reactants are converted almost entirely to products, so we can assume that the reaction proceeds 100% to completion. When we solve this type of problem, we view the system as equilibrating from the products side of the reaction rather than the reactants side. This approach is illustrated in Example 12.6.6

✔ Example 12.6.6

The chemical equation for the reaction of hydrogen with ethylene (C_2H_4) to give ethane (C_2H_6) is as follows:

$$H_{2(g)} + C_2H_{4(g)} \overset{Ni}{\rightleftharpoons} C_2H_{6(g)}$$

with $K = 9.6 \times 10^{18}$ at 25°C. If a mixture of 0.200 M H_2 and 0.155 M C_2H_4 is maintained at 25°C in the presence of a powdered nickel catalyst, what is the equilibrium concentration of each substance in the mixture?

Given: balanced chemical equation, K, and initial concentrations of reactants

Asked for: equilibrium concentrations

Strategy:

A. Construct a table showing initial concentrations, concentrations that would be present if the reaction were to go to completion, changes in concentrations, and final concentrations.
B. Write the equilibrium constant expression for the reaction. Then substitute values from the table into the expression to solve for x (the change in concentration).

C. Calculate the equilibrium concentrations. Check your answers by substituting these values into the equilibrium equation.

Solution:

A From the magnitude of the equilibrium constant, we see that the reaction goes essentially to completion. Because the initial concentration of ethylene (0.155 M) is less than the concentration of hydrogen (0.200 M), ethylene is the limiting reactant; that is, no more than 0.155 M ethane can be formed from 0.155 M ethylene. If the reaction were to go to completion, the concentration of ethane would be 0.155 M and the concentration of ethylene would be 0 M. Because the concentration of hydrogen is greater than what is needed for complete reaction, the concentration of unreacted hydrogen in the reaction mixture would be 0.200 M − 0.155 M = 0.045 M. The equilibrium constant for the forward reaction is very large, so the equilibrium constant for the reverse reaction must be very small. The problem then is identical to that in Example 12.6.5. If we define −x as the change in the ethane concentration for the reverse reaction, then the change in the ethylene and hydrogen concentrations is +x. The final equilibrium concentrations are the sums of the concentrations for the forward and reverse reactions.

$$H_{2(g)} + C_2H_{4(g)} \overset{Ni}{\rightleftharpoons} C_2H_{6(g)}$$

IACE	$[H_{2(g)}]$	$[C_2H_{4(g)}]$	$[C_2H_{6(g)}]$
Initial	0.200	0.155	0
Assuming 100% reaction	0.045	0	0.155
Change	+x	+x	−x
Final	(0.045 + x)	(0 + x)	(0.155 − x)

B Substituting values into the equilibrium constant expression,

$$K = \frac{[C_2H_6]}{[H_2][C_2H_4]} = \frac{0.155 - x}{(0.045 + x)x} = 9.6 \times 10^{18}$$

Once again, the magnitude of the equilibrium constant tells us that the equilibrium will lie far to the right as written, so the reverse reaction is negligible. Thus x is likely to be very small compared with either 0.155 M or 0.045 M, and the equation can be simplified [(0.045 + x) = 0.045 and (0.155 − x) = 0.155] as follows:

$$K = \frac{0.155}{0.045x} = 9.6 \times 10^{18}$$

$$x = 3.6 \times 10^{-19}$$

C The small x value indicates that our assumption concerning the reverse reaction is correct, and we can therefore calculate the final concentrations by evaluating the expressions from the last line of the table:

- $[C_2H_6]_f = (0.155 - x)\ M = 0.155\ M$
- $[C_2H_4]_f = x\ M = 3.6 \times 10^{-19} M$
- $[H_2]_f = (0.045 + x)\ M = 0.045\ M$

We can verify our calculations by substituting the final concentrations into the equilibrium constant expression:

$$K = \frac{[C_2H_6]}{[H_2][C_2H_4]} = \frac{0.155}{(0.045)(3.6 \times 10^{-19})} = 9.6 \times 10^{18}$$

This K value agrees with our initial value at the beginning of the example.

? Exercise 12.6.6

Hydrogen reacts with chlorine gas to form hydrogen chloride:

$$H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)}$$

with $K_p = 4.0 \times 10^{31}$ at 47°C. If a mixture of 0.257 M H_2 and 0.392 M Cl_2 is allowed to equilibrate at 47°C, what is the equilibrium composition of the mixture?

Answer

$[H_2]_f = 4.8 \times 10^{-32}\ M$

$[Cl_2]_f = 0.135\ M$

$[HCl]_f = 0.514\ M$

Summary

Various methods can be used to solve the two fundamental types of equilibrium problems:

1. those in which we calculate the concentrations of reactants and products at equilibrium and
2. those in which we use the equilibrium constant and the initial concentrations of reactants to determine the composition of the equilibrium mixture.

When an equilibrium constant is calculated from equilibrium concentrations, molar concentrations or partial pressures are substituted into the equilibrium constant expression for the reaction. Equilibrium constants can be used to calculate the equilibrium concentrations of reactants and products by using the quantities or concentrations of the reactants, the stoichiometry of the balanced chemical equation for the reaction, and a tabular format to obtain the final concentrations of all species at equilibrium.

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12.7: Reaction Directions (Empirical Explanation)

Learning Objectives

- To predict in which direction a reaction will proceed.
- Describe the ways in which an equilibrium system can be stressed
- Predict the response of a stressed equilibrium using Le Chatelier's principle

We previously saw that knowing the magnitude of the equilibrium constant under a given set of conditions allows chemists to predict the extent of a reaction. Often, however, chemists must decide whether a system has reached equilibrium or if the composition of the mixture will continue to change with time. In this section, we describe how to quantitatively analyze the composition of a reaction mixture to make this determination.

The Reaction Quotient

To determine whether a system has reached equilibrium, chemists use a quantity called the Reaction Quotient (Q). The expression for the Reaction Quotient has precisely the same form as the equilibrium constant expression from the Law of Mass Action, except that Q may be derived from a set of values measured at any time during the reaction of any mixture of the reactants and the products, regardless of whether the system is at equilibrium. Therefore, for the following general reaction:

$$aA + bB \rightarrow cC + dD \tag{12.7.1}$$

the Reaction Quotient is defined as follows:

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{12.7.2}$$

To understand how information is obtained using a Reaction Quotient, consider the dissociation of dinitrogen tetroxide to nitrogen dioxide,

$$\mathrm{N_2O_4(g) \rightleftharpoons 2\,NO_2(g).} \tag{12.7.3}$$

For this reaction, $K = 4.65 \times 10^{-3}$ at 298 K. We can write Q for this reaction as follows:

$$Q = \frac{[NO_2]^2}{[N_2O_4]} \tag{12.7.4}$$

The following table lists data from three experiments in which samples of the reaction mixture were obtained and analyzed at equivalent time intervals, and the corresponding values of Q were calculated for each. Each experiment begins with different proportions of product and reactant:

Table 12.7.1: Three Conditions of the dissociation of dinitrogen tetroxide to nitrogen dioxide (Equation 12.7.1)

Experiment	$[NO_2]$ (M)	$[N_2O_4]$ (M)	$Q = \frac{[NO^2]^2}{[N^2O^4]}$
1	0	0.0400	$\frac{0^2}{0.0400} = 0$
2	0.0600	0	$\frac{(0.0600)^2}{0} = \text{undefined}$
3	0.0200	0.0600	$\frac{(0.0200)^2}{0.0600} = 6.67 \times 10^{-3}$

As these calculations demonstrate, Q can have any numerical value between 0 and infinity (undefined); that is, Q can be greater than, less than, or equal to K.

Comparing the magnitudes of Q and K enables us to determine whether a reaction mixture is already at equilibrium and, if it is not, predict how its composition will change with time to reach equilibrium (i.e., whether the reaction will proceed to the right or to the left as written). All you need to remember is that the composition of a system not at equilibrium will change in a way that makes Q

approach K. If $Q = K$, for example, then the system is already at equilibrium, and no further change in the composition of the system will occur unless the conditions are changed. If $Q < K$, then the ratio of the concentrations of products to the concentrations of reactants is less than the ratio at equilibrium. Therefore, the reaction will proceed to the right as written, forming products at the expense of reactants. Conversely, if $Q > K$, then the ratio of the concentrations of products to the concentrations of reactants is greater than at equilibrium, so the reaction will proceed to the left as written, forming reactants at the expense of products. These points are illustrated graphically in Figure 12.7.1.

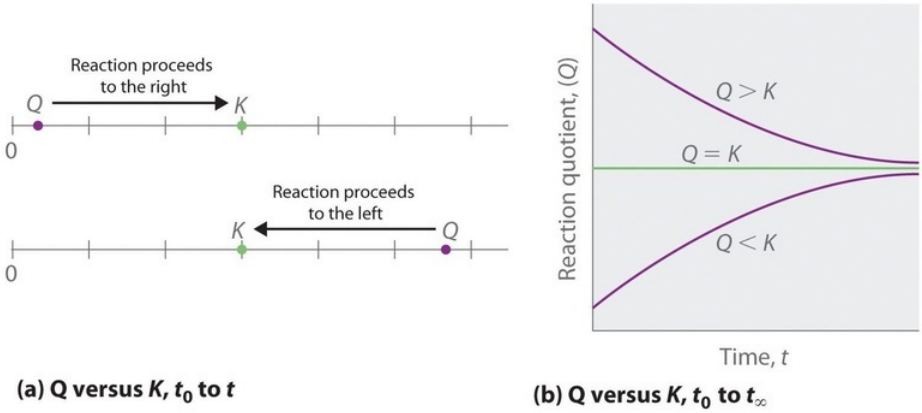


Figure 12.7.1: Two Different Ways of Illustrating How the Composition of a System Will Change Depending on the Relative Values of Q and K.(a) Both Q and K are plotted as points along a number line: the system will always react in the way that causes Q to approach K. (b) The change in the composition of a system with time is illustrated for systems with initial values of $Q > K$, $Q < K$, and $Q = K$.

If $Q < K$, the reaction will proceed to the right as written. If $Q > K$, the reaction will proceed to the left as written. If $Q = K$, then the system is at equilibrium.

Example 12.7.1: steam-reforming

At elevated temperatures, methane (CH_4) reacts with water to produce hydrogen and carbon monoxide in what is known as a steam-reforming reaction:

$$\mathrm{CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3\,H_2(g)}$$

$K = 2.4 \times 10^{-4}$ at 900 K. Huge amounts of hydrogen are produced from natural gas in this way and are then used for the industrial synthesis of ammonia. If 1.2×10^{-2} mol of CH_4, 8.0×10^{-3} mol of H_2O, 1.6×10^{-2} mol of CO, and 6.0×10^{-3} mol of H_2 are placed in a 2.0 L steel reactor and heated to 900 K, will the reaction be at equilibrium or will it proceed to the right to produce CO and H_2 or to the left to form CH_4 and H_2O?

Given: balanced chemical equation, K, amounts of reactants and products, and volume

Asked for: direction of reaction

Strategy:

A. Calculate the molar concentrations of the reactants and the products.
B. Use Equation 12.7.2to determine Q. Compare Q and K to determine in which direction the reaction will proceed.

Solution:

A: We must first find the initial concentrations of the substances present. For example, we have $1.2 \times 10^{-2} mol$ of CH_4 in a 2.0 L container, so

$$[CH_4] = \frac{1.2 \times 10^{-2} mol}{2.0\ L}$$
$$= 6.0 \times 10^{-3} M$$

We can calculate the other concentrations in a similar way:

- $[H_2O] = 4.0 \times 10^{-3} M$,
- $[CO] = 8.0 \times 10^{-3} M$, and
- $[H_2] = 3.0 \times 10^{-3} M$.

B: We now compute Q and compare it with K:

$$\begin{aligned} Q &= \frac{[CO][H_2]^3}{[CH_4][H_2O]} \\ &= \frac{(8.0 \times 10^{-3})(3.0 \times 10^{-3})^3}{(6.0 \times 10^{-3})(4.0 \times 10^{-3})} \\ &= 9.0 \times 10^{-6} \end{aligned}$$

Because $K = 2.4 \times 10^{-4}$, we see that $Q < K$. Thus the ratio of the concentrations of products to the concentrations of reactants is less than the ratio for an equilibrium mixture. The reaction will therefore proceed to the right as written, forming $\mathrm{H_2}$ and CO at the expense of H_2O and CH_4.

? Exercise 12.7.1

In the water–gas shift reaction introduced in Example 12.7.1, carbon monoxide produced by steam-reforming reaction of methane reacts with steam at elevated temperatures to produce more hydrogen:

$$\mathrm{CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)}$$

$K = 0.64$ at 900 K. If 0.010 mol of both CO and $\mathrm{H_2O}$, 0.0080 mol of $\mathrm{CO_2}$, and 0.012 mol of $\mathrm{H_2}$ are injected into a 4.0 L reactor and heated to 900 K, will the reaction proceed to the left or to the right as written?

Answer

$Q = 0.96$ (Q > K), so the reaction will proceed to the left, and CO and H_2O will form.

Predicting the Direction of a Reaction with a Graph

By graphing a few equilibrium concentrations for a system at a given temperature and pressure, we can readily see the range of reactant and product concentrations that correspond to equilibrium conditions, for which $Q = K$. Such a graph allows us to predict what will happen to a reaction when conditions change so that Q no longer equals K, such as when a reactant concentration or a product concentration is increased or decreased.

Lead carbonate decomposes to lead oxide and carbon dioxide according to the following equation:

$$\mathrm{PbCO_3(s) \rightleftharpoons PbO(s) + CO_2(g)} \tag{12.7.5}$$

Because $PbCO_3$ and PbO are solids, the equilibrium constant is simply $K = [CO_2]$. At a given temperature, therefore, any system that contains solid $PbCO_3$ and solid PbO will have exactly the same concentration of CO_2 at equilibrium, regardless of the ratio or the amounts of the solids present. This situation is represented in Figure 12.7.2, which shows a plot of $[CO_2]$ versus the amount of $PbCO_3$ added. Initially, the added $PbCO_3$ decomposes completely to CO_2 because the amount of $PbCO_3$ is not sufficient to give a CO_2 concentration equal to K. Thus the left portion of the graph represents a system that is not at equilibrium because it contains only CO2(g) and PbO(s). In contrast, when just enough $PbCO_3$ has been added to give $[CO_2] = K$, the system has reached equilibrium, and adding more $PbCO_3$ has no effect on the CO_2 concentration: the graph is a horizontal line. Thus any CO_2 concentration that is not on the horizontal line represents a nonequilibrium state, and the system will adjust its composition to achieve equilibrium, provided enough $PbCO_3$ and PbO are present. For example, the point labeled A in Figure 12.7.2 lies above the horizontal line, so it corresponds to a $[CO_2]$ that is greater than the equilibrium concentration of CO_2 (Q > K). To reach equilibrium, the system must decrease $[CO_2]$, which it can do only by reacting CO_2 with solid PbO to form solid $PbCO_3$. Thus the reaction in Equation 12.7.5 will proceed to the left as written, until $[CO_2] = K$. Conversely, the point labeled B in Figure 12.7.2 lies below the horizontal line, so it corresponds to a $[CO_2]$ that is less than the equilibrium concentration of CO_2 (Q < K). To reach equilibrium, the system must increase $[CO_2]$, which it can do only by decomposing solid $PbCO_3$ to form CO_2 and solid PbO. The reaction in Equation 12.7.5 will therefore proceed to the right as written, until $[CO_2] = K$.

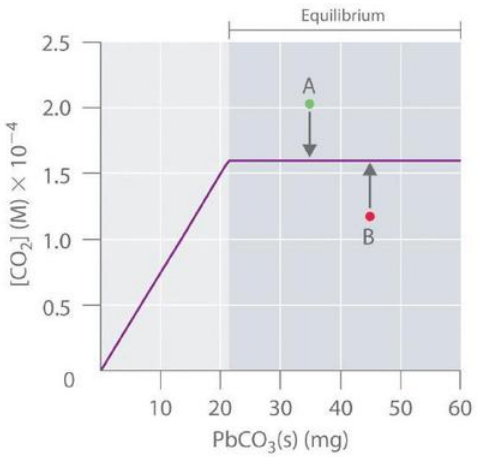


Figure 12.7.2: The Concentration of Gaseous CO_2 in a Closed System at Equilibrium as a Function of the Amount of Solid $PbCO_3$ Added. Initially the concentration of CO2(g) increases linearly with the amount of solid $PbCO_3$ added, as $PbCO_3$ decomposes to CO2(g) and solid PbO. Once the CO_2 concentration reaches the value that corresponds to the equilibrium concentration, however, adding more solid $PbCO_3$ has no effect on $[CO_2]$, as long as the temperature remains constant.

In contrast, the reduction of cadmium oxide by hydrogen gives metallic cadmium and water vapor:

$$\mathrm{CdO(s) + H_2(g) \rightleftharpoons Cd(s) + H_2O(g)} \tag{12.7.6}$$

and the equilibrium constant K is $[H_2O]/[H_2]$. If $[H_2O]$ is doubled at equilibrium, then [H2] must also be doubled for the system to remain at equilibrium. A plot of $[H_2O]$ versus $[H_2]$ at equilibrium is a straight line with a slope of K (Figure 12.7.3). Again, only those pairs of concentrations of H_2O and H_2 that lie on the line correspond to equilibrium states. Any point representing a pair of concentrations that does not lie on the line corresponds to a nonequilibrium state. In such cases, the reaction in Equation 12.7.6 will proceed in whichever direction causes the composition of the system to move toward the equilibrium line. For example, point A in Figure 12.7.3 lies below the line, indicating that the $[H_2O]/[H_2]$ ratio is less than the ratio of an equilibrium mixture (Q < K). Thus the reaction in Equation 12.7.6 will proceed to the right as written, consuming H_2 and producing H_2O, which causes the concentration ratio to move up and to the left toward the equilibrium line. Conversely, point B in Figure 12.7.3 lies above the line, indicating that the $[H_2O]/[H_2]$ ratio is greater than the ratio of an equilibrium mixture (Q > K). Thus the reaction in Equation 12.7.6 will proceed to the left as written, consuming H_2O and producing H_2, which causes the concentration ratio to move down and to the right toward the equilibrium line.

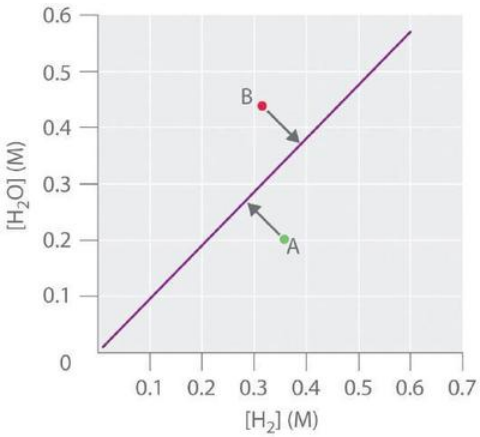


Figure 12.7.3: The Concentration of Water Vapor versus the Concentration of Hydrogen for the $CdO_{(s)} + H_{2(g)} \rightleftharpoons Cd_{(s)} + H_2O_{(g)}$ System at Equilibrium. For any equilibrium concentration of $H_2O_{(g)}$, there is only one equilibrium concentration of H2(g). Because the magnitudes of the two concentrations are directly proportional, a large $[H_2O]$ at equilibrium requires a large $[H_2]$ and vice versa. In this case, the slope of the line is equal to K.

In another example, solid ammonium iodide dissociates to gaseous ammonia and hydrogen iodide at elevated temperatures:

$$NH_4I_{(s)} \rightleftharpoons NH_{3(g)} + HI_{(g)} \tag{12.7.7}$$

For this system, K is equal to the product of the concentrations of the two products: $[NH_3][HI]$. If we double the concentration of NH3, the concentration of HI must decrease by approximately a factor of 2 to maintain equilibrium, as shown in Figure 12.7.4 As a result, for a given concentration of either HI or NH_3, only a single equilibrium composition that contains equal concentrations of both NH_3 and HI is possible, for which $[NH_3] = [HI] = K^{1/2}$. Any point that lies below and to the left of the equilibrium curve (such as point A in Figure 12.7.4) corresponds to $Q < K$, and the reaction in Equation 12.7.7 will therefore proceed to the right as written, causing the composition of the system to move toward the equilibrium line. Conversely, any point that lies above and to the right of the equilibrium curve (such as point B in Figure 12.7.4) corresponds to $Q > K$, and the reaction in Equation 12.7.7 will therefore proceed to the left as written, again causing the composition of the system to move toward the equilibrium line. By graphing equilibrium concentrations for a given system at a given temperature and pressure, we can predict the direction of reaction of that mixture when the system is not at equilibrium.

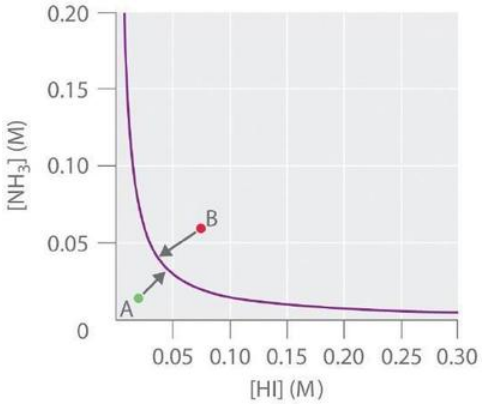


Figure 12.7.4: The Concentration of $NH_{3(g)}$ versus the Concentration of $HI_{(g)}$ for the $NH_4I_{(s)} \rightleftharpoons NH_{3(g)} + HI_{(g)}$ System at Equilibrium. Only one equilibrium concentration of $NH_{3(g)}$ is possible for any given equilibrium concentration of HI(g). In this case, the two are inversely proportional. Thus a large $[HI]$ at equilibrium requires a small $[NH_3]$ at equilibrium and vice versa.

Effect of Change in Pressure on Equilibrium

Sometimes we can change the position of equilibrium by changing the pressure of a system. However, changes in pressure have a measurable effect only in systems in which gases are involved, and then only when the chemical reaction produces a change in the total number of gas molecules in the system. An easy way to recognize such a system is to look for different numbers of moles of gas on the reactant and product sides of the equilibrium. While evaluating pressure (as well as related factors like volume), it is important to remember that equilibrium constants are defined with regard to concentration (for K_c) or partial pressure (for K_p). Some changes to total pressure, like adding an inert gas that is not part of the equilibrium, will change the total pressure but not the partial pressures of the gases in the equilibrium constant expression. Thus, addition of a gas not involved in the equilibrium will not perturb the equilibrium.



Video 12.7.1: See www.youtube.com/watch?v=pnU7ogsgUW8 to see a dramatic visual demonstration of how equilibrium changes with pressure changes.

As we increase the pressure of a gaseous system at equilibrium, either by decreasing the volume of the system or by adding more of one of the components of the equilibrium mixture, we introduce a stress by increasing the partial pressures of one or more of the components. In accordance with Le Chatelier's principle, a shift in the equilibrium that reduces the total number of molecules per unit of volume will be favored because this relieves the stress. The reverse reaction would be favored by a decrease in pressure.

Consider what happens when we increase the pressure on a system in which NO, O_2, and NO_2 are at equilibrium:

$$2\,NO_{(g)} + O_{2(g)} \rightleftharpoons 2\,NO_{2(g)} \tag{12.7.8}$$

The formation of additional amounts of NO_2 decreases the total number of molecules in the system because each time two molecules of NO_2 form, a total of three molecules of NO and O_2 are consumed. This reduces the total pressure exerted by the system and reduces, but does not completely relieve, the stress of the increased pressure. On the other hand, a decrease in the pressure on the system favors decomposition of NO_2 into NO and O_2, which tends to restore the pressure.

Now consider this reaction:

$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g) \tag{12.7.9}$$

Because there is no change in the total number of molecules in the system during reaction, a change in pressure does not favor either formation or decomposition of gaseous nitrogen monoxide.

Effect of Change in Temperature on Equilibrium

Changing concentration or pressure perturbs an equilibrium because the Reaction Quotient is shifted away from the equilibrium value. Changing the temperature of a system at equilibrium has a different effect: A change in temperature actually changes the value of the equilibrium constant. However, we can qualitatively predict the effect of the temperature change by treating it as a stress on the system and applying Le Chatelier's principle.

When hydrogen reacts with gaseous iodine, heat is evolved.

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g) \quad \Delta H = -9.4\ \text{kJ (exothermic)} \tag{12.7.10}$$

Because this reaction is exothermic, we can write it with heat as a product.

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g) + \text{heat} \tag{12.7.11}$$

Increasing the temperature of the reaction increases the internal energy of the system. Thus, increasing the temperature has the effect of increasing the amount of one of the products of this reaction. The reaction shifts to the left to relieve the stress, and there is an increase in the concentration of H_2 and I_2 and a reduction in the concentration of HI. Lowering the temperature of this system reduces the amount of energy present, favors the production of heat, and favors the formation of hydrogen iodide.

When we change the temperature of a system at equilibrium, the equilibrium constant for the reaction changes. Lowering the temperature in the HI system increases the equilibrium constant: At the new equilibrium the concentration of HI has increased and the concentrations of H_2 and I_2 decreased. Raising the temperature decreases the value of the equilibrium constant, from 67.5 at 357 °C to 50.0 at 400 °C.

Temperature affects the equilibrium between NO_2 and N_2O_4 in this reaction

$$N_2O_{4(g)} \rightleftharpoons 2\,NO_{2(g)} \quad \Delta H = 57.20\ \text{kJ} \tag{12.7.12}$$

The positive ΔH value tells us that the reaction is endothermic and could be written

$$\text{heat} + N_2O_{4(g)} \rightleftharpoons 2\,NO_{2(g)} \tag{12.7.13}$$

At higher temperatures, the gas mixture has a deep brown color, indicative of a significant amount of brown NO_2 molecules. If, however, we put a stress on the system by cooling the mixture (withdrawing energy), the equilibrium shifts to the left to supply some of the energy lost by cooling. The concentration of colorless N_2O_4 increases, and the concentration of brown NO_2 decreases, causing the brown color to fade.

Temperature is Neither a Reactant nor Product

It is not uncommon that textbooks and instructors to consider heat as a independent "species" in a reaction. While this is rigorously incorrect because one cannot "add or remove heat" to a reaction as with species, it serves as a convenient mechanism to predict the shift of reactions with changing temperature. For example, if heat is a "reactant" ($\Delta H > 0$), then the reaction favors the formation of products at elevated temperature. Similarly, if heat is a "product" ($\Delta H < 0$), then the reaction favors the formation of reactants. A more accurate, and hence preferred, description is discussed below.

Example 12.7.2: Steam Reforming of Methane

The commercial production of hydrogen is carried out by treating natural gas with steam at high temperatures and in the presence of a catalyst (“steam reforming of methane”):

$$\mathrm{CH_4 + H_2O \rightleftharpoons CH_3OH + H_2}$$

Given the following boiling points: CH_4 (methane) = –161°C, H_2O = 100°C, CH_3OH = 65°, H_2 = –253°C, predict the effects of an increase in the total pressure on this equilibrium at 50°, 75° and 120°C.

Solution

To identify the influence of changing pressure on the three reaction conditions, we need to identify the correct reaction including the phase of each reactant and product. Calculate the change in the moles of gas for each process:

Temperature	Equation	Δn_g	shift
50°	$\mathrm{CH_4(g) + H_2O(l) \rightarrow CH_3OH(l) + H_2(g)}$	0	none
75°	$\mathrm{CH_4(g) + H_2O(l) \rightarrow CH_3OH(g) + H_2(g)}$	+1	to left
120°	$\mathrm{CH_4(g) + H_2O(g) \rightarrow CH_3OH(g) + H_2(g)}$	0	none

Exercise 12.7.2

What will happen to the equilibrium when the volume of the system is decreased?

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

Answer

Decreasing the volume leads to an increase in pressure which will cause the equilibrium to shift towards the side with fewer moles. In this reaciton, there are three moles on the reactant side and two moles on the product side, so the new equilibrium will shift towards the products (to the right).

Summary

The Reaction Quotient (Q) is used to determine whether a system is at equilibrium and if it is not, to predict the direction of reaction. Reaction Quotient:

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

The Reaction Quotient (Q or Q_p) has the same form as the equilibrium constant expression, but it is derived from concentrations obtained at any time. When a reaction system is at equilibrium, $Q = K$. Graphs derived by plotting a few equilibrium concentrations for a system at a given temperature and pressure can be used to predict the direction in which a reaction will proceed. Points that do not lie on the line or curve represent nonequilibrium states, and the system will adjust, if it can, to achieve equilibrium.

Systems at equilibrium can be disturbed by changes to temperature, concentration, and, in some cases, volume and pressure; volume and pressure changes will disturb equilibrium if the number of moles of gas is different on the reactant and product sides of the reaction. The system's response to these disturbances is described by Le Chatelier's principle: The system will respond in a way that counteracts the disturbance. Not all changes to the system result in a disturbance of the equilibrium. Adding a catalyst affects the rates of the reactions but does not alter the equilibrium, and changing pressure or volume will not significantly disturb systems with no gases or with equal numbers of moles of gas on the reactant and product side.

Effects of Disturbances of Equilibrium and K

Disturbance	Observed Change as Equilibrium is Restored	Direction of Shift	Effect on K
reactant added	added reactant is partially consumed	toward products	none
product added	added product is partially consumed	toward reactants	none
decrease in volume/increase in gas pressure	pressure decreases	toward side with fewer moles of gas	none
increase in volume/decrease in gas pressure	pressure increases	toward side with more moles of gas	none
temperature increase	heat is absorbed	toward products for endothermic, toward reactants for exothermic	changes
temperature decrease	heat is given off	toward reactants for endothermic, toward products for exothermic	changes

Footnotes

1. 1 Herrlich, P. “The Responsibility of the Scientist: What Can History Teach Us About How Scientists Should Handle Research That Has the Potential to Create Harm?” *EMBO Reports* 14 (2013): 759–764.

Glossary

Le Chatelier's principle

when a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance

position of equilibrium

concentrations or partial pressures of components of a reaction at equilibrium (commonly used to describe conditions before a disturbance)

stress

change to a reaction's conditions that may cause a shift in the equilibrium

Contributors and Attributions

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12.8: Distribution of a Single Species between Immiscible Phases - Extraction and Separation

A partitioning of a compound exist between a mixture of two immiscible phases at equilibrium, which is a measure of the difference in solubility of the compound in these two phases. If one of the solvents is a gas and the other a liquid, the "gas/liquid partition coefficient" is the same as the dimensionless form of the Henry's law constant. A solute can partition when one or both solvents is a solid (e.g., solid solution).

Liquid-Liquid Extractions

We call the process of moving a species from one phase to another phase an **extraction**. Simple extractions are particularly useful for separations where only one component has a favorable partition coefficient. Several important separation techniques are based on a simple extraction, including liquid–liquid, liquid–solid, solid–liquid, and gas–solid extractions. The most important group of separation techniques uses a selective partitioning of the solute between two immiscible phases. If we bring a phase containing a solute, S, into contact with a second phase, the solute partitions itself between the two phases, as shown by the following equilibrium reaction.

$$\mathrm{S_{phase\,1}} \rightleftharpoons \mathrm{S_{phase\,2}} \tag{12.8.1}$$

The equilibrium constant for this equilbrium is

$$K_\mathrm{D} = \frac{[\mathrm{S_{phase\ 2}}]}{[\mathrm{S_{phase\ 1}}]} \tag{12.8.2}$$

is called the distribution constant or **partition coefficient**. If K_D is sufficiently large, then the solute moves from phase 1 to phase 2. The solute remains in phase 1 if the partition coefficient is sufficiently small. When we bring a phase containing two solutes into contact with a second phase, if K_D is favorable for only one of the solutes a separation of the solutes is possible. The physical states of the phases are identified when describing the separation process, with the phase containing the sample listed first. For example, if the sample is in a liquid phase and the second phase is a solid, then the separation involves liquid–solid partitioning.

It often happens that two immiscible liquid phases are in contact, one of which contains a solute. How will the solute tend to distribute itself between the two phases? One's first thought might be that some of the solute will migrate from one phase into the other until it is distributed equally between the two phases, since this would correspond to the maximum dispersion (randomness) of the solute. This, however, does not take into the account the differing solubilities the solute might have in the two liquids; if such a difference does exist, the solute will preferentially migrate into the phase in which it is more soluble (Figure 12.8.1).

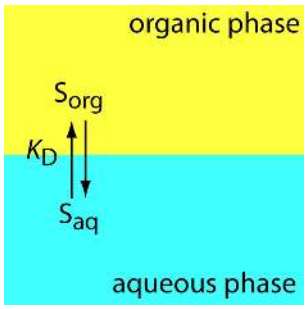


Figure 12.8.1: Scheme for a simple liquid–liquid extraction in which the solute's partitioning depends only on the K_D equilibrium.

Biomagnification

The transport of substances between different phases is of immense importance in such diverse fields as pharmacology and environmental science. For example, if a drug is to pass from the aqueous phase with the stomach into the bloodstream, it must pass through the lipid (oil-like) phase of the epithelial cells that line the digestive tract. Similarly, a pollutant such as a pesticide residue that is more soluble in oil than in water will be preferentially taken up and retained by marine organism, especially fish, whose bodies contain more oil-like substances; this is basically the mechanism whereby such residues as DDT can undergo *biomagnification* as they become more concentrated at higher levels within the food chain. For this reason, environmental

regulations now require that oil-water distribution ratios be established for any new chemical likely to find its way into natural waters. The standard “oil” phase that is almost universally used is octanol, $C_8H_{17}OH$.

In preparative chemistry it is frequently necessary to recover a desired product present in a reaction mixture by extracting it into another liquid in which it is more soluble than the unwanted substances. On the laboratory scale this operation is carried out in a **separatory funnel** as shown below. The two immiscible liquids are poured into the funnel through the opening at the top. The funnel is then shaken to bring the two phases into intimate contact, and then set aside to allow the two liquids to separate into layers, which are then separated by allowing the more dense liquid to exit through the stopcock at the bottom.



Figure 12.8.2: A separatory funnel with two solvents.

If the distribution ratio is too low to achieve efficient separation in a single step, it can be repeated; there are automated devices that can carry out hundreds of successive extractions, each yielding a product of higher purity. In these applications our goal is to exploit the Le Chatelier principle by repeatedly upsetting the phase distribution equilibrium that would result if two phases were to remain in permanent contact.



Video 12.8.1: How to perform a liquid-liquid extraction using a separating funnel.

Example 12.8.1

The distribution ratio for iodine between water and carbon disulfide is 650. Calculate the concentration of I_2 remaining in the aqueous phase after 50.0 mL of 0.10M I_2 in water is shaken with 10.0 mL of CS_2.

Solution

The equilibrium constant is

$$K_d = \frac{C_{CS_2}}{C_{H_2O}} = 650$$

Let m_1 and m_2 represent the numbers of millimoles of solute in the water and CS_2 layers, respectively. K_d can then be written as (m_2/10 mL) ÷ (m_1/50 mL) = 650. The number of moles of solute is (50 mL) × (0.10 mmol mL^{-1}) = 5.00 mmol, and mass conservation requires that $m_1 + m_2$ = 5.00 mmol, so m_2 = (5.00 – m_1) mmol and we now have only the single unknown m_1. The equilibrium constant then becomes

$$\frac{(5.00-m_1)\,mmol/10\,mL}{m_1\,mmol/50\,mL} = 650$$

Simplifying and solving for m_1 yields

$$\frac{(0.50-0.1)m_1}{0.02\,m_1} = 650$$

with m_1 = 0.0382 mmol.

The concentration of solute in the water layer is (0.0382 mmol) / (50 mL) = **0.000763 M**, showing that almost all of the iodine has moved into the CS_2 layer.

Chromatographic Separations

In an extraction, the sample is one phase and we extract the analyte or the interferent into a second phase. We also can separate the analyte and interferents by continuously passing one sample-free phase, called the mobile phase, over a second sample-free phase that remains fixed or stationary. The sample is injected into the mobile phase and the sample's components partition themselves between the mobile phase and the stationary phase. Those components with larger partition coefficients are more likely to move into the stationary phase, taking a longer time to pass through the system. This is the basis of all chromatographic separations. Chromatography provides both a separation of analytes and interferents, and a means for performing a qualitative or quantitative analysis for the analyte.

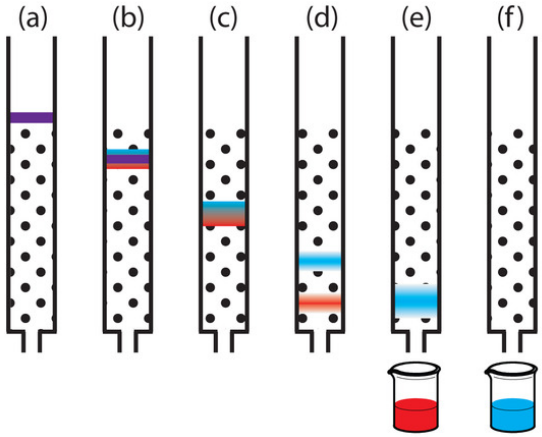


Figure 12.8.3: Progress of a column chromatographic separation of a two-component mixture. In (a) the sample is layered on top of the stationary phase. As mobile phase passes through the column, the sample separates into two solute bands (b–d). In (e) and (f), we collect each solute as it elutes from the column.

Of the two methods for bringing the stationary phase and the mobile phases into contact, the most important is column chromatography. In this section we develop a general theory that we may apply to any form of column chromatography. Figure 12.8.3 provides a simple view of a liquid–solid column chromatography experiment. The sample is introduced at the top of the column as a narrow band. Ideally, the solute's initial concentration profile is rectangular (Figure 12.8.1*a*). As the sample moves down the column the solutes begin to separate (Figures 12.8.1*b*, *c*), and the individual solute bands begin to broaden and develop a Gaussian profile. If the strength of each solute's interaction with the stationary phase is sufficiently different, then the solutes separate into individual bands (Figure 12.8.1*d*).

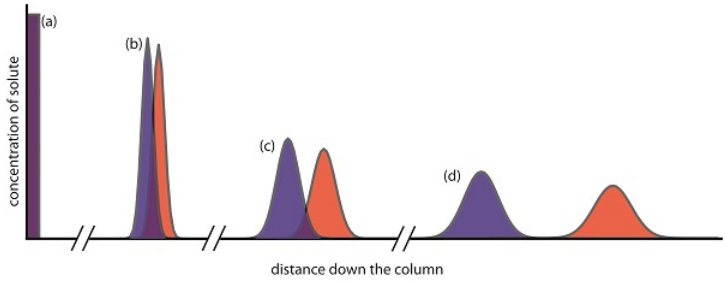


Figure 12.8.4: An alternative view of the separation in Figure 12.8.3 showing the concentration of each solute as a function of distance down the column.

We can follow the progress of the separation either by collecting fractions as they elute from the column (Figure 12.8.4), or by placing a suitable detector at the end of the column. A plot of the detector's response as a function of elution time, or as a function of the volume of mobile phase, is known as a **chromatogram** (Figure 12.8.5), and consists of a peak for each solute.

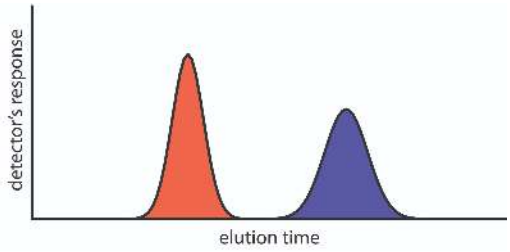


Figure 12.8.5: Chromatogram for the separation shown in Figure 12.8.3 showing the detector's response as a function of the elution time.

Contributors and Attributions

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12.E: Chemical Equilibria (Exercises)

These are homework exercises to accompany the Textmap created for "Principles of Modern Chemistry" by Oxtoby et al. Complementary General Chemistry question banks can be found for other Textmaps and can be accessed here.

Q1

Write an expression for the equilibrium constant K_c for each reaction below.

a. $2\,NO(g) + O_2(g) \rightleftharpoons 2\,NO_2(g)$
b. $N_2H_4(g) + 3\,O_2(g) \rightleftharpoons 2\,NO_2(g) + H_2O(g)$
c. $O_3(g) + H_2O(l) \rightleftharpoons H_2(g) + 2\,O_2(g)$

Solution

For a general reaction $aA + bB \rightleftharpoons cC + dD$ then Law of Mass Action argues we can construct an equilibrium constant thusly

$$K_c = \frac{[C]c[D]d}{[A]a[B]b}$$

This is the general equations to substitute the reactants and product concentrations (with coefficients as exponents).

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

a. $K_c = \dfrac{[NO_2]^2}{[NO]^2[O_2]}$
b. $K_c = \dfrac{[H_2O][NO_2]^2}{[N_2H_4][O_2]^3}$
c. $K_c = \dfrac{[O_2]^2[H_2]}{[O_3]}$

Note that for part c, $H_2O(l)$ is not included because pure solids and liquids are not included in the equilibrium constant.

Q3

Gaseous chlorine reacts with water vapor to form hydrogen chloride and oxygen gas. Write down the equilibrium expression (K_p) for the reaction.

Solution

First, a balanced reaction is constructed to ensure the equilibrium expression will be correctly states.

$$2\,Cl_2 + 2\,H_2O \rightleftharpoons 4\,HCl + O_2$$

Equilibrium expression K_p is as follows:

$$K_p = \frac{p_{HCl}^4 p_{O_2}}{p_{Cl_2}^2 p_{H_2O}^2}$$

Q11

For each thermodynamics equilibrium expressions outlined below, determine one possible chemical reaction related to each.

a. $$K = \frac{a\{CO\}^2}{a\{CO_2\}}$$

b. $$K = \frac{a\{H_2O\}^2}{a\{H_2\}^2 a\{O_2\}}$$

c. $$K = \frac{a\{Cl_2O\}^2}{a\{Cl_2\}^2 a\{O_2\}}$$

d. $$K = \frac{a\{COCl_2\}}{a\{CO\} \cdot a\{Cl_2\}}$$

Solution

a. $$CO_2(g) + C(s) \rightleftharpoons 2\,CO(g)$$

b. $$2\,H_2(g) + O_2(g) \rightleftharpoons 2\,H_2O(g)$$

c. $$2\,Cl_2(g) + O_2(g) \rightleftharpoons 2\,Cl_2O(g)$$

d. $$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

Q15A

Based on the following data, calculate the equilibrium constant and the value of ΔG at 273 K.

a. $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$ with

- $[CO_2]_{eq} = 0.0954\,M$
- $[H_2]_{eq} = 0.0454\,M$
- $[CO]_{eq} = 0.0046\,M$
- $[H_2O]_{eq} = 0.0046\,M$

b. $2\,NO(g) + 2\,H_2(g) \rightleftharpoons N_2(g) + 2\,H_2O(g)$ with

- $[NO]_{eq} = 0.45\,M$
- $[H_2]_{eq} = 0.63\,M$
- $[N_2]_{eq} = 0.95\,M$
- $[H_2O]_{eq} = 1.3\,M$

Solution

a)

$$K = \frac{[CO][H_2O]}{[CO_2][H_2]}$$
$$= \frac{(0.0046)(0.0046)}{(0.0954)(0.0454)}$$
$$= 4.9 \times 10^{-3}$$

$$\Delta G = RT\ln(K) = (8.3145\,J/(K\,mol))(273\,K)\ln(4.9 \times 10^{-3}) = -12072.288\,J/mol$$

b)

$$K = \frac{[N_2][H_2O]^2}{[NO]^2[H_2]^2} = \frac{[0.95][1.3]^2}{[0.45]^2[0.63]^2} = 19.98$$

$$\Delta G = RT\ln(K) = (8.3145\,J/K\,mol)(273\,K)\ln(19.98) = 6797.62\,J/mol$$

Q15B

Calculate the appropriate K value for the following reactions using the information provided. Assume that they are preformed under standard conditions (and 298.15 K).

a. $$2\,NO_2(g) \rightleftharpoons 2\,NO(g) + O_2(g)$$

b. $$NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq)$$

c. Jim's brother, Txeltoqlztop, goes to the bathroom only to find out that his sibling did not refill the toilet paper roll! To get revenge, Txeltoqlztop decides to fill his brother's room with carbon monoxide, via the following reaction:

$$2\,CH_4(g) + 3\,O_2(g) \rightleftharpoons 2\,CO(g) + 4\,H_2O(g)$$

Calculate the K value for this equation under standard conditions, interpret what it means in regards to the direction this equation will go, and compare it to the other two.

Solution

The core of this problem is to find the K value and understanding what information it can describe about the reaction. Since the problem provides many, many ΔG_f, it is likely that to calculate the K value, a relationship needs to be drawn from ΔG to K. This relationship is as follows:

$$\Delta G^\circ_{rxn} = -RT\ln(K_p)$$

Relevant Information obtained from the thermodynamic tables

$\Delta G_f^\circ\ NO_2(g) = 51.30\frac{kJ}{mol}$ $\Delta G_f^\circ\ H_3O^+(aq) = -103.45\frac{kJ}{mol}$

$\Delta G_f^\circ\ NO(g) = 86.57\frac{kJ}{mol}$ $\Delta G_f^\circ\ NH_3(aq) = -26.5\frac{kJ}{mol}$

$\Delta G_f^\circ\ O_2(g) = 0\frac{kJ}{mol}$ $\Delta G_f^\circ\ CH_4(g) = -50.84\frac{kJ}{mol}$

$\Delta G_f^\circ\ NH_4^+(aq) = -79.37\frac{kJ}{mol}$ $\Delta G_f^\circ\ CO(g) = -137.28\frac{kJ}{mol}$

$\Delta G_f^\circ\ H_2O(l) = -237.14\frac{kJ}{mol}$ $\Delta G_f^\circ\ H_2O(g) = -228.61\frac{kJ}{mol}$

Note that the relationship here is between ΔG and K_p, which is:

$$K_p \approx \frac{P_{products}}{P_{reactants}}$$

Where P is partial pressure of the products or reactants. The reason this is an approximation is because the equilibrium actually measures the *activities* of the species, but by using just the partial pressures a good estimate is procured. Since the equation relating K_p and ΔG only has these two variables as unknown, once ΔG is found, algebra can find K_p. The process for utilizing Hess's Law to find state variables is outlined extensively. The values below were found using the exact same process, now for ΔG (Just in case, the Hess law formula is provided).

$$\Delta G^\circ = \sum n_{products} \times \Delta G^\circ_{f_{products}} - \sum n_{reactants} \times \Delta G^\circ_{f_{reactants}}$$

$$\Delta G^\circ(2\,NO_2(g) \rightleftharpoons 2\,NO(g) + O_2(g)) = 70.42\ \frac{kJ}{mol}$$

$$\Delta G^\circ(NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq)) = -437.93\frac{kJ}{mol}$$

$$\Delta G^\circ(2\,CH_4(g) + 3\,O_2(g) \rightleftharpoons 2\,CO(g) + 4\,H_2O(l)) = -1121.44\frac{kJ}{mol}$$

To find K, plug in the ΔG into the equation above. (Note that the solution does NOT show the conversion of the gas constant from J to kJ!!)

$$\Delta G^\circ_{rxn} = -\left(8.314\ \frac{J}{mol\,K}\right)(298.15\,K) \times \ln(K_p)$$

$$70.54\frac{kJ}{mol} = -\left(8.314\frac{J}{mol\,K}\right)(298.15\,K) \times \ln(K_p)$$

$$-\frac{70.54\,\frac{\text{kJ}}{\text{mol}}}{\left(8.314\,\frac{\text{J}}{\text{molK}}\right)(298.15\,\text{K})} = \ln(K_p)$$

$$e^{-\frac{70.54\,\frac{\text{kJ}}{\text{mol}}}{\left(8.314\,\frac{\text{J}}{\text{mol K}}\right)(298.15\,\text{K})}} = K_p$$

$$K_p \approx e^{-28.457} \approx 4.3776 \times 10^{-13}$$

Thus, the K_p value for $2\,\text{NO}_2(\text{g}) \rightleftharpoons 2\,\text{NO}(\text{g}) + \text{O}_2(\text{g})$ is a very small number!. Since the equilibrium value depicts the ratio of products to reactants at the equilibrium point, this very tiny K_p value means that the reaction will heavily favor the reactants. The third reaction where Txeltoqlztop wants to poison his brother with CO also follows the same process, and the answer is such:

$$K_p \approx e^{452}$$

e^{452} is a *really* big number! That means, while the previous reaction will stay mostly on the reactant sides, this reaction heavily favors the products side, meaning that pretty much all of the methane and oxygen that Txeltoqlztop uses will be transformed into carbon monoxide, which is all the better for him!

The same method can be applied to the aqueous reaction, but the K value calculated is K_c rather than K_p.

$$K_c \approx e^{-176.65} \approx 1.898 \times 10^{-77}\ *$$

*These equilibrium constants are based solely off the calculated Gibbs energy, some of the reactions, therefore, may have actual K values much different from the ones calculated.

Abstract: use of $\Delta G^\circ_{\text{rxn}} = -RT \times \ln(K_p)$

Q15C

Use the thermodynamic data in Tables T1 and T2 to calculate the equilibrium constants for the following equations at 25°C.

a. $\text{H}_2(\text{g}) + 2\,\text{F}(\text{g}) \rightleftharpoons 2\,\text{HF}(\text{g})$
b. $\text{FeCl}_3(\text{s}) \rightleftharpoons \text{FeCl}_2(\text{s}) + \text{Cl}_2(\text{g})$
c. $\text{CaSO}_4(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$

Solution

For each of the chemical reactions, the main equation needed is

$$\Delta G_{\text{rxn}} = -R \times T \times \ln K$$

Where R is 8.134 J K^{-1} mol^{-1} and T is equal to 298K. In order to determine the value of G_{rxn}, the following the reaction is needed

$$\Delta G_{\text{rxn}} = \sum nG_f^\circ(\text{products}) - \sum nG_f^\circ(\text{reactants})$$

a. By looking in the tables, the ΔG of formation can be found and they are listed for each compound below

$H_2(g)$ = 203.3 J mol^{-1}, $F_2(g)$ = 62.3 J mol^{-1}, HF(g)=-275.4 J mol^{-1}

Next, these values are plugged into the second equation to the the change in Gibbs energy for the reaction

$$\Delta G_{\text{rxn}} = -275.4\ \text{J mol}^{-1} - (203.3\ \text{J mol}^{-1} + 62.3\ \text{J mol}^{-1}) = -514\ \text{J mol}^{-1}$$

Using the the value for the Gibbs Energy, the value of K can be determined using the first equation

$$-541\ \text{J mol}^{-1} = -8.314\ \text{J K}^{-1}\text{mol}^{-1} \times 298\ \text{K} \times \ln K$$

$$\frac{-541\ \text{J mol}^{-1}}{-8.314\ \text{J K}^{-1}\ \text{mol}^{-1} \times 298\ \text{K}} = \ln K$$

$$K = 1.25$$

b. The ΔG of formation for the compounds are

$FeCl_3(s)$ = -334.0 J mol^{-1}, $FeCl_2(s)$ = -302.3 J mol^{-1}, Cl(g)=105.3 J mol^{-1}

The calculations are

$$\Delta G_{\text{rxn}} = (-302.3\ \text{J mol}^{-1} + 105.3\ \text{J mol}^{-1}) + 334.0\ \text{J mol}^{-1} = 137\ \text{J mol}^{-1}$$

$$137\ \text{J mol}^{-1} = -8.314\ \text{J K}^{-1}\ \text{mol}^{-1} \times 298\ \text{K} \times \ln K$$

$$\frac{137\ \text{J mol}^{-1}}{-8.314\ \text{J K}^{-1}\ \text{mol}^{-1} \times 298\ \text{K}} = \ln K$$

$$K = 0.945$$

c. The ΔG of formation for the compounds are

$CaSO_4(s)$= -1322.0 J/mol, $Ca^{2+}(aq)$ = -553.58 J/mol, $SO_4^{2-}(aq)$ = -744.53 J/mol

The calculations are

$$\Delta G_{\text{rxn}} = (-553.58\ \text{J mol}^{-1} - 744.53\ \text{J mol}^{-1}) + 1322.0\ \text{J mol}^{-1} = 23.89\ \text{J mol}^{-1}$$

$$23.89\ \text{J mol}^{-1} = -8.314\ \text{J K}^{-1}\ \text{mol}^{-1} \times 298\ \text{K} \times \ln K$$

$$\frac{23.89\ \text{J mol}^{-1}}{-8.314\ \text{J K}^{-1}\ \text{mol}^{-1} \times 298\ \text{K}} = \ln K$$

$$K = 0.99$$

Q17

To ignite this house on fire, you dowsed the house in some ethanol and used a combustion reaction:

$$C_2H_5OH(l) + O_2(g) \rightleftharpoons H_2O(l) + CO_2(g)$$

This reaction has an equilibrium constant of K_1. If you multiply this equation by 5, will the equilibrium constant change? If so, write this new equilibrium constant, K_2, in terms of K_1.

Solution

Because:

$$K = \frac{[A]^a[B]^b}{[C]^c[D]^d}$$

If we multiply a chemical equation by a constant, the exponents of K will be multiplied by that multiple as well.

For this question, first balance this chemical equation,

$$C_2H_5OH(l) + 3\ O_2(g) \rightleftharpoons 3\ H_2O(l) + 2\ CO_2(g)$$

the corresponding equilibrium constant is

$$K_1 = \frac{[CO_2]^2}{[O_2]^3}$$

since liquid is ignored.

When we multiply this equation by 5, the chemical equation becomes,

$$5\,C_2H_5OH(l) + 15\,O_2(g) \rightleftharpoons 15\,H_2O(l) + 10\,CO_2(g)$$

the corresponding equilibrium constant is

$$K_2 = \frac{[CO_2]^{10}}{[O_2]^{15}} = \left(\frac{[CO_2]^2}{[O_2]^3}\right)^5$$

Therefore, for this reaction, the equilibrium constant changes and $K_2 = K_1^5$.

Q21

An unknown gas B_5D_{10} reacts at room temperature and becomes $B_{10}D_{20}$, the reaction is illustrated with the equation

$$2\,B_5D_{10}(g) \rightleftharpoons B_{10}D_{20}(g)$$

At room temperature the equilibrium partial pressure of B_5D_{10} is 1.23×10^{-4} atm and that of $B_{10}D_{20}$ is 3.14×10^{-16} atm. Given these constants, what is K_p of this reaction at room temperature.

Solution

Given that we already know the partial pressures and this reaction is at equilibrium, we simply substitute the values into the equilibrium equation and solve for K_p.

$$K_p = \frac{[\text{products}]}{[\text{reactants}]}$$

$$K_p = \frac{[3.14 \times 10^{-16}]}{[1.23 \times 10^{-4}]^2} = 2.08 \times 10^{-8}$$

$$K_p = 2.08 \times 10^{-8}$$

Q23A

Suppose there exists a compound that can be found in two forms, red and blue, such that

$$X_{red} \rightleftharpoons X_{blue}$$

During equilibrium at 25.0°C, 17% of the substance is determined to be in blue form. What is the equilibrium constant for this reaction?

Solution

The equilibrium constant, K_{eq}, for the chemical equation

$$X_{red} \rightleftharpoons X_{blue}$$

can be calculated by constructing the following equation:

$$K_{eq} = \frac{[X_{blue}]}{[X_{red}]}$$

Given that 17% of the concentration is X_{blue}, that means the remaining 83% is X_{red}, which can be plugged into the equation to yield

$$K_{eq} = \frac{[0.17]}{[0.83]} = 0.205$$

which can be further reinforced by viewing it as the fact that since $K_{eq} < 1$, the concentration of products present is expected to be smaller than the concentration of reactants.

Q23B

1,2-dimethylcyclohexane can exist in both boat and chair conformation. There is equilibrium between the two forms. What is the equilibrium constant for the reaction of boat conformation to chair conformation if the molecules in the boat form are 68.7%?

Solution

$$[\text{Boat}] \longrightarrow [\text{Chair}]$$

Let B stand for Boat and C stand for Chair, then the equilibrium constant for this reaction is

$$K = \frac{[\text{C}]}{[\text{B}]}$$

For [C] and [B] here, we can use the molar concentration $c = n/V$, then

$$[\text{C}] = n(\text{C})/V$$

$$[\text{B}] = n(\text{B})/V$$

So

$$K = \frac{n(\text{C})/V}{n(\text{B})/V} = \frac{n(\text{C})}{n(\text{B})} = \frac{n(\text{C})/n_{\text{tot}}}{n(\text{B})/n_{\text{tot}}}$$

From the question, it consists only with boat and chair conformation, so $n(\text{C})/n_{\text{tot}} = 0.687$, and the remaining is for boat, so $n(\text{B})/n_{\text{tot}} = 1 - 0.687 = 0.313$.

Therefore, the equilibrium constant is

$$K = \frac{n(\text{C})/n_{\text{tot}}}{n(\text{B})/n_{\text{tot}}} = \frac{0.687}{0.313} = 2.19$$

Q28

The K_p for the following reaction is 3.0 at 1000 K.

$$\text{CO}_2(\text{g}) + \text{C}(\text{s}) \rightleftharpoons 2\,\text{CO}(\text{g})$$

a. If the pressure in the container where the reaction occurs was initially 0.48 bar, calculate the partial pressures of CO_2 and CO at equilibrium.
b. Calculate the percentage of CO_2 that has been dissociated.

Solution

a)

$$\text{CO}_2(\text{g}) + \text{C}(\text{s}) \rightleftharpoons 2\,\text{CO}(\text{g})$$

	$\text{CO}_2(\text{g})$	$\text{CO}(\text{g})$
Initial	0.48	0
Change	$-x$	$+2x$
Equilibrium	$0.48 - x$	$2x$

$$K_p = \frac{p(\text{CO})^2}{p(\text{CO}_2)}$$

⇒

$$3 = \frac{(2x)^2}{(0.48 - x)}$$

⇒

$$4x^2 = 3(0.48 - x)$$

⇒

$$4x^2 = 1.44 - 3x$$

⇒

$$4x^2 + 3x - 1.44 = 0$$

By solving the quadratic equation, the positive value we get is

$$x = 0.33$$

Hence at equilibrium,

$$p(\mathrm{CO}) = 2x = 0.66$$

$$p(\mathrm{CO_2}) = 0.48 - x = 0.48 - 0.33 = 0.15 \text{ bar}$$

b) For fraction that has not reacted,

$$\frac{p(\mathrm{CO_2(final)})}{p(\mathrm{CO_2(initial)})} \times 100\%$$

The unreacted percentage is

$$= \frac{0.15}{0.48} \times 100\% = 31.25\%$$

Hence, 68.75% of the CO_2 has reacted.

Q29

A 100.0 mL glass bulb was filled which a weighed sample of solid $\mathrm{XO_3}$, where X is an unknown element. The bulb was then attached to a pressure gauge and heated to 325 K, at which, the pressure was read to be 0.891 atm. Given that all of the $\mathrm{XO_3}$ in the bulb at 325 K was in the gas phase, and it also partially dissociated into $\mathrm{O_2(g)}$ and $\mathrm{XO(g)}$:

$$\mathrm{XO_3(g) \rightleftharpoons O_2(g) + XO(g)}$$

At 325 K, K_p = 3.14 for this reaction. Calculate the partial pressures of all three species in the bulb at equilibrium.

Solution

$$\mathrm{XO_3(g) \rightleftharpoons O_2(g) + XO(g)}$$

Let Y be the initial partial pressure of X_2O_5, and x is the change in partial pressure of O_2:

ICE	$\mathrm{XO_3}$	$\mathrm{O_2}$	XO
Initial	y	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$y - x$	x	x

The total pressure is 0.891 atm, therefore:

$$(y - x) + x + x = 0.891 \text{ atm}$$

$$y + x = 0.891 \text{ atm}$$

$$y = 0.891 - x$$

So the ICE table now would be:

ICE	XO_3	O_2	XO
Initial	$0.891 - x$	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.891 - 2x$	x	x

$$K_p = 3.14 = \frac{P_{XO} \cdot P_{O_2}}{P_{XO_3}} = \frac{x^2}{0.891 - 2x}$$

$$x^2 + 6.28x - 2.80 = 0$$

$$x = 0.418$$

$$P_{O_2} = P_{XO} = 0.418 \text{ atm}$$

$$P_{XO_3} = 0.891 - 2(0.418) = 0.055 \text{ atm}$$

Q31

The equilibrium constant K_c for the reaction

$$\mathrm{F_2(g) + H_2(g) \rightleftharpoons 2\,HF(g)}$$

at 298 K is 5.07×10^4. Hydrogen with a partial pressure of 0.03500 atm is mixed with fluorine with a partial pressure of 0.06800 atm, and allowed to reach the equilibrium. What is the partial pressure of each of the gasses at the equilibrium?

Solution

We are looking for partial pressures of the reactants and we have starting partial pressures and a K_c value. First we need to convert K_c to K_p

$$K_p = K_c(RT)^{\Delta n_{gas}}$$

$$K_p = (5.07 \times 10^4) \times (0.0821 \times 298 \text{ K})^0 = 5.07 \times 10^4$$

The equilibrium constant can be constructed from the equation given

$$K_p = \frac{[HF]^2}{[H_2][F_2]}$$

Use an ICE table to find the equilibrium partial pressures of the equilibrium

Reaction	$H_2(g)$	$F_2(g)$	$2\,HF(g)$
I	0.035	0.068	0
C	$-x$	$-x$	$+2x$
E	$0.035 - x$	$0.068 - x$	$2x$

$$5.07 \times 10^4 = \frac{[2x]^2}{[0.035 - x]^2[0.068 - x]^2}$$

Simplify the equation and solve as you wish. You can't use the quadratic formula because you end up with a degree three equation but you can put the equation into a graphing calculator and solve for x using the zero function.

$$x = 0.0286 \text{ atm}$$

$$[\mathrm{HF}] = 2x = 0.0571\ \mathrm{atm}$$

$$[\mathrm{H_2}] = 0.035 - x = 0.00643\ \mathrm{atm}$$

$$[\mathrm{F_2}] = 0.068 - x = 0.0394\ \mathrm{atm}$$

Q33

At 25 °C, the equilibrium constant for the reaction below has the value of 1.7×10^{-13}:

$$\mathrm{N_2O(g)} + \tfrac{1}{2}\mathrm{O_2(g)} \rightleftharpoons 2\,\mathrm{NO(g)}$$

In a container where $\mathrm{N_2O}$ has an initial partial pressure of 0.62 atm, $\mathrm{O_2}$ has a pressure of 0.24 atm, and NO has an initial pressure of 0.08 atm, what will the partial pressure of the three gases be after reaching equilibrium at the same temperature?

Q35

The reaction:

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

has an equilibrium constant $K_c = 1.82 \times 10^{-2}$ at 698 K. If the reaction took place in a tank at 698 K and started off with HI having a partial pressure of 1 atm, what would the partial pressures of all the gases be at equilibrium?

Solution

First, we need to convert K_c into K_p with the equation

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

$$K_p = 1.82 \times 10^{-2}(0.0821\ \mathrm{L\ atm\ /\ K\ mol} \times 698\ \mathrm{K})^{2-2}$$

$$K_p = 1.82 \times 10^{-2}$$

An ICE table can also be constructed for the reaction:

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

ICE Table	$2\,\mathrm{HI(g)}$	$\mathrm{H_2(g)}$	$\mathrm{I_2(g)}$
Initial	1	0	0
Change	$-2x$	$+x$	$+x$
Equilibrium	$1-2x$	x	x

$$0.82 \times 10^{-2} = \frac{x^2}{1-2x}$$

$$x^2 = 1.82 \times 10^{-2} - 0.0368x$$

$$x = 0.118488$$

$$\text{partial pressure of HI} = 0.763\ \mathrm{atm}$$

$$\text{partial pressure of } \mathrm{H_2} = \text{partial pressure of } \mathrm{I_2} = 0.1189\ \mathrm{atm}$$

Q37

What is the concentration of a XY that will be found in equilibrium at room temperature, given that $\mathrm{X_2}$ has a concentration of 3.14×10^{-15} M, $\mathrm{Y_2}$ has a concentration of 1.23×10^{-4} M, and the K_c of the reaction is 2.22×10^{-7} M.

Solution

First we must state what the formulas for both the reaction and K_c and then we can substitute the known values and solve for the concentration of XY as an unknown variable.

$$2\,\mathrm{XY(g)} \rightleftharpoons \mathrm{X_2(g)} + \mathrm{Y_2(g)}$$

$$K_c = \frac{[\text{Products}]}{[\text{Reactants}]}$$

$$K_c = \frac{[\mathrm{X_2}][\mathrm{Y_2}]}{[\mathrm{XY}]^2} = \frac{[3.14 \times 10^{-15}][1.23 \times 10^{-4}]}{[\mathrm{XY}]^2} = 2.22 \times 10^{-7}$$

$$K_c = \frac{[3.86 \times 10^{-19}]}{[\mathrm{XY}]^2} = 2.22 \times 10^{-7}$$

$$K_c = 3.86 \times 10^{-19} = 2.22 \times 10^{-7}[\mathrm{XY}]^2$$

$$[\mathrm{XY}] = 1.32 \times 10^{-6}$$

So the concentration of XY is 1.32×10^{-6} M in equilibrium at 25ºC.

Q41

Hydrogen and oxygen gas react with each other to form gaseous water with an equilibrium constant for the reaction is $K_c = 1.33 \times 10^{20}$ at 1000 K.

a. Consider a system at 1000.0 K in which 4.00 atm of oxygen is mixed with 0.500 atm of hydrogen and no water is initially present. What is the concentration of hydrogen gas after equilibration.
b. Consider a system, also at 1000.0 K, where 0.250 atm of oxygen is mixed with 0.500 atm of hydrogen and 2.000 atm of water. What is the concentration of hydrogen and oxygen gas after equilibration.

Solution

a)

$$2\,\mathrm{H_2(g)} + \mathrm{O_2(g)} \rightleftharpoons 2\,\mathrm{H_2O(l)}$$

$$K = 3.4 = \frac{1}{P_{\mathrm{H_2}}^2 P_{\mathrm{O_2}}}$$

$$P_{\mathrm{H_2}} = 1.2\,\text{atm}$$

$$3.4 = \frac{1}{(1.2)^2 P_{\mathrm{O_2}}}$$

$$P_{\mathrm{O_2}} = \frac{1}{(1.2)^2(3.4)} = 0.204\,\text{atm}$$

b) Excess $\mathrm{H_2O(l)}$ is added drive the reaction to the left towards the reactant to reach the equilibrium; therefore, pressure of H_2 and O_2 increased.

	$2\,\mathrm{H_2(g)}$	$\mathrm{O_2(g)}$	$2\,\mathrm{H_2O(l)}$
Initial	0	0.3	N/A
Change	$+2x$	$+x$	N/A
Equilibrium	$2x$	$0.3 + x$	N/A

$$K = \frac{1}{(2x)^2(0.3+x)} = 3.4$$

$$3.4(0.3+x)(2x)^2 = 1$$

$$x = 0.339\ \text{atm}$$

$$P_{O_2} = 0.3 + 0.339 = 0.639\ \text{atm}$$

$$P_{H_2} = 2(0.339) = 0.678\ \text{atm}$$

Q43

If you decompose ammonium nitrate into water and nitrous oxide, which further decomposes into oxygen and nitrogen gas, making the final reaction:

$$2\,NH_4NO_3(s) \rightleftharpoons 2\,N_2(g) + O_2(g) + 4\,H_2O(g)$$

This reaction takes place only in the molten salt, above its melting point of 169.6°C (for the anhydrous product). So, you get your 170°C blow torch and begin decomposing the ammonium nitrate under a sealed hood. Upon decomposition, all of the ammonium nitrate is gone, i.e. the reaction goes to completion.

a. What can be said of the equilibrium constant of this reaction at 170°C?
b. Now, in another universe, the partial pressure of $N_2(g)$ is 0.3 atm initially. Will the reaction still go to, essentially, completion?

Solution

(a) If there is no ammonium nitrate left, then the reaction was **heavily** products favoring, meaning K is extremely high at 170°C.

Note: It's more accurate to say that Q is a big number when there is no reactants left after reaction occurred. Reviewer's comment: Q stands for the current state. K is the equilibrium constant. When there is no reactant left after reaction occurred, the reaction is at the equilibrium state, so Q = K. Since Q is a big number, then K is also a big number.

(b) There would have to be an enormous amount of Nitrogen to force the reaction backwards. Because 0.3 atm is likely not enough to push back an essentially irreversible reaction, it has no noticeable affect on the amount of end product. (Note: If the reactants and products are essentially gas, we calculate the equilibrium constant not by its concentration, but by its pressure.)

Q45

Al_2Cl_6 at a partial pressure of 0.600 atm is placed in a closed container at 454 K. Al_3Cl_9 (partial pressure 1.98×10^{-3} atm) is also placed in it as well. Argon is added to raise the total pressure up to 1.00 atm.

Find whether if there is going to be net production or consumption of Al_3Cl_9 given $K_p = 1.04 \times 10^{-4}$. Then find the final pressure of Al_3Cl_9.

Solution

The reaction is

$$3\,Al_2Cl_6(g) \rightleftharpoons 2\,Al_3Cl_9(g)$$

Because argon does not react, it can be ignored.

$$Q = \frac{([Al_3Cl_9])^2}{([Al_2Cl_6])^3} = \frac{(1.98 \cdot 10^{-3})^2}{(0.600)^3} = 1.82 \cdot 10^{-5} < K_p = 1.04 \cdot 10^{-4}$$

There will be production of Al_3Cl_9.

ICE Table	Al_2Cl_6	Al_3Cl_9
Initial	0.600	1.98×10^{-3}
Change	$-3y$	$+2y$
Equilibrium	$0.6 - 3y$	$1.98 \times 10^{-3} + 2y$

$$K = 1.04 \cdot 10^{-4} \frac{([Al_3Cl_9])^2}{([Al_2Cl_6])^3} = \frac{(1.98 \times 10^{-3} + 2y)^2}{(1 - (1.98 \times 10^{-3} + 2y))^3}$$

Solving out

$$y = 0.0041 \text{ atm}$$

Al_3Cl_9 final pressure = 0.0102 atm.

Q46

The thermal decomposition of NH_4Cl solid proceeds as follows:

$$\mathrm{NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)}$$

the equilibrium constant at 275°C is 1.04×10^{-2}. If the partial pressures of $\mathrm{NH_3(g)}$ and $\mathrm{HCl(g)}$ are equal, and the total partial pressure of the system is 0.200 atm, in what direction does the reaction proceed? What will be formed?

Solution

First, we make two equations to solve out the partial pressures. To get the first equation, we sum over the partial pressures to the total pressure. $\mathrm{NH_4Cl}$ is a solid, so it doesn't contribute to the partial pressure

$$P_{\mathrm{NH_3}} + P_{\mathrm{HCl}} = 0.200 \text{ atm}$$

The second equation is from the question that partial pressures of $\mathrm{NH_3(g)}$ and $\mathrm{HCl(g)}$ are equal

$$P_{\mathrm{NH_3}} = P_{\mathrm{HCl}}$$

Hence,

$$P_{\mathrm{NH_3}} = P_{\mathrm{HCl}} = 0.100 \text{ atm}$$

$$Q(\text{reaction quotient}) = P_{\mathrm{NH_3}} P_{\mathrm{HCl}} = (0.100)^2$$

$$10^{-2} < 1.04 \times 10^{-2}$$

$$Q < K$$

Hence, the reaction will slightly proceed more in the forward direction.

NH_3 and HCl will be formed.

Q47

A tube contains a mixture of NO_2 and N_2O_4 gas is set at 298K, in which the initial partial pressure NO_2 is 0.38 atm, and the initial partial pressure of N_2O_4 is 0.59 atm. NO_2 is a brownish gas, while N_2O_4 is a colorless gas.

$$\mathrm{2\,NO_2(g) \rightleftharpoons N_2O_4(g)}$$

a. What is the reaction quotient at the start of this reaction?
b. As the reaction shown above reaches equilibrium, the mixture becomes more brown. With this in mind, is the equilibrium constant, K_p, greater than or less than the Q calculated in part a?

Solution

a)

$$\mathrm{2\,NO_2(g) \rightleftharpoons N_2O_4(g)}$$

$$P_{\mathrm{N_2O_4}} = 0.59 \text{ atm} \quad P_{\mathrm{NO_2}} = 0.38 \text{ atm}$$

$$Q_p = \frac{P_{\mathrm{N_2O_4}}}{(P_{\mathrm{NO_2}})^2}$$

$$Q_p = \frac{0.59}{0.38^2} = 4.1$$

b) Since the mixture becomes more brown as the reaction reaches equilibrium, more NO gas is being produced, therefore the reverse reaction is favored, so $Q_p > k_p$, in conclusion, $K_p < 4.1$.

Q49

At 500 K the equilibrium constant for the reaction:

$$\mathrm{PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)}$$

is $K_{eq} = 2.1$. Suppose the equilibrium is disturbed and shifts, while temperature remains constant. Calculate the reaction quotient for each one of the possible changes in equilibrium concentration given below and evaluate in what direction the reaction will shift to reestablish equilibrium.

a. [PCl_3]= 0.0563, [Cl2]= 0.0784, [PCl_5]= 0.8934.
b. [PCl_3]=0.4390 , [Cl2]= 0.3547, [PCl_5]= 0.1048.
c. [PCl_3]= 0.4018, [Cl2]= 0.8690, [PCl_5]= 0.7205.

Q48

NO_2 has a brownish color. At elevated temperatures, NO_2 reacts with CO

$$\mathrm{NO_2(g) + CO(g) \rightleftharpoons NO(g) + CO_2(g)}$$

The other gases in this equation are colorless. When a gas mixture is prepared at 600K, in which 9.6 atm is the initial partial pressure of both NO_2 and CO, and 5.4 atm is the partial pressure of both NO and CO_2, the brown color of the mixture observed begins to get stronger as the reaction progresses toward equilibrium. Give a condition that must be satisfied by the equilibrium constant K.

Q51

The equilibrium constant (K_p) for the reaction

$$\mathrm{As_4(g) \rightleftharpoons 2\ As_2(g)}$$

is 5.5837×10^{-4} at 1090 K.

a. The initial molarity of $[\mathrm{As_4}]$ is 2.3 M and the initial molarity of $[\mathrm{As_2}]$ is 0.001 M. Calculate the reaction quotient Q and determine which way the reaction proceeds.
b. Calculate the molarity of each compound at the equilibrium.
c. Which direction will the reaction proceed if the pressure on the reaction decreases? Explain your answer.

Solution

(a) First, because you are given the initial molarities of your products and reactants and a Kp instead of a Kc value, you have to convert Kp to Kc using the formula:

$$K_p = K_c(RT)^{\Delta n_{\text{gas}}}$$

Plug in your given values

$$5.5837 \times 10^{-4} = K_c(0.0821 \times 1090)^{2-1} = 89.489K_c$$

$$K_c = 6.24 \times 10^{-6}$$

Set up a reaction quotient for the equation given

$$Q = \frac{[\mathrm{As_2}]^2}{[\mathrm{As_4}]} = \frac{[0.001]^2}{[2.3]} = 4.35 \times 10^{-7}$$

Reaction will progress towards the right to reach equilibrium

(b) Set up an ice chart to find the equilibrium molarities

Reaction	P_4	2 P_2
I	2.3	0.001
C	$-x$	$+2x$
E	$2.3-x$	$0.001+2x$

$$6.24\times10^{-6}=\frac{[0.001+2x]^2}{[2.3-x]}$$

$$4x^2+0.00400624x-1.3352\times10^{-5}=0$$

Use the quadratic equation to find x

$$x=-0.0024,0.00139$$

-0.0024 is negative, which can't happen in real life so we know \(x) actually equals 0.00139.

[P_4]= 2.29861 M

[P_2]= 0.00378 M

(c) The reaction will progress towards the right because as pressure decreases, the reaction moves towards the side with the most moles of gas, which is the products.

Q55

Consider a reaction involving only gaseous compounds. The product yield at equilibrium decreases when the temperature and volume increase.

a. Is this reaction endothermic or exothermic?
b. Does the number of gas molecules in this reaction increase or decrease?

Solution

a. Exothermic. In exothermic reactions, product yield is indirectly related to temperature. In endothermic reactions, product yield is directly related to temperature. These properties can be further explained when heat is thought of as a reactant or a product. In exothermic reactions, heat is a product, and in endothermic reactions, heat is a reactant. When heat is added to a reaction, the equilibrium shifts to the opposite side to relieve stress on the system.

b. Decreases. The number of gas molecules is directly related to the volume of the container in which the reaction is happening. For example, if the volume of the container is decreased, the reaction will shift to whichever side has fewer moles of gas.

Q57

the Haber process, also called the Haber–Bosch process, is an artificial nitrogen fixation process and is the main industrial procedure for the production of ammonia today.

$$\mathrm{N_3+3\,H_2\rightleftharpoons 2\,NH_3}\quad(\Delta H=-92.4\,\mathrm{kJ/mol})$$

Determine the best condition of temperature and pressure to yield the most ammonia.

Solution

Because Haber process is an exothermic reaction, a lower temperature will maximize the yield of product. Also, according to the ideal gas law, because the moles of gas are proportional to the volume, and the volume is inverse proportional to the pressure; a higher pressure is required to maximize the yield of product.

Q59

At room temperature, a vessel is filled with gaseous carbon dioxide. Some water is added at 2.00 atm. It is well-shaken, integrating carbon dioxide gas into the water. 0.5 kg of the solution is taken out and boiled to extract 2.50 L of carbon dioxide. The system is at 10 degree Celsius and 1.00 atm. What is the Henry's Law constant for carbon dioxide in water?

Solution

given that the extracted solution:

$$PV = nRT \tag{12.E.1}$$

$$n = \frac{PV}{RT} = \frac{1\,\text{atm} \times 2.5\,\text{L}}{0.082 \frac{\text{L atm}}{\text{mol K}} \times 283.15\,\text{L}} = 0.1077\,\text{mol} \tag{12.E.2}$$

$$m_{CO_2} = n_{CO_2} \times \text{molar mass} = 0.1077\,\text{mol} \times 44\,\text{g/mol} = 4.7388\,\text{g} \tag{12.E.3}$$

$$m_{H_2O} = 500\,\text{g} - 4.7388\,\text{g} = 495.29\,\text{g} \tag{12.E.4}$$

$$n_{H_2O} = \frac{495.29\,\text{g}}{18\,\text{g/mol}} = 27.5\,\text{mol} \tag{12.E.5}$$

$$\text{Solubility of } \ce{CO2} \text{ in water} = \frac{0.1077\,\text{mol}}{0.5\,\text{kg}} = 0.2154\,\text{mol/kg} \tag{12.E.6}$$

Due to the Ideal gas law, the ratio of moles equals to the ratio of pressure

pressure: pressure = mol:mol = 0.1077: 27.51

because the total pressure is 2 atm, partial pressure of CO_2 = 0.0724 atm

Due to Henry's law:

$$k = \frac{c}{P} = \frac{0.2154 mol/kg}{0.0724\ atm} = 2.9751 \frac{mol}{kg\ atm} \tag{12.E.7}$$

Q61

The equilibrium constant for a reaction increases from $\text{K}=4 \cdot 5 \times 10^{-2}$ to $\text{K}=4 \cdot 5$ as the temperature increases from 0.00°C to 300.0°C. Assuming the change in enthalpy (ΔH) and change in entropy (ΔS) are constant over this range of temperatures, what is ΔS for this reaction? Is this reaction endothermic or exothermic?

Solution

Assuming ΔH and ΔS are constant, we can set up a system of equations as follows:

$$\begin{cases} \Delta G_{0.00^{\circ}\text{C}} = \Delta\text{H} - \text{T}\Delta\text{S} \\ \Delta G_{300.0^{\circ}\text{C}} = \Delta\text{H} - \text{T}\Delta\text{S} \end{cases}$$

We can determine $\Delta G_{0.00^{\circ}\text{C}}$ and $\Delta G_{300.0^{\circ}\text{C}}$ by utilizing the equation below that relates ΔG to K_{eq}:

$$\Delta G = -\text{RT}\ln(\text{K}) \quad \text{Easily remembered using the mnemonic: "}\Delta\text{Get in the }-\text{RighT lane, K?"}$$

$$\Delta G_{0.00^{\circ}\text{C}} = -\left(8.314 \frac{\text{J}}{\text{K} \times \text{mol}}\right)(273.15\text{K})\left(\ln(4.5 \times 10^{-2})\right) = 7042.5 \frac{\text{J}}{\text{mol}}$$

$$\Delta G_{300.0^{\circ}\text{C}} = -\left(8.314 \frac{\text{J}}{\text{K} \times \text{mol}}\right)(573.15\text{K})\left(\ln(4.5)\right) = -7167.2 \frac{\text{J}}{\text{mol}}$$

These values can then be plugged back into the original system of equations to obtain

$$\begin{cases} \Delta G_{0.00^{\circ}\text{C}} = 7042.5 \frac{\text{J}}{\text{mol}} = \Delta\text{H} - (273.15\text{K})\,\Delta\text{S} \\ \Delta G_{300.0^{\circ}\text{C}} = -7167.2 \frac{\text{J}}{\text{mol}} = \Delta\text{H} - (573.15\text{K})\,\Delta\text{S} \end{cases}$$

To calculate the values of the remaining two unknown variables, a substitution can be made that expresses ΔH in terms of ΔS.

$$-7167.2 \frac{\text{J}}{\text{mol}} + (573.15\text{K})\,\Delta\text{S} = \Delta\text{H}$$

This substitution can be plugged into the first equation to calculate the value for ΔS.

$$7042.5\,\tfrac{\text{J}}{\text{mol}} = -7167.2\,\tfrac{\text{J}}{\text{mol}} + (573.15\text{K})\,\Delta\text{S} - (273.15\text{K})\,\Delta\text{S}$$

$$\Delta\text{S} = 47.37\,\tfrac{\text{J}}{\text{K}\times\text{mol}}$$

ΔH can be calculated now by plugging in the value for ΔS into either one of the equations in the original set.

$$7042.5\,\tfrac{\text{J}}{\text{mol}} = \Delta\text{H} - (273.15\text{K})\left(47.37\,\tfrac{\text{J}}{\text{K}\times\text{mol}}\right)$$

$$\Delta\text{H} = 19980\,\tfrac{\text{J}}{\text{mol}} = 19.98\,\tfrac{\text{kJ}}{\text{mol}}$$

Because ΔH is positive, we know the reaction is endothermic.

Q63A

The equilibrium constant for the reaction $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\,\text{NO}_2(\text{g})$ is measured to be 5.9×10^{-3} at 298\;K and 1.3×10^{-6} at 398 K

a. Calculate ΔG° at 298 K for the reaction.
b. Calculate ΔH and ΔS°, assuming the enthalpy and entropy changes are independent of temperature between 298 K and 398 K.

Solution

a.Use the equation $\Delta G^\circ = -RT\ln K$

$\Delta G^\circ = -RT\ln K = (-8.3145\ \text{J K mol}^{-1}) \times (298\ \text{K})(\ln 5.9\times10^{-3}) = -1.29\times10^4\ \text{J mol}^{-1}$

For one mole of the reaction as written, ΔG° is -1290 kJ.

b. Use van't Hoff equation and the values of K at 298 K and at 398 K to obtain ΔH°. Then get ΔS° from ΔG° and the equation $\Delta G^\circ = -RT\ln K$

$\ln(\frac{1.3\times10^{-6}}{5.9\times10^{-3}}) = \frac{\Delta H^\circ}{8.3145\ \text{J K}^{-1}\,\text{mol}^{-1}}(\frac{1}{398\ K} - \frac{1}{298\ K})$

$\Delta\ H^\circ = 83.0\ kJ$

The answer equals both $\Delta\ H^\circ$ at 298 K and 398 K because it is assumed in the derivation of the van't Hoff equation that $\Delta\ H^\circ$ is independent of temperature. Next,

$\Delta\ S^\circ = \frac{\Delta\ H^\circ - \Delta\ G^\circ}{T} = \frac{83.0\times10^3\ J - (-1.29\times10^4\ J)}{298\ K} = 323\ J\ K^{-1}$

Q63B

For the reaction: $\text{Br}_2(\text{g}) \rightleftharpoons 2\,\text{Br}(\text{g})$, the equilibrium constant is 4.64×10^{-29} at 25ºC and 1.1×10^{-3} at 1280 K.

a. What is ΔG of the reaction at 298 K?
b. Assuming that ΔH^o and ΔS^o are independent of temperature, what are the values of enthalpy and entropy when the temperature changes to 1280 K?

Solution

a. ΔG = RTln(k)

= $(8.3145\text{JK}^{-1}\text{mol}^{-1})(298\text{K})\ln(4.64\text{x}10^{-29})$

= -161.65kJ

a)

$$ln\left(\frac{1.1x10^{-3}}{4.64x10^{-29}}\right) = \frac{-\Delta H}{R}\left(\frac{1}{1280K} - \frac{1}{298K}\right)$$

Solve for Δ H.

Δ H = 188.70 KJ

$$ln\,(k) = \frac{-\Delta H}{RT} + \frac{\Delta S}{R}$$

ln \left({1.1x10^{-3}}\right) = \dfrac{-188699.30}{(8.3245;\ {JK^{-1}mol^{-1}})(1280:\K} + \dfrac{ ΔS}{R} \nonumber

ΔS =90.78 $JK^{-1}mol^{-1}$

Q65

Calculate the equilibrium constant for the reaction,

$$2\ NO_2\ (g) \rightleftharpoons N_2O_4\ (g) \text{ at } 500\ K,$$

given the equilibrium constant K = 4.65 x 10^{-3} at 298 K, and ΔH° = -57.2 kJ mol^{-1}. Assume that ΔH° does not change between 298 K and 500 K

Solution

Use the van 't Hoff equation to calculate K_{500} from K_{298} and the standard enthalpy of the reaction ΔH°:

$$ln\frac{K_{500}}{K_{298}} = -\frac{\Delta H^\circ}{R}(\frac{1}{T_1} - \frac{1}{T_2})$$

=> K_{500} = 3.366 x 10^{-7}

Solve for the unknown variable, in this case it is K_{500}. T_1 is equal to 298K while T_2 is equal to 500K.

Q69

The equilibrium constant for the following reaction was experientially calculated at different temperatures.

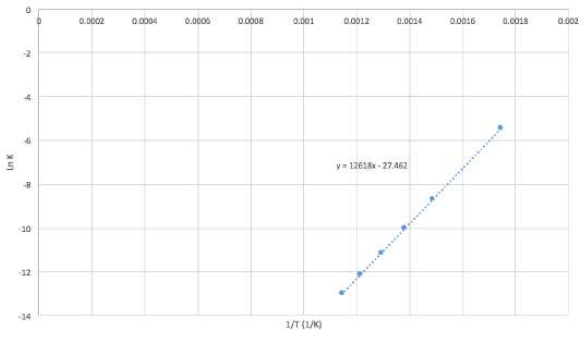
$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

Temperature (°C)	300	400	450	500	550	600
Equilibrium Constant (K_{eq})	4.34 x 10^{-3}	1.64 x 10^{-4}	4.51 x 10^{-5}	1.45 x 10^{-5}	5.38 x 10^{-6}	2.25 x 10^{-6}

a. Plot $\ln K$ as a function of $1/T$ (K^{-1})
b. What is ΔH^o of the equilibrium reaction with ammonia? HINT: use the slope to find the ΔH^o

Solution

The graph bellow shows what the graph should look like:



First we must write the van't Hoff equation:

$$\ln K = -\frac{\Delta H^o}{R}\frac{1}{T} + \frac{\Delta S^o}{R}$$

Writing the equation like this how it can be compared with y = mx + b. With this information we then know that the slope of the graphe is equal to -ΔH^o/R. So:

$$\Delta H^o = \text{-mR were R = 8.3145 J K}^{-1}\text{mol}^{-1}$$

$$\Delta H^o = \text{-104.9 kJ mol}^{-1}$$

Q71

At a certain temperature, $0.5\text{ mol I}_{2\text{ (aq)}}$ is dissolved in $2\text{ L H}_2\text{O}$ and shaken vigorously in a container with 2 L of CCl_4, an immiscible liquid. The container is then left to equilibrate during which time the iodine redistributes itself between the layers of H_2O and CCl_4 as indicated by the following reaction:

$$\text{I}_{2\text{ (aq)}} \rightleftharpoons \text{I}_2(\text{CCl}_4)$$

The final concentration of $\text{I}_{2\text{ (aq)}}$ is determined to be 0.0710 M. What is the partition coefficient (K) for this process?

Solution

The word "equilibrate" is a dead giveaway for "ICE Table" so we can establish the following ICE Table based on the information provided for the reaction provided.

$\text{I}_{2\text{ (aq)}} \rightleftharpoons \text{I}_2(\text{CCl}_4)$

ICE Table	$\text{I}_{2\text{ (aq)}}$	$\text{I}_2(\text{CCl}_4)$
Initial	0.250M	0M
Change	$-\text{x}$	$+\text{x}$
Equilibrium	0.0710M	$+\text{x}$

x can be calculated by solving the following equation:

$$0.250\text{M} - \text{x} = 0.0710\text{M}$$

$$\text{x} = 0.179\text{M}$$

This value can then be plugged into the ICE Table to obtain equilibrium values for $\text{I}_{2\text{ (aq)}}$ and $\text{I}_2(\text{CCl}_4)$. (Remember that the two liquids are immiscible so the molarity isn't 0.125Mas $\text{I}_2(\text{CCl}_4)$ does not contribute to the initial molarity of the solution.)

ICE Table	$\text{I}_{2\text{ (aq)}}$	$\text{I}_2(\text{CCl}_4)$
Initial	0.250M	0M
Change	-0.179M	$+0.179\text{M}$
Equilibrium	0.0710M	$+0.179\text{M}$

The equilibrium concentrations of $\text{I}_{2\text{ (aq)}}$ and $\text{I}_2(\text{CCl}_4)$ can then be plugged into the equilibrium constant expression and solve for the partition coefficient.

$$\text{K} = \frac{0.179\text{M}}{0.0710\text{M}}$$

$$\text{K} = 2.52$$

Q73

At 25°C, 0.130 g/L of chloroacetic acid ($C_2H_3ClO_2$) dissolve in of water, and at the same temperature 0.2834 g/L of chloroacetic acid dissolve in 1-octanol.

a. Calculate the following equilibrium constants

$$C_2H_2ClO_2H(s) \rightleftharpoons C_2H_2ClO_2H_{(aq)}$$

$$C_2H_2ClO_2H(s) \rightleftharpoons C_2H_2ClO_2H_{(octanol)}$$

b. Calculate the *participation coefficient*, K, of the combined reactions.

$$C_2H_2ClO_2H(aq) \rightleftharpoons C_2H_2ClO_2H_{(octanol)}$$

Solution

First, we will need g/L to M so that we can calculate the equilibrium constant.

$$\left(\frac{0.130\ \cancel{g\ C_2H_3ClO_2}}{1\ L}\right)\left(\frac{1\ mol}{94.494\ \cancel{g\ C_2H_3ClO_2}}\right) = 0.0013757\ M$$

$$\left(\frac{0.2834\ \cancel{g\ C_2H_3ClO_2}}{1\ L}\right)\left(\frac{1\ mol}{94.494\ \cancel{g\ C_2H_3ClO_2}}\right) = 3.00x10^{-3}\ M$$

$$K = \frac{K_{forminde}}{K_{aq}} = \frac{3.00 \times 10^{-3}}{0.001376} = 2.18$$

$$\log_{10} K_{oct/wat} = 0.338$$

Q75

At 298 K, the two gases NOBr and Br_2 have the number of moles of 1.25 and 8.5 x 10^{-5} at equilibrium with a sufficient amount of solid NO. Determine the equilibrium constant of the reaction:

$$2NOBr_{(g)} \rightleftharpoons 2NO_{(s)} + Br_{2(g)}$$

Solution

Use: $P_{gas} = n_{gas}(RT/V)$

$K = P_{Br2} / P^2_{NOBr} = n_{Br2} / n^2_{NOBr} = 5.44 \times 10^{-5}$

The volume is needed to solve this problem. It is necessary to find the value of K regardless of it is K_p or K_c.

Q79

At 300 K and 1 atm, N_2O_4 is partly dissociated into NO_2. The density of the equilibrium mixture was 2.076 g/L. What is the degree of dissociation of N_2O_4 under these circumstances?

Solution

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

moles of N_2O_4 at equilibrium = 1-x moles of NO_2 at equilibrium = 2x

Therefore, the degree of dissociation of SO_3 is 0.8.

(Multiplying number of moles by molar mass to get the total mass)

92*(1- x) + [46*(2x)/ (1+x)]= [2.076 g/L * 0.08206 (L*atm)/(mol*K)] / 1 atm

On solving the equation, we get the equation, x= 0.8

Q85

The decompressions of calcium carbonate ($CaCO_3$) occurs according to the following reaction:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

100 g of solid calcium carbonate ($\mathrm{CaCO_3}$) and 50 g of calcium oxide (CaO) are placed in an evacuated round bottom flask that is heated up to 35°C. At this temperature the pressure in the round bottom flask is found to be 0.5 atm.

a. What is the equilibrium constant of the decompressions of calcium carbonate ($\mathrm{CaCO_3}$) at 35°C?
b. If 100 g of calcium oxide (CaO) at 35°C was added to the flask what would be the new total pressure of the flask and why?
c. If the pressure in the round bottom flask would to increase to 1.0 atm, then what would would be the new equilibrium constant?

Solution

a. First we need to write the equilibrium expression for the reaction:

$$K_{eq} = p\mathrm{CO_2}] \tag{12.E.8}$$

Now we just need to plug in the pressure of CO_2: K_{eq} = [0.5] = 0.5

b. The total pressure would still be 0.5 atm because solids have an activity of 1 so they don't effect the equilibrium pressure.
c. The new equilibrium constant would be 1.0 atm.

Q87

Let's say you have the reaction:

$$A(s) + B(g) \leftrightharpoons C(s) + D(g)$$

At 25°C, this reaction has an equilibrium constant of 157.2. Find the partial pressures of $B(g)$ and $D(g)$ when the total pressure of the system is equal to 4.3 atm.

Solution

First, the equilibrium expression of this reaction is

$$K_c = \frac{D(g)}{B(g)} = 157.2$$

Note, the A(s) and C(s) are not included in this expression because they are solids. Solids have an activity equal to 1 which basically means they do not affect the equilibrium of the reaction.

To calculate the partial pressure of our unknowns, we can use Dalton's Law of partial pressures:

$$P_A = X_A P_{Total}$$

Since we are looking for the partial pressure of each of our gases, and we already have the total pressure of the system, we need to find the mole fraction of each of our gases. To find it, we can manipulate the above equilibrium expression to get:

$$D(g) = 157.2\ B(g)$$

Here, we see that at equilibrium, there are 157.2 molecules of $D(g)$ for every 1 molecule of $B(g)$

Now that we have the ratio of molecules in this reaction, we can construct workable mole fractions.

$$X_D = \frac{157.2}{1+157.2}$$
$$X_B = \frac{1}{1+157.2}$$

Finally, we can plug everything in to find our partial pressures.

$$P_D = \frac{157.2}{158.2} \times (4.3\ atm) = 4.27\ atm$$
$$P_B = \frac{1}{157.8} \times (4.3\ atm) = 0.027\ atm$$

Q91

Given the reaction

$$C_3H_5N(g) + 3\ H_2(g) \leftrightharpoons C_5H_{11}N(g)$$

whose equilibrium constant is solved by this equation

$$log_{10}(K) = -20.28 + \frac{10.56\ K}{T}$$

a. Solve for K when $T = 200\ K$
b. What is partial pressure of $C_3H_5N(g)$ when $T = 200\ K$ and the partial pressure of hydrogen is 1.0 atm and the partial pressure of $C_5H_{11}N(g)$ is 2.0×10^{-5} atm.

Solution

Part a)

$$log_{10}(K) = -20.28 + \frac{10.56\ K}{200\ K}$$

$$K = 10^{-20.23} = 5.89 \times 10^{-21}$$

part b)

Set up the equilibrium constant of the reaction, plug in your partial pressures, and solve for $C_3H_5N(g)$

$$K = \frac{[C_5H_{11}N]}{[C_5H_5N]\ [H_2]^3}$$

$$K = \frac{2.0 \times 10^{-5}}{[C_5H_5N]\ [1]}$$

$$[C_5H_5N] = 3.40 \times 10^{15}$$

Q93

Two equal volume solutions of 2M $HCOO^-$ and 2M HCOOH are mixed together. Assume that the volumes are additive. The value of the equilibrium constant Ka for HCOOH is 1.77 x 10^{-4}. What is the ratio between the amounts of HCOOH and $HCOO^-$ in the solution at equilibrium?

Solution

The chemical equation for this reaction is

$$HCOOH_{(aq)} + H_2O_l \leftrightarrow H_3O^+_{(aq)} + HCOO^-_{(aq)}$$

This indicates that

$$K_a = \frac{[HCOO^-][H_3O^+]}{[HCOOH]}$$

Because the volumes are equal and additive, the concentrations of the two solutions become half of what they were initially.

At equilibrium,

$$[HCOO^-] = 1 + x$$

$$[H_3O^+] = x$$

$$[HCOOH] = 1 - x$$

Plugging in these values into the equilibrium expression gives

$$1.77 \bullet 10^{-4} = \frac{[1+x][x]}{[1-x]}$$

Solving the equation for x gives

$$x = 1.77 \bullet 10^{-4} M$$

The ratio of HCOOH and $HCOO^-$ is

$$\frac{1+x}{1-x}$$

and due to x being such a small value, the ratio between the amounts of HCOOH and $HCOO^-$ is essentially 1.

Q101

The \(ΔG_f^o\) of $PbO(s)$ is -188.95 kJ mol^{-1}. Calculate the equilibrium pressure of O_2(g) over a sample of pure PbO(s) in contact with pure Pb(s) at 25°C. PbO(s) decomposes according to the equation

$$PbO_{(s)} \rightleftharpoons Pb(s) + \frac{1}{2}O_2(g)$$

Solution

Since $G_f°$ for O_2(g) and Pb_s(s) is 0, for the reaction

$$\Delta G^\circ = (0+0) - (-188.95 kJ mol^{-1}) = 188.95 kJ mol^{-1}$$

The equilibrium constant of the reaction can be computed by

$$lnK = -\frac{\Delta G^\circ}{RT} = -76.22$$

$$K = 7.898 \bullet 10^{-34}$$

From the chemical equation, we can tell

$$K = (P_{O_2})^{1/2}$$

Therefore the equilibrium pressure of O_2 at 25°C

$$P_{O_2} = 6.2 \bullet 10^{-67} atm$$

Q105

If that weren't enough, Jim's sister, ., knocked his grass juice (a mixture of 1-Hexanol, Cl_2, $CaCl_2$, and cyclohexane) into the family's benzene-ethanol vat! Assume that the two solvents in the vat are immiscible with each other but are miscible with the grass juice components. Jim separates the benzene and ethanol, and drinks the one with the greater amount of 1-Hexanol. Which one does he drink? Which of the two solvents have the highest concentration of the other components of the grass juice?

Solution

There are two immiscible solvents in the family vat. What this means is that they do not mix/ dissolve well in each other. Consequently, when . poured the grass juice into this vat, the solution technically contains two solvents. Evidently, what this means is that each of the solutes (which are the grass juice constituents mentioned in the question) dissolves to a different extent in each solvent. When the question asks which solvent has the greater amount of 1-Hexanol, it is the same as asking does 1-Hexanol dissolve "more" in either benzene or ethanol (the two solvents). The concept of "like dissolves like" is very important here, and to solve this problem first benzene must be identified as non-polar and driven by dispersion forces, while ethanol is polar. Since polar solvents dissolve polar solutes, then ethanol should be able to dissolve $CaCl_2$ and 1-Hexanol, both polar solutes, much better, while benzene can dissolve Cl_2 and cyclohexane, which are nonpolar, to a greater extent. The aptitude that each solvent has in dissolving the solutes directly correlate to the concentrations of solutes that are present in the solvent.

Thus, Jim would drink the ethanol, since it has the highest concentration of the polar 1-Hexanol. Also, the benzene would have the highest concentration of Cl_2 and cyclohexane, and the ethanol would also have the highest concentration of $CaCl_2$, which is ionic and therefore "very polar".

Abstract: "Like dissolves Like": polar solvents dissolve polar solutes, and nonpolar solvents dissolve polar solutes

Q107

Calculate the pH of a 0.5 M H_3PO_4 acid solution given that $K_{a1} = 7.1 \times 10^{-3}$, $K_{a2} = 6.3 \times 10^{-8}$ and $K_{a3} = 4.2 \times 10^{-13}$.

Solution

A14.107V2

1.25

H14.107V2

Review on how to calculate the pH of a polyprotic acids here.

S14.107V2

$$7.1 \times 10^{-3} = \frac{x^2}{(0.5 - x)}$$

$$x = 0.0561\ M = [H^+]$$

$$pH = -\log[H^+] = 1.25$$

We assume that all of the H^+ in solution comes from the dissociation of the first H^+ because the second and the third is too small to have a significant effect in the pH of the solution.

Q107

The Haber-Bosch process is a method invented in the 20th century as a method for hydrogen fixation. It is widely used in industry today, and involves reacting nitrogen and hydrogen in the following manner:

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

Calculate ΔG°_{rxn}. If the pressure of the products and reaction are all kept constant at the same value, in which direction will the reaction go?

Relevant information:

$\Delta G^\circ_f\ NH_{2\ (g)} = 199.83 \frac{kJ}{mol}$

Solution

The process of calculating ΔG should be very familiar after reading Q15, so this solution will not elaborate much on this method. With that being said, the ΔG°_{rxn} is as follows:

$$\Delta G^\circ_{rxn} = 399.66 \frac{kJ}{mol}$$

Both N_2 and H_2 have respective ΔG_f of zero. Now, remember that if ΔG°_{rxn} is negative (ΔG°_{rxn}<0), then the reaction is spontaneous in the direction mentioned. However, in this case the ΔG°_{rxn} is definitely NOT less than zero, so it is not spontaneous in the direction $N_{2\ (g)} + 3H_{2\ (g)} \rightarrow 2NH_{3\ (g)}$. However, if the chemical formula is "flipped" so that it goes from $N_{2\ (g)} + 3H_{2\ (g)} \leftarrow 2NH_{3\ (g)}$, Hess's law states that the corresponding ΔG°_{rxn} is also "flipped" from positive to negative (or vice versa, depending on the value. For this situation, however, the ΔG°_{rxn} does turn negative). What information can be drawn from this is that, since a negative ΔG°_{rxn} means that the reaction will be spontaneous, then it can be inferred that the reaction will favor going from $N_{2\ (g)} + 3H_{2\ (g)} \leftarrow 2NH_{3\ (g)}$, rather than $N_{2\ (g)} + 3H_{2\ (g)} \rightarrow 2NH_{3\ (g)}$. Without even having to calculate the equilibrium constant, from this information alone, it can be inferred that, at equilibrium, the reactants are favored over the products. Therefore, if both gasses are kept at constant pressure, the reaction will tend to increase concentration of reactants. Thus, the reaction will go left.

Abstract: Find the ΔG°_{rxn}, understand what implications it has in regards to equilibrium, and apply this knowledge to infer that the reaction will favor the reactants.

Q109

At 273 K, the equation: $H_2(g) + I_2(g) \rightarrow 2HI(g)$ has an equilibrium constant of 60.2

a. Solve for ΔG° at 273 K
b. How does G change when the pressure of HI is 2 atm, I_2 is 4 atm and H_2 is 6 atm?
c. Is this reaction spontaneous?

Solution

a) $\Delta G° = -RT \ln(K)$

ΔG° = -(8.3145 J/K mol)(273 K) ln(60.2)

ΔG° = -9301.1 J/mol

b) ΔG = ΔG° + RT ln(Q)

ΔG = -9301.1 J/mol + (8.3145 J/K mol)(273 K) ln(P_{HI} / $P_{H2}P_{I2}$)

ΔG = -9301.1 J/mol + (8.3145 J/K mol)(273 K) ln(2 / (6x4))

ΔG = -14941.49 J/mol.

c) This reaction proceeds spontaneously in the forward direction.

Q109

At 773 K the equilibrium constant for the Haber-Bosch process is 1.45x10^{-5}. The chemical reaction involved in the Haber-Bosch process is:

$$N_{2\,(g)} + 3H_{2\,(g)} \rightleftharpoons 2NH_{3\,(g)}$$

a. What is $\Delta G^{\circ}(773)$ for this reaction?
b. What is ΔG at 773 K for transforming 1 mole of N_2 and 3 moles H_2 held at 30 atm to 2 moles of NH_3 held at 1 atm?
c. In which direction would the previous reaction run spontaneously?

Solution

a. The value of $\Delta G^{\circ}(773)$ can be found using the equation $\Delta G^{\circ} = -RT \ln K$ where T and K are already known to be 773 K and 1.45x10^{-5} respectively while R=8.134 J K^{-1} mol^{-1}.

$$\Delta G^{\circ} = -8.314\ J\ K^{-1}\ mol^{-1} \times 773K \times ln(1.45 \times 10^{-5}) = 70052\ J$$

$$\Delta G^{\circ} = 70052\ J$$

b. The equation needed to determine ΔG is $\Delta G = RTln(Q/K)$. The values of R, T, and K are known while Q is

$$Q = \frac{P_{NH_3}^2 / P_{ref}}{(P_{N_2}/P_{ref})(P_{H_2}^3/P_{ref})}$$

P_{ref} =1 atm and the other pressures are stated in the question. So to find Q, the pressures have to be plugged into the equation

$$Q = \frac{(1)^2}{(20)(20)^3} = \frac{1}{160000} = 6.25 \times 10^{-6}$$

Now that the value of Q is known, ΔG can be found

$$\Delta G = -8.314\ J\ K^{-1}\ mol^{-1} \times 773K \times ln(\frac{6.25 \times 10^{-6}}{1.45 \times 10^{-5}}) = -5291\ J$$

$$\Delta G = -5291\ J$$

c. The previous reaction would run towards the products spontaneously because $\Delta G < 0$.

Q111

The following reaction is exothermic

$$\mathrm{SnO_2(s) + 2\,H_2(g) \rightarrow Sn(g) + 2\,H_2O(l)}$$

a. What is the equilibrium expression based on this chemical equation?
b. What happens to the reaction if more H_2 is added? SnO_2 is added into the system?
c. What effect would an increase in temperature have on the system?
d. What affect would an increase in pressure have on the system?

Solution

a. Add texts here. Do not delete this text first.K = [Sn] / [H_2] This is because solids are not included in the equilibrium expression
b. If H_2 were added, the reaction would shift right, towards the products, more Sn is produced. If SnO_2 were added, there would be no effect on the equilibrium because SnO_2 is not involve in the equilibrium process (K).
c. The reaction would shift towards the reactants. The reaction is exothermic, so heat is treated like a product.
d. An increase in pressure would shift the reaction towards the side that has less mole of gas. Therefore, in this reaction, an increased in pressure would shift the reaction to the right, more products are produced. Q111

Q112

Given the chemical reaction

$$\mathrm{SnO_2(s) \rightleftharpoons Sn(s) + O_2(g)}$$

a. Formulate the equilibrium expression using activities
b. State the effect on $p\mathrm{O_2}$ at equilibrium if more $\mathrm{SnCl_4(l)}$ is added to the system
c. State the effect on $p\mathrm{O_2}$ at equilibrium if more $\mathrm{O_2(g)}$ is added to the system

Solution

a. The activities of solids and liquids are always equal to 1. The activities of gases are equal to the partial pressure of the gas in bars. Therefore the equilibrium expression would be

$$K = P_{O_2}$$

b. P_{O_2} would not change because the activity of a liquid is always 1 meaning it has no effect on the equilibrium constant

c. P_{O_2} would decrease because the extra gas would push the system out of equilibrium and in order for the system to return to equilibrium, some of the O_2 gas would have to react with some of the $Sn_{(s)}$. This would decrease the amount of $O_{2(g)}$ present in the system and therefore decrease the the pressure of $O_{2(g)}$.

Q113

Arrange the following solutions in order of most acidic to basic: NaOH, NaCN, H_2SO_4, NH_4NO_3, NaCl

Solution

$$\mathrm{H_2SO_4 > NH_4NO_3 > NaCl > NaCN > NaOH} \tag{12.E.9}$$

Review acids bases here.

- H_2SO_4 is a strong acid.
- NH_4NO_3 is formed by a weak base (NH_4OH) and a strong acid (HNO_3). Hence, NH_4NO_3 is acidic.
- NaCl is formed by a strong base (NaOH) and a strong acid (HCl). Hence, it is a neutral salt.
- NaCN is formed by a strong base (NaOH) and a weak acid (HCN). Hence, NaCN is basic.
- NaOH is a strong base.

Q115

Given that the K_b values for $\mathrm{NH_3}$ and $\mathrm{NH_2NH_2}$ are 1.8×10^{-5} and 8.5×10^{-7}, respectively. Which is the stronger acid?

Solution

$$\mathrm{NH_2NH_2}$$

Calculate the K_a values first. Review on how to identify the strength of an acid from its K_a value here.

For NH_3,

$$K_a = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10}$$

For NH_2NH_2,

$$K_a = \frac{(1.0 \times 10^{-14}}{8.5 \times 10^{-7}} = 1.18 \times 10^{-8}$$

Since the Ka value of NH_2NH_2 is larger, NH_2NH_2 is the stronger acid.

Q119

Calculate the pH of the following solutions.

a. 0.5 M NaCN (K_a of $HCN = 6.2 \times 10^{-10}$)
b. 0.01 M NH_4Cl (K_b of $NH_3 = 1.8 \times 10^{-5}$)

Solution

11.5 5.63

Ka=(1*10^{-14})/(1.8*10^{-5})=5.56*10^{-10}
5.56*10^{-10}=x^2/(0.01-x)
x=2.36*10^{-6}
pH= -log(x)= 5.63

H14.119V2

Review on the properties of salts here.

\[\ce{CN$^-$ (aq) + H$_2$O (l) <=> HCN (aq) + OH$^-$ (aq)}\]

Kb=(1*10^{-14})/(6.2*10^{-10})=1.62*10^{-5}

$$1.62 \times 10^{-5} = \frac{x^2}{0.5 - x} \tag{12.E.10}$$

x=0.00283

pOH= -log(x)= 2.55

pH= 14-pOH= 11.5

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq) \tag{12.E.11}$$

Q131

Identify the stronger acid in each of the following combination. Explain.

a. HF and HBr
b. H_2SO_4 and H_2SO_3
c. HOCl and HOBr

Solution

14.131V2

HBr H_2SO_4 HOCl

Study the effect of structure on acids and bases.

S14.131V2

1. HBr is the stronger acid because Br less electronegative and therefore less polar as compared to HF.
2. H_2SO_4 is the stronger acid because as the number of attached oxygen on the O-H bonds increases, the less polar the molecule is.
3. For oxyacids, the less polar oxyacids are the ones that are more electronegative. Since Cl is more electronegative than Br, HOCl is the stronger acid.

Q137

Identify the Lewis acid and Lewis base for each of the following reaction.

a. $H^+(aq) + NH_3(aq) \rightleftharpoons NH_4^+(aq)$
b. $Al^{3+}(aq) + 6\,H_2O(l) \rightleftharpoons Al(H_2O)_6^{3+}(aq)$
c. $CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$

Solution

	Lewis acid	Lewis base
1.	H^+	NH_3
2.	Al^{3+}	H_2O
3.	CO_2	H_2O

H14.137V2

Study the concept of electron pairs here.

S14.137V2

H^+ is the electron-pair acceptor while NH_3 is the electron-pair donor. Al^{3+} is the electron-pair acceptor while H_2O is the electron-pair donor. CO_2 is the electron-pair acceptor while H_2O is the electron-pair donor.

Q139

Beryllium hydroxide is an amphoteric compound. It can react as an acid as well as a base. Please write the reactions of $Be(OH)_2$ and describe its role base on Brønsted-Lowry and Lewis theories.

Solution

$Be(OH)_2(s)+2H^+(aq)$-> $Be^{2+}(aq)+2H_2O(l)$ (Brønsted-Lowry base, $2H^+$ acceptor)

$Be(OH)_2(s)+2OH^-(aq)$-> $Be(OH)_4^{2-}(aq)$ (Lewis acid, electron pair acceptor)

H14.139.2P

Consider Brønsted-Lowry and Lewis theories.

http://chemwiki.ucdavis.edu/Textbook...cids_and_Bases

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SECTION OVERVIEW

13.1: Solids, Liquids, and Phase Transitions

An General Chemistry Libretexts Textmap organized around the textbook

Principles of Modern Chemistry

by Oxtoby, Gillis, and Campion

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Template:HideTOC

Gas, liquid, and solid are known as the three states of matter or material, but each of solid and liquid states may exist in one or more forms. Thus, another term is required to describe the various forms, and the term phase is used. Each distinct form is called a phase, but the concept of phase defined as a homogeneous portion of a system, extends beyond a single material, because a phase may also involve several materials. A solid has a definite shape and volume. A liquid has a definite volume but it takes the shape of a container whereas a gas fills the entire volume of a container. You already know that diamond and graphite are solids made up of the element carbon. They are two phases of carbon, but both are solids.Solids are divided into subclasses of amorphous (or glassy) solids and crystalline solids. Arrangements of atoms or molecules in crystalline solids are repeated regularly over a very long range of millions of atoms, but their arrangements in amorphous solids are somewhat random or short range of say some tens or hundreds of atoms. In general, there is only one liquid phase of a material. However, there are two forms of liquid helium, each have some unique properties. Thus, the two forms are different (liquid) phases of helium. At a definite temperature and pressure, the two phases co-exist.

13.1.1: Bulk Properties of Liquids - Molecular Interpretation

13.1.2: Intermolecular Forces - Origins in Molecular Structure

13.1.3: Intermolecular Forces in Liquids

13.1.4: Phase Equilibrium

13.1.5: Phase Transitions

13.1.6: Phase Diagrams

13.1.E: Solids, Liquids, and Phase Transitions (Exercises)

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13.1.1: Bulk Properties of Liquids - Molecular Interpretation

Learning Objectives

- To describe the unique properties of liquids.
- To know how and why the vapor pressure of a liquid varies with temperature.
- To understand that the equilibrium vapor pressure of a liquid depends on the temperature and the intermolecular forces present.

Although you have been introduced to some of the interactions that hold molecules together in a liquid, we have not yet discussed the consequences of those interactions for the bulk properties of liquids. We now turn our attention to four unique properties of liquids that intimately depend on the nature of intermolecular interactions:

1. surface tension,
2. capillary action,
3. viscosity, and
4. boiling point.

Surface Tension

If liquids tend to adopt the shapes of their containers, then why do small amounts of water on a freshly waxed car form raised droplets instead of forming a thin, continuous film? The answer lies in a property called **surface tension**, which depends on intermolecular forces. Surface tension is the energy required to increase the surface area of a liquid by a unit amount and varies greatly from liquid to liquid based on the nature of the intermolecular forces, e.g., water with hydrogen bonds has a surface tension of *[Math Processing Error]* (at 20°C), while mercury with metallic (electrostatic) bonds has as surface tension that is 6.5-times greater: *[Math Processing Error]* (at 20°C).

Figure *[Math Processing Error]* presents a microscopic view of a liquid droplet. A typical molecule in the *interior* of the droplet is surrounded by other molecules that exert attractive forces from all directions. Consequently, there is no *net* force on the molecule that would cause it to move in a particular direction. In contrast, a molecule on the *surface* experiences a net attraction toward the drop because there are no molecules on the outside to balance the forces exerted by adjacent molecules in the interior. Because a sphere has the smallest possible surface area for a given volume, intermolecular attractive interactions between water molecules cause the droplet to adopt a spherical shape. This maximizes the number of attractive interactions and minimizes the number of water molecules at the surface. Hence raindrops are almost spherical, and drops of water on a waxed (nonpolar) surface, which does not interact strongly with water, form round beads. A dirty car is covered with a mixture of substances, some of which are polar. Attractive interactions between the polar substances and water cause the water to spread out into a thin film instead of forming beads.

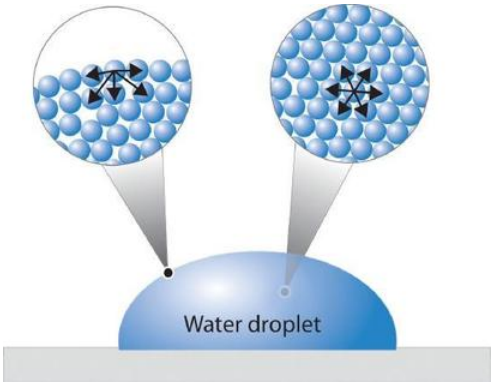


Figure *[Math Processing Error]*: A Representation of Surface Tension in a Liquid. Molecules at the surface of water experience a net attraction to other molecules in the liquid, which holds the surface of the bulk sample together. In contrast, those in the interior experience uniform attractive forces. (CC BY-SA-NC; anonymous)

The same phenomenon holds molecules together at the surface of a bulk sample of water, almost as if they formed a skin. When filling a glass with water, the glass can be overfilled so that the level of the liquid actually extends *above* the rim. Similarly, a sewing needle or a paper clip can be placed on the surface of a glass of water where it “floats,” even though steel is much denser

than water. Many insects take advantage of this property to walk on the surface of puddles or ponds without sinking. This is better demonstrated in the zero-gravity conditions of space (Figure *[Math Processing Error]*).



Figure *[Math Processing Error]*: The Effects of the High Surface Tension of Liquid Water. The Full video can be found at https://youtu.be/o8TssbmY-GM.

Such phenomena are manifestations of surface tension, which is defined as the energy required to increase the surface area of a liquid by a specific amount. Surface tension is therefore measured as energy per unit area, such as joules per square meter (J/m^2). The values of the surface tension of some representative liquids are listed in Table *[Math Processing Error]*. Note the correlation between the surface tension of a liquid and the strength of the intermolecular forces: the stronger the intermolecular forces, the higher the surface tension. For example, water, with its strong intermolecular hydrogen bonding, has one of the highest surface tension values of any liquid, whereas low-boiling-point organic molecules, which have relatively weak intermolecular forces, have much lower surface tensions. Mercury is an apparent anomaly, but its very high surface tension is due to the presence of strong metallic bonding.

Table *[Math Processing Error]*: Surface Tension, Viscosity, Vapor Pressure (at 25°C Unless Otherwise Indicated), and Normal Boiling Points of Common Liquids

Substance	Surface Tension ($\times 10^{-3}$ J/m^2)	Viscosity (mPa•s)	Vapor Pressure (mmHg)	Normal Boiling Point (°C)
Organic Compounds				
diethyl ether	17	0.22	531	34.6
n-hexane	18	0.30	149	68.7
acetone	23	0.31	227	56.5
ethanol	22	1.07	59	78.3
ethylene glycol	48	16.1	~0.08	198.9
Liquid Elements				
bromine	41	0.94	218	58.8
mercury	486	1.53	0.0020	357
Water				
0°C	75.6	1.79	4.6	—
20°C	72.8	1.00	17.5	—
60°C	66.2	0.47	149	—
100°C	58.9	0.28	760	—

Adding soaps and detergents that disrupt the intermolecular attractions between adjacent water molecules can reduce the surface tension of water. Because they affect the surface properties of a liquid, soaps and detergents are called surface-active agents, or surfactants. In the 1960s, US Navy researchers developed a method of fighting fires aboard aircraft carriers using “foams,” which are aqueous solutions of fluorinated surfactants. The surfactants reduce the surface tension of water below that of fuel, so the fluorinated solution is able to spread across the burning surface and extinguish the fire. Such foams are now used universally to fight large-scale fires of organic liquids.

Surface Energies and Surface Tension

Any material - solid, liquid or (non-ideal) gas - wants to bond to itself. This is why condensed phase materials "sticks" together in the first place. However, a surface disrupts this bonding, and so incurs an energy penalty. This is why liquids in zero gravity ball up into spherical drops (Figure *[Math Processing Error]*) - the sphere is the shape with the lowest surface area for a fixed volume. We can describe this *surface energy* with dimensions of energy per unit area, which is the amount of extra energy needed to create new surface or extend a surface (e.g., cracking a solid or parting a liquid). Hence, surface tension is typically given in J/m^2 units (Table *[Math Processing Error]*).

Capillary Action

Intermolecular forces also cause a phenomenon called capillary action, which is the tendency of a polar liquid to rise against gravity into a small-diameter tube (a *capillary*), as shown in Figure *[Math Processing Error]*. When a glass capillary is put into a dish of water, water is drawn up into the tube. The height to which the water rises depends on the diameter of the tube and the temperature of the water but *not* on the angle at which the tube enters the water. The smaller the diameter, the higher the liquid rises. The height of the water does *not* depend on the angle at which the capillary is tilted.

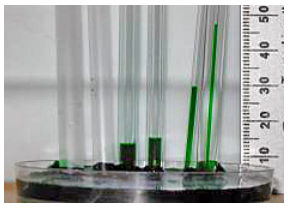


Figure *[Math Processing Error]*: The Phenomenon of Capillary Action. Capillary action seen as water climbs to different levels in glass tubes of different diameters. (Dr. Clay Robinson, PhD, West Texas A&M University)

Capillary action is the net result of two opposing sets of forces: cohesive forces, which are the intermolecular forces that hold a liquid together, and adhesive forces, which are the attractive forces between a liquid and the substance that composes the capillary.

- Cohesive forces bind molecules of the same type together
- Adhesive forces bind a substance to a surface

Water has both strong adhesion to glass, which contains polar *[Math Processing Error]* groups, and strong intermolecular cohesion. When a glass capillary is put into water, the surface tension due to cohesive forces constricts the surface area of water within the tube, while adhesion between the water and the glass creates an upward force that maximizes the amount of glass surface in contact with the water. If the adhesive forces are stronger than the cohesive forces, as is the case for water, then the liquid in the capillary rises to the level where the downward force of gravity exactly balances this upward force. If, however, the cohesive forces are stronger than the adhesive forces, as is the case for mercury and glass, the liquid pulls itself down into the capillary below the surface of the bulk liquid to minimize contact with the glass (part (a) in Figure *[Math Processing Error]*). The upper surface of a liquid in a tube is called the meniscus, and the shape of the meniscus depends on the relative strengths of the cohesive and adhesive forces. In liquids such as water, the meniscus is concave; in liquids such as mercury, however, which have very strong cohesive forces and weak adhesion to glass, the meniscus is convex (Figure *[Math Processing Error]*).

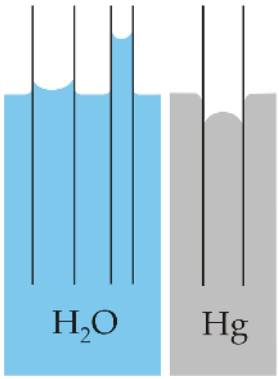


Figure *[Math Processing Error]*: The Phenomenon of Capillary Action. Capillary action of water compared to mercury, in each case with respect to a polar surface such as glass. (a) This drawing illustrates the shape of the meniscus and the relative height of a mercury column when a glass capillary is put into liquid mercury. The meniscus is convex and the surface of the liquid inside the tube is *lower* than the level of the liquid outside the tube. (b) Because water adheres strongly to the polar surface of glass, it has a concave meniscus, whereas mercury, which does not adhere to the glass, has a convex meniscus. (CC BY-SA 3.0; MesserWoland via Wikipedia)

Fluids and nutrients are transported up the stems of plants or the trunks of trees by capillary action. Plants contain tiny rigid tubes composed of cellulose, to which water has strong adhesion. Because of the strong adhesive forces, nutrients can be transported from the roots to the tops of trees that are more than 50 m tall. Cotton towels are also made of cellulose; they absorb water because the tiny tubes act like capillaries and "wick" the water away from your skin. The moisture is absorbed by the entire fabric, not just the layer in contact with your body.

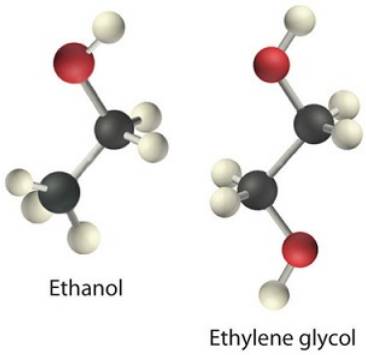
> *Polar substances are drawn up a glass capillary and generally have concave meniscuses and nonpolar substances general avoid the capillary and exhibit convex meniscuses.*

Viscosity

Viscosity (η) is the resistance of a liquid to flow. Some liquids, such as gasoline, ethanol, and water, flow very readily and hence have a *low viscosity*. Others, such as motor oil, molasses, and maple syrup, flow very slowly and have a *high viscosity*. The two most common methods for evaluating the viscosity of a liquid are

1. to measure the time it takes for a quantity of liquid to flow through a narrow vertical tube and
2. to measure the time it takes steel balls to fall through a given volume of the liquid.

The higher the viscosity, the slower the liquid flows through the tube and the steel balls fall. Viscosity is expressed in units of the poise (mPa•s); the higher the number, the higher the viscosity. The viscosities of some representative liquids are listed in Table *[Math Processing Error]* and show a correlation between viscosity and intermolecular forces. Because a liquid can flow only if the molecules can move past one another with minimal resistance, strong intermolecular attractive forces make it more difficult for molecules to move with respect to one another. The addition of a second hydroxyl group to ethanol, for example, which produces ethylene glycol ($HOCH_2CH_2OH$), increases the viscosity 15-fold. This effect is due to the increased number of hydrogen bonds that can form between hydroxyl groups in adjacent molecules, resulting in dramatically stronger intermolecular attractive forces.



Comparison of structures of ethanol (left) with ethylene glycol (right). (CC BY-SA-NC; anonymous)

There is also a correlation between viscosity and molecular shape. Liquids consisting of long, flexible molecules tend to have higher viscosities than those composed of more spherical or shorter-chain molecules. The longer the molecules, the easier it is for them to become “tangled” with one another, making it more difficult for them to move past one another. London dispersion forces also increase with chain length. Due to a combination of these two effects, long-chain hydrocarbons (such as motor oils) are highly viscous.

> *Viscosity increases as intermolecular interactions or molecular size increases.*

Application: Motor Oils

Motor oils and other lubricants demonstrate the practical importance of controlling viscosity. The oil in an automobile engine must effectively lubricate under a wide range of conditions, from subzero starting temperatures to the 200°C that oil can reach in an engine in the heat of the Mojave Desert in August. Viscosity decreases rapidly with increasing temperatures because the kinetic energy of the molecules increases, and higher kinetic energy enables the molecules to overcome the attractive forces that prevent the liquid from flowing (Table *[Math Processing Error]*). As a result, an oil that is thin enough to be a good lubricant in a cold engine will become too “thin” (have too low a viscosity) to be effective at high temperatures.



Viscosity of motor Oils. youtu.be/V5a4kP-5Jiw

The viscosity of motor oils is described by an SAE (Society of Automotive Engineers) rating ranging from SAE 5 to SAE 50 for engine oils: the lower the number, the lower the viscosity. So-called *single-grade oils* can cause major problems. If they are viscous enough to work at high operating temperatures (SAE 50, for example), then at low temperatures, they can be so viscous that a car is difficult to start or an engine is not properly lubricated. Consequently, most modern oils are *multigrade*, with designations such as SAE 20W/50 (a grade used in high-performance sports cars), in which case the oil has the viscosity of an SAE 20 oil at subzero temperatures (hence the W for winter) and the viscosity of an SAE 50 oil at high temperatures. These properties are achieved by a careful blend of additives that modulate the intermolecular interactions in the oil, thereby controlling the temperature dependence of the viscosity. Many of the commercially available oil additives “for improved engine performance” are highly viscous materials that increase the viscosity and effective SAE rating of the oil, but overusing these additives can cause the same problems experienced with highly viscous single-grade oils.

Table *[Math Processing Error]*: Dynamic Viscosity (N s/m^2)

SAE	Temperature (^oC)			
	0	20	50	100
10	0.31	0.079	0.020	0.005
20	0.72	0.170	0.033	0.007

SAE	Temperature (^oC)			
	0	20	50	100
30	1.53	0.310	0.061	0.010
40	2.61	0.430	0.072	0.012
50	3.82	0.630	0.097	0.015

Example *[Math Processing Error]*

Based on the nature and strength of the intermolecular cohesive forces and the probable nature of the liquid–glass adhesive forces, predict what will happen when a glass capillary is put into a beaker of SAE 20 motor oil. Will the oil be pulled up into the tube by capillary action or pushed down below the surface of the liquid in the beaker? What will be the shape of the meniscus (convex or concave)? (Hint: the surface of glass is lined with Si–OH groups.)

Given: substance and composition of the glass surface

Asked for: behavior of oil and the shape of meniscus

Strategy:

A. Identify the cohesive forces in the motor oil.
B. Determine whether the forces interact with the surface of glass. From the strength of this interaction, predict the behavior of the oil and the shape of the meniscus.

Solution:

A Motor oil is a nonpolar liquid consisting largely of hydrocarbon chains. The cohesive forces responsible for its high boiling point are almost solely London dispersion forces between the hydrocarbon chains.

B Such a liquid cannot form strong interactions with the polar Si–OH groups of glass, so the surface of the oil inside the capillary will be lower than the level of the liquid in the beaker. The oil will have a convex meniscus similar to that of mercury.

Exercise *[Math Processing Error]*

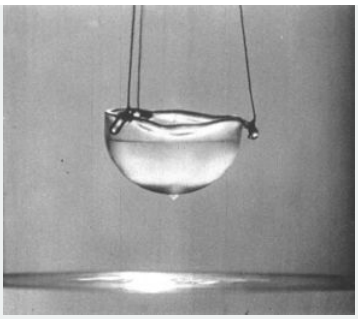
Predict what will happen when a glass capillary is put into a beaker of ethylene glycol. Will the ethylene glycol be pulled up into the tube by capillary action or pushed down below the surface of the liquid in the beaker? What will be the shape of the meniscus (convex or concave)?

Answer

Capillary action will pull the ethylene glycol up into the capillary. The meniscus will be concave.

Oddity of Science: Superfluid Helium-4

Superfluid helium-4 is the superfluid form of helium-4, an isotope of the element helium. A superfluid is a state of matter in which the matter behaves like a fluid with zero viscosity. The substance, which looks like a normal liquid, flows without friction past any surface, which allows it to continue to circulate over obstructions and through pores in containers which hold it, subject only to its own inertia.



The liquid helium is in the superfluid phase. A thin invisible film creeps up the inside wall of the cup and down on the outside. A drop forms. It will fall off into the liquid helium below. This will repeat until the cup is empty - provided the liquid remains superfluid. (Public Domain; Alfred Leitner).

Many ordinary fluids, like alcohol or petroleum, creep up solid walls, driven by their surface tension. However, in the case of superfluid helium-4, the flow of the liquid in the layer is not restricted by its viscosity but by a critical velocity which is about 20 cm/s. This is a fairly high velocity so superfluid helium can flow relatively easily up the wall of containers, over the top, and down to the same level as the surface of the liquid inside the container. In a container, lifted above the liquid level, it forms visible droplets as seen above.

Boiling Points

The **vapor pressure** of a liquid is defined as the pressure exerted by a vapor in equilibrium with its condensed phases (solid or liquid) at a given temperature in a closed system (discussed in more detail in next Sections of Chapter). As the temperature of a liquid increases, the vapor pressure of the liquid increases until it equals the external pressure, or the atmospheric pressure in the case of an open container. Bubbles of vapor begin to form throughout the liquid, and the liquid begins to boil. The temperature at which a liquid boils at exactly 1 atm pressure is the normal boiling point of the liquid. For water, the normal boiling point is exactly 100°C. The normal boiling points of the other liquids in Figure *[Math Processing Error]* are represented by the points at which the vapor pressure curves cross the line corresponding to a pressure of 1 atm.

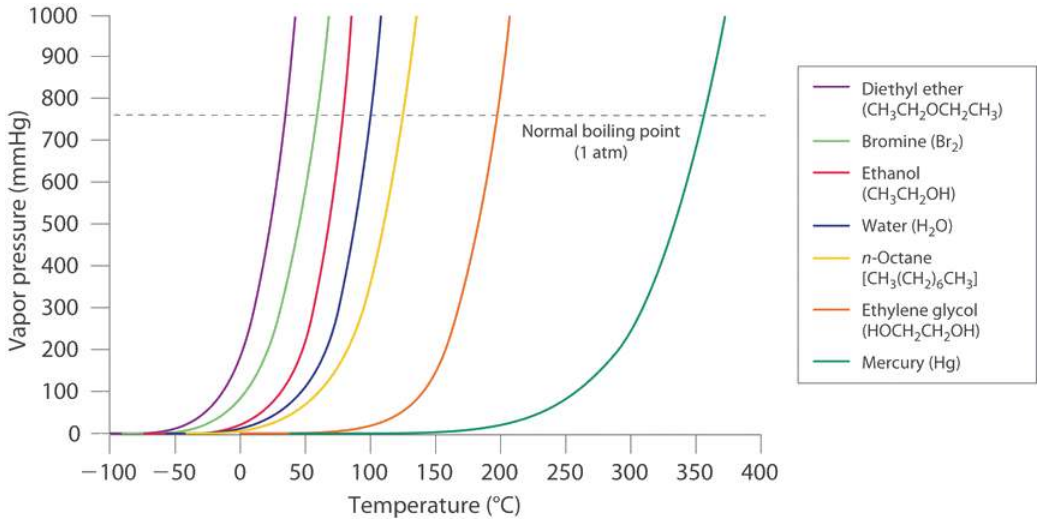


Figure *[Math Processing Error]*: The Vapor Pressures of Several Liquids as a Function of Temperature. The point at which the vapor pressure curve crosses the P = 1 atm line (dashed) is the normal boiling point of the liquid. (CC BY-SA-NC; anonymous)

Although we usually cite the normal boiling point of a liquid, the *actual* boiling point depends on the pressure. At a pressure greater than 1 atm, water boils at a temperature greater than 100°C because the increased pressure forces vapor molecules above the surface to condense. Hence the molecules must have greater kinetic energy to escape from the surface. Conversely, at pressures less than 1 atm, water boils below 100°C.

Table *[Math Processing Error]*: The Boiling Points of Water at Various Locations on Earth

Place	Altitude above Sea Level (ft)	Atmospheric Pressure (mmHg)	Boiling Point of Water (°C)
Mt. Everest, Nepal/Tibet	29,028	240	70
Bogota, Colombia	11,490	495	88
Denver, Colorado	5280	633	95
Washington, DC	25	759	100
Dead Sea, Israel/Jordan	−1312	799	101.4

Typical variations in atmospheric pressure at sea level are relatively small, causing only minor changes in the boiling point of water. For example, the highest recorded atmospheric pressure at sea level is 813 mmHg, recorded during a Siberian winter; the lowest sea-level pressure ever measured was 658 mmHg in a Pacific typhoon. At these pressures, the boiling point of water changes minimally, to 102°C and 96°C, respectively. At high altitudes, on the other hand, the dependence of the boiling point of water on pressure becomes significant. Table *[Math Processing Error]* lists the boiling points of water at several locations with different altitudes. At an elevation of only 5000 ft, for example, the boiling point of water is already lower than the lowest ever recorded at sea level. The lower boiling point of water has major consequences for cooking everything from soft-boiled eggs (a "three-minute egg" may well take four or more minutes in the Rockies and even longer in the Himalayas) to cakes (cake mixes are often sold with separate high-altitude instructions). Conversely, pressure cookers, which have a seal that allows the pressure inside them to exceed 1 atm, are used to cook food more rapidly by raising the boiling point of water and thus the temperature at which the food is being cooked.

> *As pressure increases, the boiling point of a liquid increases and vice versa.*

Example *[Math Processing Error]*: Boiling Mercury

Use Figure *[Math Processing Error]* to estimate the following.

a. the boiling point of water in a pressure cooker operating at 1000 mmHg
b. the pressure required for mercury to boil at 250°C



Mercury boils at 356 °C at room pressure. To see video go to www.youtube.com/watch?v=0iizsbXWYoo

Given: data in Figure *[Math Processing Error]*, pressure, and boiling point

Asked for: corresponding boiling point and pressure

Strategy:

A. To estimate the boiling point of water at 1000 mmHg, refer to Figure *[Math Processing Error]* and find the point where the vapor pressure curve of water intersects the line corresponding to a pressure of 1000 mmHg.
B. To estimate the pressure required for mercury to boil at 250°C, find the point where the vapor pressure curve of mercury intersects the line corresponding to a temperature of 250°C.

Solution:

a. The vapor pressure curve of water intersects the P = 1000 mmHg line at about 110°C; this is therefore the boiling point of water at 1000 mmHg.
b. The vertical line corresponding to 250°C intersects the vapor pressure curve of mercury at $P \approx 75$ mmHg. Hence this is the pressure required for mercury to boil at 250°C.

? Exercise *[Math Processing Error]*: Boiling Ethylene Glycol

Ethylene glycol is an organic compound primarily used as a raw material in the manufacture of polyester fibers and fabric industry, and polyethylene terephthalate resins (PET) used in bottling. Use the data in Figure *[Math Processing Error]* to estimate the following.

a. the normal boiling point of ethylene glycol
b. the pressure required for diethyl ether to boil at 20°C.

Answer a

200°C

Answer b

450 mmHg

Summary

Surface tension, capillary action, boiling points, and viscosity are unique properties of liquids that depend on the nature of intermolecular interactions. **Surface tension** is the energy required to increase the surface area of a liquid by a given amount. The stronger the intermolecular interactions, the greater the surface tension. **Surfactants** are molecules, such as soaps and detergents, that reduce the surface tension of polar liquids like water. **Capillary action** is the phenomenon in which liquids rise up into a narrow tube called a capillary. It results when **cohesive forces**, the intermolecular forces in the liquid, are weaker than **adhesive forces**, the attraction between a liquid and the surface of the capillary. The shape of the **meniscus**, the upper surface of a liquid in a tube, also reflects the balance between adhesive and cohesive forces. The **viscosity** of a liquid is its resistance to flow. Liquids that have strong intermolecular forces tend to have high viscosities. The **boiling point** of a liquid is the temperature when the **vapor pressure** of the liquid equals the external pressure, or the atmospheric pressure in the case of an open container.

Contributors and Attributions

- Modified by Joshua Halpern (Howard University)

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13.1.2: Intermolecular Forces - Origins in Molecular Structure

Learning Objectives

- To describe the intermolecular forces in liquids.

The properties of liquids are intermediate between those of gases and solids, but are more similar to solids. In contrast to *intra*molecular forces, such as the covalent bonds that hold atoms together in molecules and polyatomic ions, *inter*molecular forces hold molecules together in a liquid or solid. Intermolecular forces are generally much weaker than covalent bonds. For example, it requires 927 kJ to overcome the intramolecular forces and break both O–H bonds in 1 mol of water, but it takes only about 41 kJ to overcome the intermolecular attractions and convert 1 mol of liquid water to water vapor at 100°C. (Despite this seemingly low value, the intermolecular forces in liquid water are among the strongest such forces known!) Given the large difference in the strengths of intra- and intermolecular forces, changes between the solid, liquid, and gaseous states almost invariably occur for molecular substances *without breaking covalent bonds*.

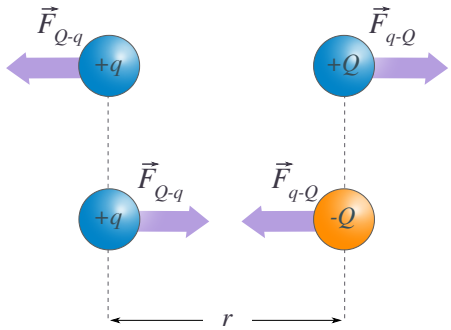
The properties of liquids are intermediate between those of gases and solids but are more similar to solids.

Intermolecular forces determine bulk properties such as the melting points of solids and the boiling points of liquids. Liquids boil when the molecules have enough thermal energy to overcome the intermolecular attractive forces that hold them together, thereby forming bubbles of vapor within the liquid. Similarly, solids melt when the molecules acquire enough thermal energy to overcome the intermolecular forces that lock them into place in the solid.

Coulombic Interactions

Through various experiments, Charles Augustin de Coulomb found a way to explain the interactions between charged particles, which in turn helped to explain where the stabilities and instabilities of various particles come from. While the entities that hold atoms together within a molecule can be attributed to bonds, the forces that create these bonds can be explained by Coulomb Forces. Thus, the physical basis behind the bonding of two atoms can be explained.

Coulomb's findings indicate that like charges repel each other and unlike charges attract one another. Thus electrons, which are negatively charged, repel each other but attract protons. Likewise, protons repel each other.



The absolute value of the force F between two point charges q and Q relates to the distance between the point charges and to the simple product of their charges. The diagram shows that like charges repel each other, and opposite charges attract each other. (CC BY-NC; Ümit Kaya)

Each atom is made up of a nucleus in the center, which consists of a number of protons and neutrons, depending upon the element in question. Surrounding the nucleus are electrons that float around the nucleus in what can be thought of as a cloud. As two atoms approach one another, the protons of one atom attract the electrons of the other atom. Similarly, the protons of the other atom attract the electrons of the first atom. As a result, the simultaneous attraction of the components from one atom to another create a bond. This interaction can be summarized mathematically and is known as Coulombic forces:

$$F = k\frac{q_1 q_2}{r^2} \tag{13.1.2.1}$$

In this mathematical representation of Coulomb's observations,

- F is the electrical force acting between two atoms
- with q_1 and q_2 representing the magnitude of the charges of each atom,
- r is the distance between the two atoms.
- and k is a constant.

From Equation 13.1.2.1, the electrostatic force between two charges is *inversely* proportional to the *square* of the distance separating the two atoms.

Ion–Ion Interactions

The interactions between ions (ion - ion interactions or charge-charge interactions) are the easiest to understand since such interactions are just a simple application of Coulombic forces (Equation 13.1.2.1). This specific interaction operates over relatively long distances in the gas phase and is responsible for the attraction of opposite charge ions and the repulsion of like charged ions.

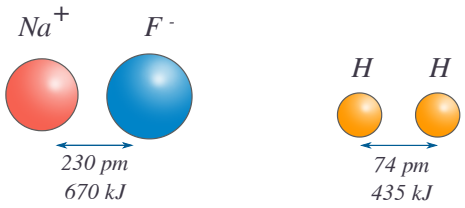


Figure 13.1.2.1: Ion-Ion attraction in NaF (left) exceeds the covalent bond energy of $\mathrm{H_2}$ (right). (CC BY-NC; Ümit Kaya)

Coulombic forces are also involved in all forms of chemical bonding; when they act between separate charged particles they are especially strong. Thus the energy required to pull a mole of $\mathrm{Na^+}$ and $\mathrm{F^-}$ ions apart in the sodium fluoride crystal is greater than that needed to break the a covalent bonds of a mole of $\mathrm{H_2}$. The effects of ion-ion attraction are seen most directly in salts such as NaF and NaCl that consist of oppositely-charged ions arranged in inter-penetrating crystal lattices.

According to Coulomb's Law the force between two charged particles is given by

$$\underbrace{F = \frac{q_1 q_2}{4\pi\epsilon_0 r^2}}_{\text{ion-ion Force}} \tag{13.1.2.2}$$

Instead of using SI units, chemists often prefer to express atomic-scale distances in picometers and charges as electron charge (±1, ±2, etc.) Using these units, the proportionality constant $1/4\pi\epsilon$ works out to $2.31 \times 10^{16}\ J\ pm$. The sign of F determines whether the force will be attractive (–) or repulsive (+); notice that the latter is the case whenever the two q's have the same sign. Two oppositely-charged particles flying about in a vacuum will be attracted toward each other, and the force becomes stronger and stronger as they approach until eventually they will stick together and a considerable amount of energy will be required to separate them.

Figure 13.1.2.2: Ion - Ion Interactions in the Gas Phase. (Gary L. Bertrand).

They form an *ion-pair*, a new particle which has a positively-charged area and a negatively-charged area. There are fairly strong interactions between these ion pairs and free ions, so that these clusters tend to grow, and they will eventually fall out of the gas phase as a liquid or solid (depending on the temperature).

Equation 13.1.2.2 is an example of an *inverse square law*; the force falls off as the square of the distance. A similar law governs the manner in which the illumination falls off as you move away from a point light source; recall this the next time you walk away from a street light at night, and you will have some feeling for what an inverse square law means.

The stronger the attractive force acting between two particles, the greater the amount of work required to separate them. Work represents a flow of energy, so the foregoing statement is another way of saying that when two particles move in response to a force, their potential energy is lowered. This work is found by integrating the negative of the force function with respect to distance over the distance moved. Thus the energy that must be supplied in order to completely separate two oppositely-charged particles initially at a distance r_0 is given by

$$w = -\int_{r_o}^{\infty} \frac{q_1 q_2}{4\pi\epsilon_0 r^2} dr = -\frac{q_1 q_2}{4\pi\epsilon_0 r_o} \tag{13.1.2.3}$$

hence, the potential ($V_{ion-ion}$) responsible for the ion-ion force is

$$\underbrace{V_{ion-ion} = \frac{q_1 q_2}{4\pi\epsilon_0 r}}_{\text{ion-ion potential}} \tag{13.1.2.4}$$

Example 13.1.2.1

When sodium chloride is melted, some of the ion pairs vaporize and form neutral NaCl dimers. How much energy would be released when one mole of Na^+ and Cl^- ions are brought together to generate dimers in this way? The bondlength of NaCl is 237 pm.

Solution

The interactions involved in forming NaCl dimers is the ion-ion forces with a potential energy given by Equation 13.1.2.4 However, this is the energy of interaction for one pair of Na^+ and Cl^- ion and needs to be scaled by a mole. So the energy released will be

$$\begin{aligned} E &= N_a V(\text{NaCl}) \\ &= N_a \frac{q_1 q_2}{4\pi\epsilon_0 r} \end{aligned}$$

The r in this equation is the distance between the two ions, which is the bondlength of 237 pm ($237 \times 10^{-12} m$).

$$\begin{aligned} E &= (6.022 \times 10^{23}) \underbrace{(8.987 \times 10^9 Nm^2/C^2)}_{1/4\pi\epsilon_o} \frac{(+1.6 \times 10^{-19} C)(-1.6 \times 10^{-19} C)}{237 \times 10^{-12} m} \\ &= -584\ kJ/mol \end{aligned}$$

This is not the energy needed to separate one mole of NaCl since that is a lattice and has more than pairwise interactions and require addressing the geometric orientation of the lattice (see Madelung Constants for more details).

Intermolecular forces are electrostatic in nature; that is, they arise from the electrostatic interaction between positively and negatively charged species. Like covalent and ionic bonds, intermolecular interactions are the sum of both attractive and repulsive components. Because electrostatic interactions fall off rapidly with increasing distance between molecules, intermolecular interactions are most important for solids and liquids, where the molecules are close together. These interactions become important for gases only at very high pressures, where they are responsible for the observed deviations from the ideal gas law at high pressures (i.e., real gases).

Ion-Dipole Interactions

A dipole that is close to a positive or negative ion will orient itself so that the end whose partial charge is opposite to the ion charge will point toward the ion. This kind of interaction is very important in aqueous solutions of ionic substances; H_2O is a highly polar molecule, so that in a solution of sodium chloride, for example, the Na^+ ions will be enveloped by a shell of water molecules with

their oxygen-ends pointing toward these ions, while H_2O molecules surrounding the Cl^- ions will have their hydrogen ends directed inward. As a consequence of ion-dipole interactions, all ionic species in aqueous solution are hydrated; this is what is denoted by the suffix in formulas such as K^+(aq), etc.

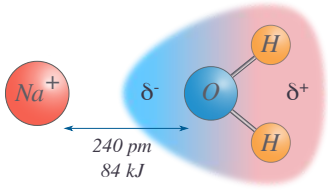


Figure 13.1.2.3: Ion - Dipole Interaction. (CC BY-NC; Ümit Kaya)

The strength of ion-dipole attraction depends on the magnitude of the dipole moment and on the charge density of the ion. This latter quantity is just the charge of the ion divided by its volume. Owing to their smaller sizes, positive ions tend to have larger charge densities than negative ions, and they should be more strongly hydrated in aqueous solution. The hydrogen ion, being nothing more than a bare proton of extremely small volume, has the highest charge density of any ion; it is for this reason that it exists entirely in its hydrated form H_3O^+ in water.

Since there is now both attractive and repulsive interactions and they both get weaker as the ion and dipole distance increases while also approaching each other in strength, the net ion-dipole is an inverse square relationship as shown in Equation 13.1.2.5.

$$\underbrace{E \propto \frac{-|q_1|\mu_2}{r^2}}_{\text{ion-dipole potential}} \tag{13.1.2.5}$$

- r is the distance of separation.
- q is the charge of the ion (only the magnitude of the charge is shown here.)
- μ is the permanent dipole moment of the polar molecule.

$$\vec{\mu} = q' \vec{d} \tag{13.1.2.6}$$

where q' is the partial charge of each end of the dipole and d is the separation between the charges within the dipole

Ion-Ion vs. Ion-Dipole potentials

There are several differences between ion-ion potential (Equation 13.1.2.4) and the ion-dipole potential (Equation 13.1.2.5) interactions.

- First, the potential of ion/dipole interactions are negative and net interaction will always be attractive, since the attraction of the opposite dipole to the ion will make it closer than the dipole with the like charge. By using the absolute value of the charge of the ion, and placing a negative sign in front of the equation, this results in a lowering of the potential energy (μ is positive).
- Second, the potential drops off quicker in Equation 13.1.2.5, where it is an inverse square relationship to the radius ($1/r^2$), while a simple charge-charge interaction (Equation 13.1.2.4) has a linear inverse relationship ($1/r$). This means the ion-dipole are a shorter range interaction and diminish more rapidly the father the polar molecule is from the ion.
- Third, note that the units of the two equations are the same, as μ has the units of charge X distance. However, the distance in μ is the distance between the dipoles of the polar molecule, while the distance denoted by the "r" is the distance between the ion and the dipole.

It needs to be understood that the molecules in a solution are rotating and vibrating and actual systems are quite complicated (Figure 13.1.2.4). What is important to realize is that these interactions are Coulombic in nature and how the mathematical equations describe this in terms of the magnitude of the charges and their distances from each other. In this course we will not be calculating dipole moments or the magnitudes of them, but understanding how to read the equations, and developing qualitative understandings that allow us to predict trends.

Figure 13.1.2.4: Ion-Dipole Interactions in the gas phase. (Gary L. Bertrand).

Dipole–Dipole Interactions

Polar covalent bonds behave as if the bonded atoms have localized fractional charges that are equal but opposite (i.e., the two bonded atoms generate a *dipole*). If the structure of a molecule is such that the individual bond dipoles do not cancel one another, then the molecule has a net dipole moment. Molecules with net dipole moments tend to align themselves so that the positive end of one dipole is near the negative end of another and vice versa, as shown in part (a) in Figure 13.1.2.1.

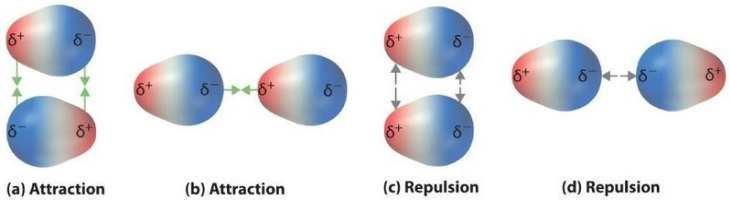


Figure 13.1.2.5: Attractive and Repulsive Dipole–Dipole Interactions. (a and b) Molecular orientations in which the positive end of one dipole (δ^+) is near the negative end of another (δ^-) (and vice versa) produce attractive interactions. (c and d) Molecular orientations that juxtapose the positive or negative ends of the dipoles on adjacent molecules produce repulsive interactions.

These arrangements are more stable than arrangements in which two positive or two negative ends are adjacent (Figure 13.1.2.1*c*). Hence dipole–dipole interactions, such as those in Figure 13.1.2.5*b*, are *attractive intermolecular interactions*, whereas those in Figure 13.1.2.5*d* are *repulsive intermolecular interactions*. Because molecules in a liquid move freely and continuously, molecules always experience both attractive and repulsive dipole–dipole interactions simultaneously, as shown in Figure 13.1.2.2 On average, however, the attractive interactions dominate.

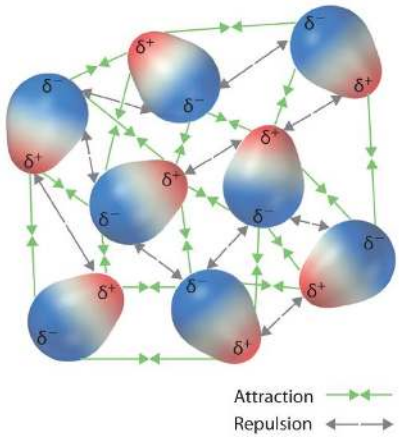


Figure 13.1.2.6: Both Attractive and Repulsive Dipole–Dipole Interactions Occur in a Liquid Sample with Many Molecules

Because each end of a dipole possesses only a fraction of the charge of an electron, dipole–dipole interactions are substantially weaker than the interactions between two ions, each of which has a charge of at least ±1, or between a dipole and an ion, in which one of the species has at least a full positive or negative charge. In addition, the attractive interaction between dipoles falls off much more rapidly with increasing distance than do the ion–ion interactions. Recall that the attractive energy between two ions is proportional to $1/r$, where r is the distance between the ions. Doubling the distance ($r \rightarrow 2r$) decreases the attractive energy by one-half.

In contrast, the energy of the interaction of two dipoles is proportional to $1/r^6$, so doubling the distance between the dipoles decreases the strength of the interaction by 2^6, or 64-fold:

$$V = -\frac{2\mu_A^2\mu_B^2}{3(4\pi\epsilon_0)^2 r^6}\frac{1}{k_B T} \tag{13.1.2.7}$$

Thus a substance such as HCl, which is partially held together by dipole–dipole interactions, is a gas at room temperature and 1 atm pressure, whereas NaCl, which is held together by interionic interactions, is a high-melting-point solid. Within a series of compounds of similar molar mass, the strength of the intermolecular interactions increases as the dipole moment of the molecules increases, as shown in Table 13.1.2.1 Using what we learned about predicting relative bond polarities from the electronegativities of the bonded atoms, we can make educated guesses about the relative boiling points of similar molecules.

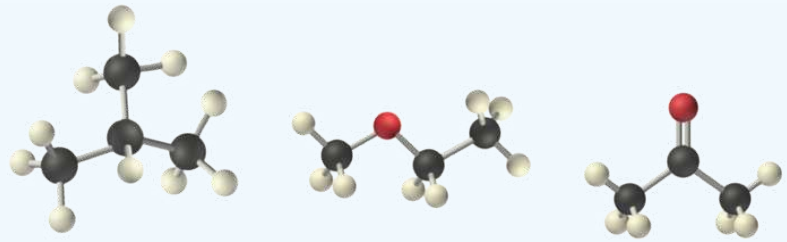
Table 13.1.2.1: Relationships between the Dipole Moment and the Boiling Point for Organic Compounds of Similar Molar Mass

Compound	Molar Mass (g/mol)	Dipole Moment (D)	Boiling Point (K)
C_3H_6 (cyclopropane)	42	0	240
CH_3OCH_3 (dimethyl ether)	46	1.30	248
CH_3CN (acetonitrile)	41	3.9	355

The attractive energy between two ions is proportional to $1/r$, whereas the attractive energy between two dipoles is proportional to $1/r^6$.

Example 13.1.2.2

Arrange ethyl methyl ether ($CH_3OCH_2CH_3$), 2-methylpropane [isobutane, $(CH_3)_2CHCH_3$], and acetone (CH_3COCH_3) in order of increasing boiling points. Their structures are as follows:



Given: compounds

Asked for: order of increasing boiling points

Strategy:

Compare the molar masses and the polarities of the compounds. Compounds with higher molar masses and that are polar will have the highest boiling points.

Solution:

The three compounds have essentially the same molar mass (58–60 g/mol), so we must look at differences in polarity to predict the strength of the intermolecular dipole–dipole interactions and thus the boiling points of the compounds. The first compound, 2-methylpropane, contains only C–H bonds, which are not very polar because C and H have similar electronegativities. It should therefore have a very small (but nonzero) dipole moment and a very low boiling point. Ethyl methyl ether has a structure similar to H_2O; it contains two polar C–O single bonds oriented at about a 109° angle to each other, in addition to relatively nonpolar C–H bonds. As a result, the C–O bond dipoles partially reinforce one another and generate a significant dipole moment that should give a moderately high boiling point. Acetone contains a polar C=O double bond oriented at about 120° to two methyl groups with nonpolar C–H bonds. The C–O bond dipole therefore corresponds to the molecular dipole, which should result in both a rather large dipole moment and a high boiling point. Thus we predict the following order of

boiling points: 2-methylpropane < ethyl methyl ether < acetone. This result is in good agreement with the actual data: 2-methylpropane, boiling point = −11.7°C, and the dipole moment (μ) = 0.13 D; methyl ethyl ether, boiling point = 7.4°C and μ = 1.17 D; acetone, boiling point = 56.1°C and μ = 2.88 D.

? Exercise 13.1.2.1

Arrange carbon tetrafluoride (CF_4), ethyl methyl sulfide ($CH_3SC_2H_5$), dimethyl sulfoxide [$(CH_3)_2S{=}O$], and 2-methylbutane [isopentane, $(CH_3)_2CHCH_2CH_3$] in order of decreasing boiling points.

Answer

dimethyl sulfoxide (boiling point = 189.9°C) > ethyl methyl sulfide (boiling point = 67°C) > 2-methylbutane (boiling point = 27.8°C) > carbon tetrafluoride (boiling point = −128°C)

London Dispersion Forces

Thus far we have considered only interactions between polar molecules, but other factors must be considered to explain why many nonpolar molecules, such as bromine, benzene, and hexane, are liquids at room temperature, and others, such as iodine and naphthalene, are solids. Even the noble gases can be liquefied or solidified at low temperatures, high pressures, or both (Table 13.1.2.2).

What kind of attractive forces can exist between nonpolar molecules or atoms? This question was answered by Fritz London (1900–1954), a German physicist who later worked in the United States. In 1930, London proposed that temporary fluctuations in the electron distributions within atoms and nonpolar molecules could result in the formation of short-lived instantaneous dipole moments, which produce attractive forces called London dispersion forces between otherwise nonpolar substances.

Table 13.1.2.2: Normal Melting and Boiling Points of Some Elements and Nonpolar Compounds

Substance	Molar Mass (g/mol)	Melting Point (°C)	Boiling Point (°C)
Ar	40	−189.4	−185.9
Xe	131	−111.8	−108.1
N_2	28	−210	−195.8
O_2	32	−218.8	−183.0
F_2	38	−219.7	−188.1
I_2	254	113.7	184.4
CH_4	16	−182.5	−161.5

Consider a pair of adjacent He atoms, for example. On average, the two electrons in each He atom are uniformly distributed around the nucleus. Because the electrons are in constant motion, however, their distribution in one atom is likely to be asymmetrical at any given instant, resulting in an instantaneous dipole moment. As shown in part (a) in Figure 13.1.2.3, the instantaneous dipole moment on one atom can interact with the electrons in an adjacent atom, pulling them toward the positive end of the instantaneous dipole or repelling them from the negative end. The net effect is that the first atom causes the temporary formation of a dipole, called an induced dipole, in the second. Interactions between these temporary dipoles cause atoms to be attracted to one another. These attractive interactions are weak and fall off rapidly with increasing distance. London was able to show with quantum mechanics that the attractive energy between molecules due to temporary dipole–induced dipole interactions falls off as $1/r^6$. Doubling the distance therefore decreases the attractive energy by 2^6, or 64-fold.

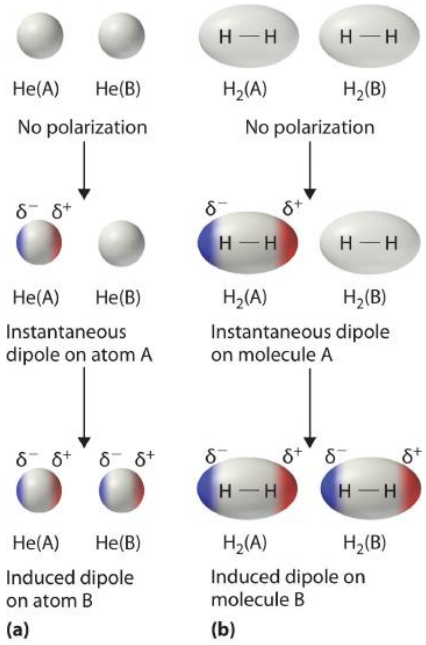


Figure 13.1.2.3: Instantaneous Dipole Moments. The formation of an instantaneous dipole moment on one He atom (a) or an H_2 molecule (b) results in the formation of an induced dipole on an adjacent atom or molecule.

Instantaneous dipole–induced dipole interactions between nonpolar molecules can produce intermolecular attractions just as they produce interatomic attractions in monatomic substances like Xe. This effect, illustrated for two H_2 molecules in part (b) in Figure 13.1.2.3, tends to become more pronounced as atomic and molecular masses increase (Table 13.1.2.2). For example, Xe boils at −108.1°C, whereas He boils at −269°C. The reason for this trend is that the strength of London dispersion forces is related to the ease with which the electron distribution in a given atom can be perturbed. In small atoms such as He, the two 1*s* electrons are held close to the nucleus in a very small volume, and electron–electron repulsions are strong enough to prevent significant asymmetry in their distribution. In larger atoms such as Xe, however, the outer electrons are much less strongly attracted to the nucleus because of filled intervening shells. As a result, it is relatively easy to temporarily deform the electron distribution to generate an instantaneous or induced dipole. The ease of deformation of the electron distribution in an atom or molecule is called its polarizability. Because the electron distribution is more easily perturbed in large, heavy species than in small, light species, we say that heavier substances tend to be much more *polarizable* than lighter ones.

> *For similar substances, London dispersion forces get stronger with increasing molecular size.*

The polarizability of a substance also determines how it interacts with ions and species that possess permanent dipoles. Thus London dispersion forces are responsible for the general trend toward higher boiling points with increased molecular mass and greater surface area in a homologous series of compounds, such as the alkanes (part (a) in Figure 13.1.2.4). The strengths of London dispersion forces also depend significantly on molecular shape because shape determines how much of one molecule can interact with its neighboring molecules at any given time. For example, part (b) in Figure 13.1.2.4 shows 2,2-dimethylpropane (neopentane) and *n*-pentane, both of which have the empirical formula C_5H_{12}. Neopentane is almost spherical, with a small surface area for intermolecular interactions, whereas *n*-pentane has an extended conformation that enables it to come into close contact with other *n*-pentane molecules. As a result, the boiling point of neopentane (9.5°C) is more than 25°C lower than the boiling point of *n*-pentane (36.1°C).

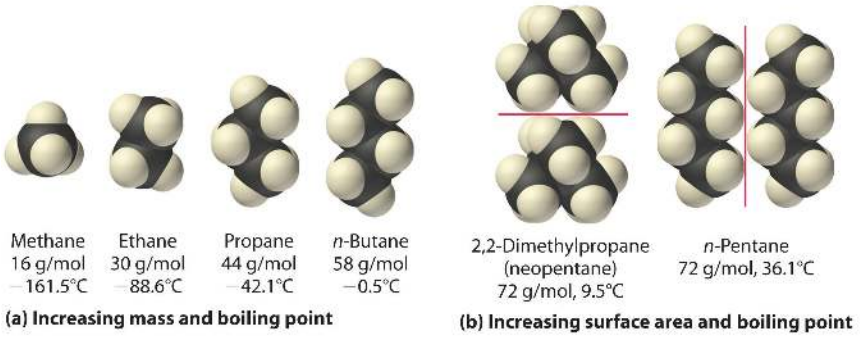


Figure 13.1.2.4: Mass and Surface Area Affect the Strength of London Dispersion Forces. (a) In this series of four simple alkanes, larger molecules have stronger London forces between them than smaller molecules and consequently higher boiling points. (b) Linear *n*-pentane molecules have a larger surface area and stronger intermolecular forces than spherical neopentane molecules. As a result, neopentane is a gas at room temperature, whereas *n*-pentane is a volatile liquid.

All molecules, whether polar or nonpolar, are attracted to one another by London dispersion forces in addition to any other attractive forces that may be present. In general, however, dipole–dipole interactions in small polar molecules are significantly stronger than London dispersion forces, so the former predominate.

✔ Example 13.1.2.2

Arrange *n*-butane, propane, 2-methylpropane [isobutene, $(CH_3)_2CHCH_3$], and *n*-pentane in order of increasing boiling points.

Given: compounds

Asked for: order of increasing boiling points

Strategy:

Determine the intermolecular forces in the compounds and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

Solution:

The four compounds are alkanes and nonpolar, so London dispersion forces are the only important intermolecular forces. These forces are generally stronger with increasing molecular mass, so propane should have the lowest boiling point and *n*-pentane should have the highest, with the two butane isomers falling in between. Of the two butane isomers, 2-methylpropane is more compact, and *n*-butane has the more extended shape. Consequently, we expect intermolecular interactions for *n*-butane to be stronger due to its larger surface area, resulting in a higher boiling point. The overall order is thus as follows, with actual boiling points in parentheses: propane (−42.1°C) < 2-methylpropane (−11.7°C) < *n*-butane (−0.5°C) < *n*-pentane (36.1°C).

? Exercise 13.1.2.2

Arrange GeH_4, $SiCl_4$, SiH_4, CH_4, and $GeCl_4$ in order of decreasing boiling points.

Answer

$GeCl_4$ (87°C) > $SiCl_4$ (57.6°C) > GeH_4 (−88.5°C) > SiH_4 (−111.8°C) > CH_4 (−161°C)

Summary

Intermolecular forces are electrostatic in nature and include van der Waals forces and hydrogen bonds. Molecules in liquids are held to other molecules by intermolecular interactions, which are weaker than the intramolecular interactions that hold the atoms together within molecules and polyatomic ions. Transitions between the solid and liquid or the liquid and gas phases are due to changes in intermolecular interactions but do not affect intramolecular interactions. The three major types of intermolecular interactions are dipole–dipole interactions, London dispersion forces (these two are often referred to collectively as **van der Waals forces**), and hydrogen bonds. **Dipole–dipole interactions** arise from the electrostatic interactions of the positive and negative ends of molecules with permanent dipole moments; their strength is proportional to the magnitude of the dipole moment and to $1/r^6$, where r is the distance between dipoles. **London dispersion forces** are due to the formation of **instantaneous dipole moments** in

polar or nonpolar molecules as a result of short-lived fluctuations of electron charge distribution, which in turn cause the temporary formation of an **induced dipole** in adjacent molecules. Like dipole–dipole interactions, their energy falls off as $1/r^6$. Larger atoms tend to be more **polarizable** than smaller ones because their outer electrons are less tightly bound and are therefore more easily perturbed.

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13.1.3: Intermolecular Forces in Liquids

Learning Objectives

- To describe the intermolecular forces in liquids.

Hydrogen Bonds

Molecules with hydrogen atoms bonded to electronegative atoms such as O, N, and F (and to a much lesser extent Cl and S) tend to exhibit unusually strong intermolecular interactions. These result in much higher boiling points than are observed for substances in which London dispersion forces dominate, as illustrated for the covalent hydrides of elements of groups 14–17 in Figure 13.1.3.1. Methane and its heavier congeners in group 14 form a series whose boiling points increase smoothly with increasing molar mass. This is the expected trend in nonpolar molecules, for which London dispersion forces are the exclusive intermolecular forces. In contrast, the hydrides of the lightest members of groups 15–17 have boiling points that are more than 100°C greater than predicted on the basis of their molar masses. The effect is most dramatic for water: if we extend the straight line connecting the points for H_2Te and H_2Se to the line for period 2, we obtain an estimated boiling point of −130°C for water! Imagine the implications for life on Earth if water boiled at −130°C rather than 100°C.

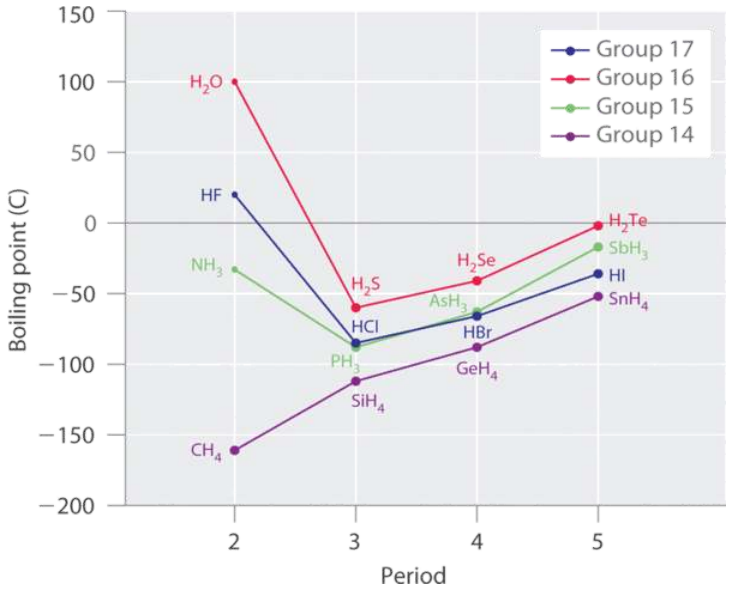


Figure 13.1.3.1: The Effects of Hydrogen Bonding on Boiling Points. These plots of the boiling points of the covalent hydrides of the elements of groups 14–17 show that the boiling points of the lightest members of each series for which hydrogen bonding is possible (HF, NH_3, and H_2O) are anomalously high for compounds with such low molecular masses.

Why do strong intermolecular forces produce such anomalously high boiling points and other unusual properties, such as high enthalpies of vaporization and high melting points? The answer lies in the highly polar nature of the bonds between hydrogen and very electronegative elements such as O, N, and F. The large difference in electronegativity results in a large partial positive charge on hydrogen and a correspondingly large partial negative charge on the O, N, or F atom. Consequently, H–O, H–N, and H–F bonds have very large bond dipoles that can interact strongly with one another. Because a hydrogen atom is so small, these dipoles can also approach one another more closely than most other dipoles. The combination of large bond dipoles and short dipole–dipole distances results in very strong dipole–dipole interactions called hydrogen bonds, as shown for ice in Figure 13.1.3.2 A hydrogen bond is usually indicated by a dotted line between the hydrogen atom attached to O, N, or F (the *hydrogen bond donor*) and the atom that has the lone pair of electrons (the *hydrogen bond acceptor*). Because each water molecule contains two hydrogen atoms and two lone pairs, a tetrahedral arrangement maximizes the number of hydrogen bonds that can be formed. In the structure of ice, each oxygen atom is surrounded by a distorted tetrahedron of hydrogen atoms that form bridges to the oxygen atoms of adjacent water molecules. The bridging hydrogen atoms are *not* equidistant from the two oxygen atoms they connect, however. Instead, each hydrogen atom is 101 pm from one oxygen and 174 pm from the other. In contrast, each oxygen atom is bonded to two H atoms at the shorter distance and two at the longer distance, corresponding to two O–H covalent bonds and two O···H hydrogen bonds from

adjacent water molecules, respectively. The resulting open, cagelike structure of ice means that the solid is actually slightly less dense than the liquid, which explains why ice floats on water rather than sinks.

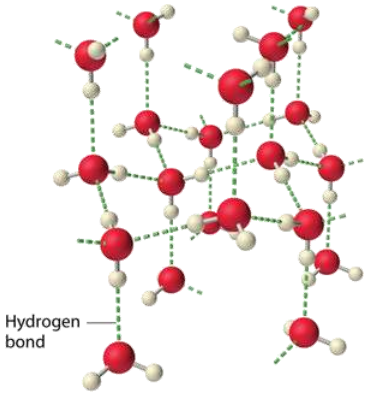


Figure 13.1.3.2: The Hydrogen-Bonded Structure of Ice

Each water molecule accepts two hydrogen bonds from two other water molecules and donates two hydrogen atoms to form hydrogen bonds with two more water molecules, producing an open, cagelike structure. The structure of liquid water is very similar, but in the liquid, the hydrogen bonds are continually broken and formed because of rapid molecular motion.

It takes two to tango...

Hydrogen bond formation requires *both* a hydrogen bond donor *and* a hydrogen bond acceptor.

Because ice is less dense than liquid water, rivers, lakes, and oceans freeze from the top down. In fact, the ice forms a protective surface layer that insulates the rest of the water, allowing fish and other organisms to survive in the lower levels of a frozen lake or sea. If ice were denser than the liquid, the ice formed at the surface in cold weather would sink as fast as it formed. Bodies of water would freeze from the bottom up, which would be lethal for most aquatic creatures. The expansion of water when freezing also explains why automobile or boat engines must be protected by “antifreeze” and why unprotected pipes in houses break if they are allowed to freeze.

Example 13.1.3.1

Considering CH_3OH, C_2H_6, Xe, and $(CH_3)_3N$, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Given: compounds

Asked for: formation of hydrogen bonds and structure

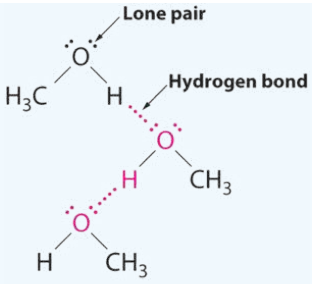
Strategy:

A. Identify the compounds with a hydrogen atom attached to O, N, or F. These are likely to be able to act as hydrogen bond donors.
B. Of the compounds that can act as hydrogen bond donors, identify those that also contain lone pairs of electrons, which allow them to be hydrogen bond acceptors. If a substance is both a hydrogen donor and a hydrogen bond acceptor, draw a structure showing the hydrogen bonding.

Solution:

A Of the species listed, xenon (Xe), ethane (C_2H_6), and trimethylamine [$(CH_3)_3N$] do not contain a hydrogen atom attached to O, N, or F; hence they cannot act as hydrogen bond donors.

B The one compound that can act as a hydrogen bond donor, methanol (CH_3OH), contains both a hydrogen atom attached to O (making it a hydrogen bond donor) and two lone pairs of electrons on O (making it a hydrogen bond acceptor); methanol can thus form hydrogen bonds by acting as either a hydrogen bond donor or a hydrogen bond acceptor. The hydrogen-bonded structure of methanol is as follows:



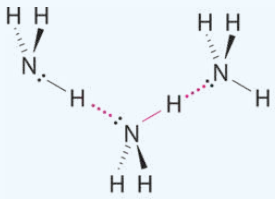
Hydrogen bonding in methanol

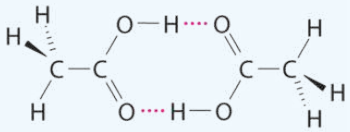
Exercise 13.1.3.1

Considering CH_3CO_2H, $(CH_3)_3N$, NH_3, and CH_3F, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Answer

CH_3CO_2H and NH_3;


Hydrogen bonding in ammonia


Hydrogen bonding in acetic acid

Although hydrogen bonds are significantly weaker than covalent bonds, with typical dissociation energies of only 15–25 kJ/mol, they have a significant influence on the physical properties of a compound. Compounds such as HF can form only two hydrogen bonds at a time as can, on average, pure liquid NH_3. Consequently, even though their molecular masses are similar to that of water, their boiling points are significantly lower than the boiling point of water, which forms *four* hydrogen bonds at a time.

Example 13.1.3.2

Arrange C_{60} (buckminsterfullerene, which has a cage structure), NaCl, He, Ar, and N_2O in order of increasing boiling points.

Spinning Buckminsterfullerene (C_{60}). (CC BY-SA 3.0; unported; Sponk).

Given: compounds

Asked for: order of increasing boiling points

Strategy:

Identify the intermolecular forces in each compound and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

Solution:

Electrostatic interactions are strongest for an ionic compound, so we expect NaCl to have the highest boiling point. To predict the relative boiling points of the other compounds, we must consider their polarity (for dipole–dipole interactions), their ability to form hydrogen bonds, and their molar mass (for London dispersion forces). Helium is nonpolar and by far the lightest, so it should have the lowest boiling point. Argon and N_2O have very similar molar masses (40 and 44 g/mol, respectively), but N_2O is polar while Ar is not. Consequently, N_2O should have a higher boiling point. A C_{60} molecule is nonpolar, but its molar mass is 720 g/mol, much greater than that of Ar or N_2O. Because the boiling points of nonpolar substances increase rapidly with molecular mass, C_{60} should boil at a higher temperature than the other nonionic substances. The predicted order is thus as follows, with actual boiling points in parentheses:

$$\text{He } (-269^\circ\text{C}) < \text{Ar } (-185.7^\circ\text{C}) < N_2O\ (-88.5^\circ\text{C}) < C_{60}\ (>280^\circ\text{C}) < \text{NaCl } (1465^\circ\text{C}).$$

Exercise 13.1.3.2

Arrange 2,4-dimethylheptane, Ne, CS_2, Cl_2, and KBr in order of decreasing boiling points.

Answer

KBr (1435°C) > 2,4-dimethylheptane (132.9°C) > CS_2 (46.6°C) > Cl_2 (−34.6°C) > Ne (−246°C)

Special Properties of Water

Besides mercury, water has the highest surface tension for all liquids. Water's high surface tension is due to the hydrogen bonding in water molecules. Water also has an exceptionally high heat of vaporization. Vaporization occurs when a liquid changes to a gas, which makes it an endothermic reaction. Water's heat of vaporization is 41 kJ/mol. Vapor pressure is inversely related to intermolecular forces, so those with stronger intermolecular forces have a lower vapor pressure. Water has very strong intermolecular forces, hence the low vapor pressure, but it's even lower compared to larger molecules with low vapor pressures.

- Viscosity is the property of fluid having high resistance to flow. We normally think of liquids like honey or motor oil being viscous, but when compared to other substances with like structures, water is viscous. Liquids with stronger intermolecular interactions are usually more viscous than liquids with weak intermolecular interactions.
- Cohesion is intermolecular forces between like molecules; this is why water molecules are able to hold themselves together in a drop. Water molecules are very cohesive because of the molecule's polarity. This is why you can fill a glass of water just barely above the rim without it spilling.

Because of water's polarity, it is able to dissolve or dissociate many particles. Oxygen has a slightly negative charge, while the two hydrogens have a slightly positive charge. The slightly negative particles of a compound will be attracted to water's hydrogen atoms, while the slightly positive particles will be attracted to water's oxygen molecule; this causes the compound to dissociate.

Besides the explanations above, we can look to some attributes of a water molecule to provide some more reasons of water's uniqueness:

- Forgetting fluorine, oxygen is the most electronegative non-noble gas element, so while forming a bond, the electrons are pulled towards the oxygen atom rather than the hydrogen. This creates two polar bonds, which make the water molecule more polar than the bonds in the other hydrides in the group.
- A 104.5° bond angle creates a very strong dipole.
- Water has hydrogen bonding which probably is a vital aspect in water's strong intermolecular interaction



Figure 13.1.3.3: Young boy with father ice fish. The fish do not freeze below the ice surface of the lake due to the unique properties of water. (Public Domain; U.S. Fish and Wildlife Service).

The properties of water make it suitable for organisms to survive in during differing weather conditions. Water expands as it freezes, which explains why ice is able to float on liquid water. During the winter when lakes begin to freeze, the surface of the water freezes and then moves down toward deeper water; this explains why people can ice skate on or fall through a frozen

lake. If ice was not able to float, the lake would freeze from the bottom up killing all ecosystems living in the lake. However ice floats, so the fish are able to survive under the surface of the ice during the winter. The surface of ice above a lake also shields lakes from the cold temperature outside and insulates the water beneath it, allowing the lake under the frozen ice to stay liquid and maintain a temperature adequate for the ecosystems living in the lake to survive.

Summary

Intermolecular forces are electrostatic in nature and include van der Waals forces and hydrogen bonds. Molecules in liquids are held to other molecules by intermolecular interactions, which are weaker than the intramolecular interactions that hold the atoms together within molecules and polyatomic ions. Transitions between the solid and liquid or the liquid and gas phases are due to changes in intermolecular interactions but do not affect intramolecular interactions. The three major types of intermolecular interactions are dipole–dipole interactions, London dispersion forces (these two are often referred to collectively as **van der Waals forces**), and hydrogen bonds. **Dipole–dipole interactions** arise from the electrostatic interactions of the positive and negative ends of molecules with permanent dipole moments; their strength is proportional to the magnitude of the dipole moment and to $1/r^6$, where r is the distance between dipoles. **London dispersion forces** are due to the formation of **instantaneous dipole moments** in polar or nonpolar molecules as a result of short-lived fluctuations of electron charge distribution, which in turn cause the temporary formation of an **induced dipole** in adjacent molecules. Like dipole–dipole interactions, their energy falls off as $1/r^6$. Larger atoms tend to be more **polarizable** than smaller ones because their outer electrons are less tightly bound and are therefore more easily perturbed. **Hydrogen bonds** are especially strong dipole–dipole interactions between molecules that have hydrogen bonded to a highly electronegative atom, such as O, N, or F. The resulting partially positively charged H atom on one molecule (the *hydrogen bond donor*) can interact strongly with a lone pair of electrons of a partially negatively charged O, N, or F atom on adjacent molecules (the *hydrogen bond acceptor*). Because of strong O···H hydrogen bonding between water molecules, water has an unusually high boiling point, and ice has an open, cagelike structure that is less dense than liquid water.

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13.1.4: Phase Equilibrium

Learning Objectives

- To know how and why the vapor pressure of a liquid varies with temperature.
- To understand that the equilibrium vapor pressure of a liquid depends on the temperature and the intermolecular forces present.
- To understand that the relationship between pressure, enthalpy of vaporization, and temperature is given by the Clausius-Clapeyron equation.

Nearly all of us have heated a pan of water with the lid in place and shortly thereafter heard the sounds of the lid rattling and hot water spilling onto the stovetop. When a liquid is heated, its molecules obtain sufficient kinetic energy to overcome the forces holding them in the liquid and they escape into the gaseous phase. By doing so, they generate a population of molecules in the vapor phase above the liquid that produces a pressure—the vapor pressure of the liquid. In the situation we described, enough pressure was generated to move the lid, which allowed the vapor to escape. If the vapor is contained in a sealed vessel, however, such as an unvented flask, and the vapor pressure becomes too high, the flask will explode (as many students have unfortunately discovered). In this section, we describe vapor pressure in more detail and explain how to quantitatively determine the vapor pressure of a liquid.

Evaporation and Condensation

Because the molecules of a liquid are in constant motion, we can plot the fraction of molecules with a given kinetic energy (KE) against their kinetic energy to obtain the kinetic energy distribution of the molecules in the liquid (Figure 13.1.4.1), just as we did for a gas. As for gases, increasing the temperature increases both the average kinetic energy of the particles in a liquid and the range of kinetic energy of the individual molecules. If we assume that a minimum amount of energy (E_0) is needed to overcome the intermolecular attractive forces that hold a liquid together, then some fraction of molecules in the liquid always has a kinetic energy greater than E_0. The fraction of molecules with a kinetic energy greater than this minimum value increases with increasing temperature. Any molecule with a kinetic energy greater than E_0 has enough energy to overcome the forces holding it in the liquid and escape into the vapor phase. Before it can do so, however, a molecule must also be at the surface of the liquid, where it is physically possible for it to leave the liquid surface; that is, only molecules at the surface can undergo evaporation (or vaporization), where molecules gain sufficient energy to enter a gaseous state above a liquid's surface, thereby creating a vapor pressure.

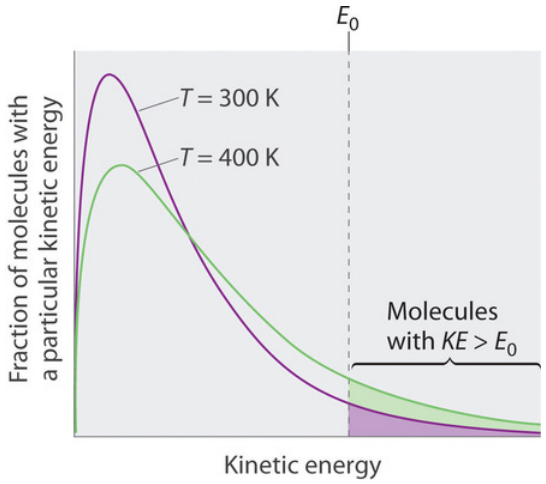


Figure 13.1.4.1: The Distribution of the Kinetic Energies of the Molecules of a Liquid at Two Temperatures. Just as with gases, increasing the temperature shifts the peak to a higher energy and broadens the curve. Only molecules with a kinetic energy greater than E_0 can escape from the liquid to enter the vapor phase, and the proportion of molecules with $KE > E_0$ is greater at the higher temperature. (CC BY-SA-NC; Anonymous by request)

Graph of fraction of molecules with a particular kinetic energy against kinetic energy. Green line is temperature at 400 kelvin, purple line is temperature at 300 kelvin.

To understand the causes of vapor pressure, consider the apparatus shown in Figure 13.1.4.2 When a liquid is introduced into an evacuated chamber (part (a) in Figure 13.1.4.2), the initial pressure above the liquid is approximately zero because there are as yet no molecules in the vapor phase. Some molecules at the surface, however, will have sufficient kinetic energy to escape from the liquid and form a vapor, thus increasing the pressure inside the container. As long as the temperature of the liquid is held constant, the fraction of molecules with $KE > E_0$ will not change, and the rate at which molecules escape from the liquid into the vapor phase will depend only on the surface area of the liquid phase.

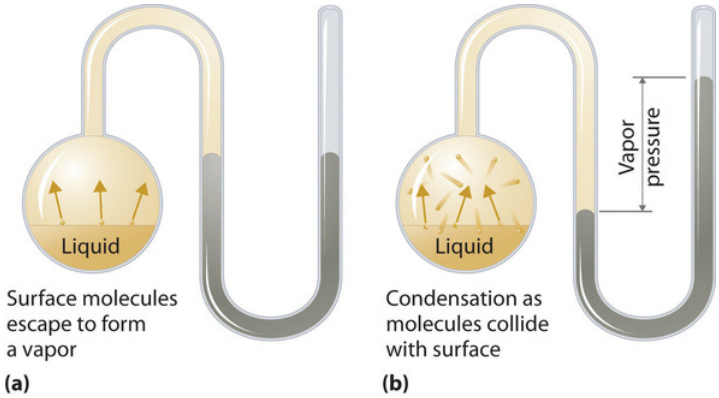


Figure 13.1.4.2: Vapor Pressure. (a) When a liquid is introduced into an evacuated chamber, molecules with sufficient kinetic energy escape from the surface and enter the vapor phase, causing the pressure in the chamber to increase. (b) When sufficient molecules are in the vapor phase for a given temperature, the rate of condensation equals the rate of evaporation (a steady state is reached), and the pressure in the container becomes constant. (CC BY-SA-NC; Anonymous by request)

As soon as some vapor has formed, a fraction of the molecules in the vapor phase will collide with the surface of the liquid and reenter the liquid phase in a process known as condensation (part (b) in Figure 13.1.4.2). As the number of molecules in the vapor phase increases, the number of collisions between vapor-phase molecules and the surface will also increase. Eventually, a *steady state* will be reached in which exactly as many molecules per unit time leave the surface of the liquid (vaporize) as collide with it (condense). At this point, the pressure over the liquid stops increasing and remains constant at a particular value that is characteristic of the liquid at a given temperature. The rates of evaporation and condensation over time for a system such as this are shown graphically in Figure 13.1.4.3

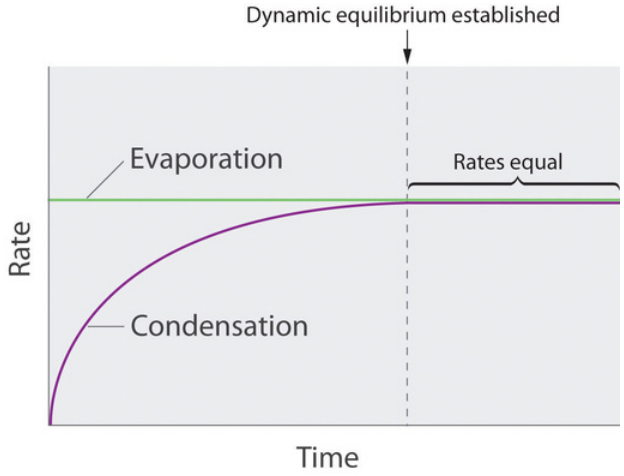


Figure 13.1.4.3: The Relative Rates of Evaporation and Condensation as a Function of Time after a Liquid Is Introduced into a Sealed Chamber. The rate of evaporation depends only on the surface area of the liquid and is essentially constant. The rate of condensation depends on the number of molecules in the vapor phase and increases steadily until it equals the rate of evaporation. (CC BY-SA-NC; Anonymous by request)

Graph of rate against time. The green line is evaporation while the pruple line is condensation. Dynamic equilibrium is established when the evaporation and condensation rates are equal.

Equilibrium Vapor Pressure

Two opposing processes (such as evaporation and condensation) that occur at the same rate and thus produce no *net* change in a system, constitute a dynamic equilibrium. In the case of a liquid enclosed in a chamber, the molecules continuously evaporate and

condense, but the amounts of liquid and vapor do not change with time. The pressure exerted by a vapor in dynamic equilibrium with a liquid is the equilibrium vapor pressure of the liquid.

If a liquid is in an *open* container, however, most of the molecules that escape into the vapor phase will *not* collide with the surface of the liquid and return to the liquid phase. Instead, they will diffuse through the gas phase away from the container, and an equilibrium will never be established. Under these conditions, the liquid will continue to evaporate until it has "disappeared." The speed with which this occurs depends on the vapor pressure of the liquid and the temperature. Volatile liquids have relatively high vapor pressures and tend to evaporate readily; nonvolatile liquids have low vapor pressures and evaporate more slowly. Although the dividing line between volatile and nonvolatile liquids is not clear-cut, as a general guideline, we can say that substances with vapor pressures greater than that of water (Figure 13.1.4.4) are relatively volatile, whereas those with vapor pressures less than that of water are relatively nonvolatile. Thus diethyl ether (ethyl ether), acetone, and gasoline are volatile, but mercury, ethylene glycol, and motor oil are nonvolatile.

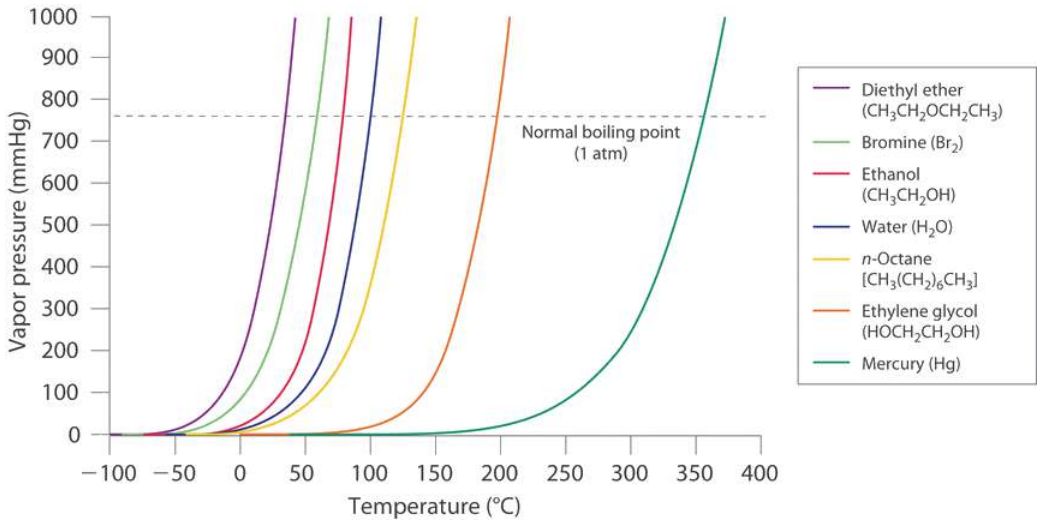


Figure 13.1.4.4: The Vapor Pressures of Several Liquids as a Function of Temperature. The point at which the vapor pressure curve crosses the P = 1 atm line (dashed) is the normal boiling point of the liquid. (CC BY-SA-NC; Anonymous by request)

The equilibrium vapor pressure of a substance at a particular temperature is a characteristic of the material, like its molecular mass, melting point, and boiling point. It does *not* depend on the amount of liquid as long as at least a tiny amount of liquid is present in equilibrium with the vapor. The equilibrium vapor pressure does, however, depend very strongly on the temperature and the intermolecular forces present, as shown for several substances in Figure 13.1.4.4 Molecules that can hydrogen bond, such as ethylene glycol, have a much lower equilibrium vapor pressure than those that cannot, such as octane. The nonlinear increase in vapor pressure with increasing temperature is *much* steeper than the increase in pressure expected for an ideal gas over the corresponding temperature range. The temperature dependence is so strong because the vapor pressure depends on the fraction of molecules that have a kinetic energy greater than that needed to escape from the liquid, and this fraction increases exponentially with temperature. As a result, sealed containers of volatile liquids are potential bombs if subjected to large increases in temperature. The gas tanks on automobiles are vented, for example, so that a car won't explode when parked in the sun. Similarly, the small cans (1–5 gallons) used to transport gasoline are required by law to have a pop-off pressure release.

> *Volatile substances have low boiling points and relatively weak intermolecular interactions; nonvolatile substances have high boiling points and relatively strong intermolecular interactions.*



A Video Discussing Vapor Pressure and Boiling Points. Video Source: Vapor Pressure & Boiling Point(opens in new window) [youtu.be]

The exponential rise in vapor pressure with increasing temperature in Figure 13.1.4.4allows us to use natural logarithms to express the nonlinear relationship as a linear one.

$$\boxed{\ln P = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T}\right) + C} \tag{13.1.4.1}$$

where

- $\ln P$ is the natural logarithm of the vapor pressure,
- ΔH_{vap} is the enthalpy of vaporization,
- R is the universal gas constant [8.314 J/(mol•K)],
- T is the temperature in kelvins, and
- C is the y-intercept, which is a constant for any given line.

Plotting $\ln P$ versus the inverse of the absolute temperature $(1/T)$ is a straight line with a slope of $-\Delta H_{vap}/R$. Equation 13.1.4.1, called the Clausius–Clapeyron Equation, can be used to calculate the ΔH_{vap} of a liquid from its measured vapor pressure at two or more temperatures. The simplest way to determine ΔH_{vap} is to measure the vapor pressure of a liquid at **two** temperatures and insert the values of P and T for these points into Equation 13.1.4.2, which is derived from the Clausius–Clapeyron equation:

$$\ln\left(\frac{P_1}{P_2}\right) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{13.1.4.2}$$

Conversely, if we know ΔH_{vap} and the vapor pressure P_1 at any temperature T_1, we can use Equation 13.1.4.2 to calculate the vapor pressure P_2 at any other temperature T_2, as shown in Example 13.1.4.1.



A Video Discussing the Clausius-Clapeyron Equation. Video Link: The Clausius-Clapeyron Equation(opens in new window) [youtu.be]

Example 13.1.4.1: Vapor Pressure of Mercury

The experimentally measured vapor pressures of liquid Hg at four temperatures are listed in the following table:

experimentally measured vapor pressures of liquid Hg at four temperatures

T (°C)	80.0	100	120	140
P (torr)	0.0888	0.2729	0.7457	1.845

From these data, calculate the enthalpy of vaporization (ΔH_{vap}) of mercury and predict the vapor pressure of the liquid at 160°C. (Safety note: mercury is highly toxic; when it is spilled, its vapor pressure generates hazardous levels of mercury vapor.)

Given: vapor pressures at four temperatures

Asked for: ΔH_{vap} of mercury and vapor pressure at 160°C

Strategy:

A. Use Equation 13.1.4.2to obtain ΔH_{vap} directly from two pairs of values in the table, making sure to convert all values to the appropriate units.

B. Substitute the calculated value of ΔH_{vap} into Equation 13.1.4.2to obtain the unknown pressure (P_2).

Solution:

A The table gives the measured vapor pressures of liquid Hg for four temperatures. Although one way to proceed would be to plot the data using Equation 13.1.4.1and find the value of ΔH_{vap} from the slope of the line, an alternative approach is to use Equation 13.1.4.2to obtain ΔH_{vap} directly from two pairs of values listed in the table, assuming no errors in our measurement. We therefore select two sets of values from the table and convert the temperatures from degrees Celsius to kelvin because the equation requires absolute temperatures. Substituting the values measured at 80.0°C (T_1) and 120.0°C (T_2) into Equation 13.1.4.2gives

$$\ln\left(\frac{0.7457\ \cancel{Torr}}{0.0888\ \cancel{Torr}}\right) = \frac{-\Delta H_{vap}}{8.314\ J/mol\cdot K}\left(\frac{1}{(120+273)\,K} - \frac{1}{(80.0+273)\,K}\right)$$

$$\ln(8.398) = \frac{-\Delta H_{vap}}{8.314\ J/mol\cdot\ \cancel{K}}\left(-2.88\times10^{-4}\ \cancel{K^{-1}}\right)$$

$$2.13 = -\Delta H_{vap}\left(-3.46\times10^{-4}\right)J^{-1}\cdot mol$$

$$\Delta H_{vap} = 61,400\ J/mol = 61.4\ kJ/mol$$

B We can now use this value of ΔH_{vap} to calculate the vapor pressure of the liquid (P_2) at 160.0°C (T_2):

$$\ln\left(\frac{P_2}{0.0888\ torr}\right) = \frac{-61,400\ \cancel{J/mol}}{8.314\ \cancel{J/mol}\ K^{-1}}\left(\frac{1}{(160+273)\,K} - \frac{1}{(80.0+273)\,K}\right)$$

Using the relationship $e^{\ln x} = x$, we have

$$\ln\left(\frac{P_2}{0.0888\ Torr}\right) = 3.86$$

$$\frac{P_2}{0.0888\ Torr} = e^{3.86} = 47.5$$

$$P_2 = 4.21 Torr$$

At 160°C, liquid Hg has a vapor pressure of 4.21 torr, substantially greater than the pressure at 80.0°C, as we would expect.

Exercise 13.1.4.1: Vapor Pressure of Nickel

The vapor pressure of liquid nickel at 1606°C is 0.100 torr, whereas at 1805°C, its vapor pressure is 1.000 torr. At what temperature does the liquid have a vapor pressure of 2.500 torr?

Answer

1896°C

Boiling Points

As the temperature of a liquid increases, the vapor pressure of the liquid increases until it equals the external pressure, or the atmospheric pressure in the case of an open container. Bubbles of vapor begin to form throughout the liquid, and the liquid begins to boil. The temperature at which a liquid boils at exactly 1 atm pressure is the normal boiling point of the liquid. For water, the normal boiling point is exactly 100°C. The normal boiling points of the other liquids in Figure 13.1.4.4 are represented by the points at which the vapor pressure curves cross the line corresponding to a pressure of 1 atm. Although we usually cite the normal boiling point of a liquid, the *actual* boiling point depends on the pressure. At a pressure greater than 1 atm, water boils at a temperature greater than 100°C because the increased pressure forces vapor molecules above the surface to condense. Hence the molecules must have greater kinetic energy to escape from the surface. Conversely, at pressures less than 1 atm, water boils below 100°C.

Table 13.1.4.1: The Boiling Points of Water at Various Locations on Earth

Place	Altitude above Sea Level (ft)	Atmospheric Pressure (mmHg)	Boiling Point of Water (°C)
Mt. Everest, Nepal/Tibet	29,028	240	70
Bogota, Colombia	11,490	495	88
Denver, Colorado	5280	633	95
Washington, DC	25	759	100
Dead Sea, Israel/Jordan	−1312	799	101.4

Typical variations in atmospheric pressure at sea level are relatively small, causing only minor changes in the boiling point of water. For example, the highest recorded atmospheric pressure at sea level is 813 mmHg, recorded during a Siberian winter; the lowest sea-level pressure ever measured was 658 mmHg in a Pacific typhoon. At these pressures, the boiling point of water changes minimally, to 102°C and 96°C, respectively. At high altitudes, on the other hand, the dependence of the boiling point of water on pressure becomes significant. Table 13.1.4.1 lists the boiling points of water at several locations with different altitudes. At an elevation of only 5000 ft, for example, the boiling point of water is already lower than the lowest ever recorded at sea level. The lower boiling point of water has major consequences for cooking everything from soft-boiled eggs (a “three-minute egg” may well take four or more minutes in the Rockies and even longer in the Himalayas) to cakes (cake mixes are often sold with separate high-altitude instructions). Conversely, pressure cookers, which have a seal that allows the pressure inside them to exceed 1 atm, are used to cook food more rapidly by raising the boiling point of water and thus the temperature at which the food is being cooked.

> *As pressure increases, the boiling point of a liquid increases and vice versa.*

Example 13.1.4.2: Boiling Mercury

Use Figure 13.1.4.4 to estimate the following.

a. the boiling point of water in a pressure cooker operating at 1000 mmHg
b. the pressure required for mercury to boil at 250°C



Mercury boils at 356 °C at room pressure. To see video go to www.youtube.com/watch?v=0iizsbXWYoo

Given: Data in Figure 13.1.4.4 pressure, and boiling point

Asked for: corresponding boiling point and pressure

Strategy:

A. To estimate the boiling point of water at 1000 mmHg, refer to Figure 13.1.4.4and find the point where the vapor pressure curve of water intersects the line corresponding to a pressure of 1000 mmHg.

B. To estimate the pressure required for mercury to boil at 250°C, find the point where the vapor pressure curve of mercury intersects the line corresponding to a temperature of 250°C.

Solution:

a. **A** The vapor pressure curve of water intersects the P = 1000 mmHg line at about 110°C; this is therefore the boiling point of water at 1000 mmHg.

b. **B** The vertical line corresponding to 250°C intersects the vapor pressure curve of mercury at $P \approx 75$ mmHg. Hence this is the pressure required for mercury to boil at 250°C.

? Exercise 13.1.4.2: Boiling Ethlyene Glycol

Ethylene glycol is an organic compound primarily used as a raw material in the manufacture of polyester fibers and fabric industry, and polyethylene terephthalate resins (PET) used in bottling. Use the data in Figure 13.1.4.4 to estimate the following.

a. the normal boiling point of ethylene glycol
b. the pressure required for diethyl ether to boil at 20°C.

Answer a

200°C

Answer b

450 mmHg

Summary

Because the molecules of a liquid are in constant motion and possess a wide range of kinetic energies, at any moment some fraction of them has enough energy to escape from the surface of the liquid to enter the gas or vapor phase. This process, called **vaporization** or **evaporation**, generates a **vapor pressure** above the liquid. Molecules in the gas phase can collide with the liquid surface and reenter the liquid via **condensation**. Eventually, a *steady state* is reached in which the number of molecules evaporating and condensing per unit time is the same, and the system is in a state of **dynamic equilibrium**. Under these conditions, a liquid exhibits a characteristic **equilibrium vapor pressure** that depends only on the temperature. We can express the nonlinear relationship between vapor pressure and temperature as a linear relationship using the **Clausius–Clapeyron equation**. This equation can be used to calculate the enthalpy of vaporization of a liquid from its measured vapor pressure at two or more temperatures. **Volatile liquids** are liquids with high vapor pressures, which tend to evaporate readily from an open container; **nonvolatile liquids** have low vapor pressures. When the vapor pressure equals the external pressure, bubbles of vapor form within the liquid, and it boils. The temperature at which a substance boils at a pressure of 1 atm is its **normal boiling point**.

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13.1.5: Phase Transitions

Learning Objectives

- To calculate the energy changes that accompany phase changes.

We take advantage of changes between the gas, liquid, and solid states to cool a drink with ice cubes (solid to liquid), cool our bodies by perspiration (liquid to gas), and cool food inside a refrigerator (gas to liquid and vice versa). We use dry ice, which is solid CO_2, as a refrigerant (solid to gas), and we make artificial snow for skiing and snowboarding by transforming a liquid to a solid. In this section, we examine what happens when any of the three forms of matter is converted to either of the other two. These changes of state are often called phase changes. The six most common phase changes are shown in Figure 13.1.5.1.

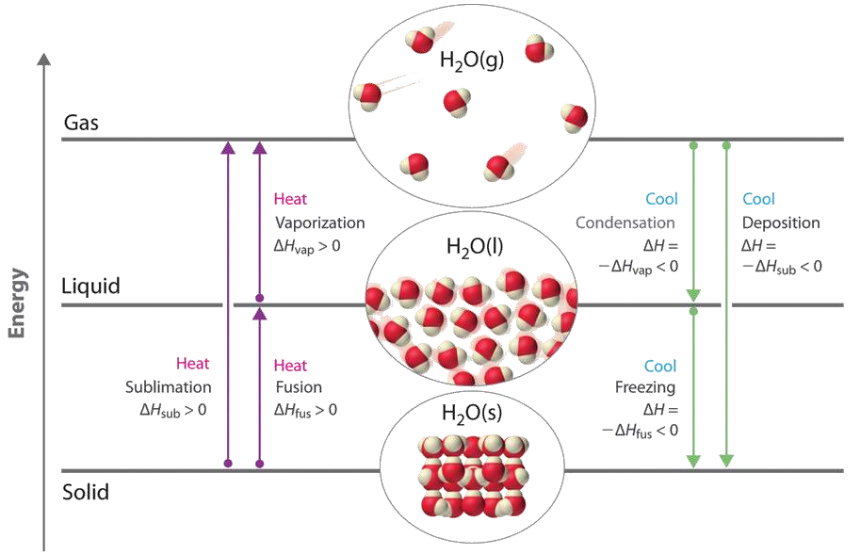


Figure 13.1.5.1: Enthalpy changes that accompany phase transitions are indicated by purple and green arrows. Purple arrows indicate heating from solid to gas, solid to liquid, and liquid to gas. Green arrows indicate cooling from gas to solid, gas to liquid, and liquid to solid. (CC BY-SA-NC; anoymous)

Energy Changes That Accompany Phase Changes

Phase changes are *always* accompanied by a change in the energy of a system. For example, converting a liquid, in which the molecules are close together, to a gas, in which the molecules are, on average, far apart, requires an input of energy (heat) to give the molecules enough kinetic energy to allow them to overcome the intermolecular attractive forces. The stronger the attractive forces, the more energy is needed to overcome them. Solids, which are highly ordered, have the strongest intermolecular interactions, whereas gases, which are very disordered, have the weakest. Thus any transition from a more ordered to a less ordered state (solid to liquid, liquid to gas, or solid to gas) requires an input of energy; it is **endothermic**. Conversely, any transition from a less ordered to a more ordered state (liquid to solid, gas to liquid, or gas to solid) releases energy; it is **exothermic**. The energy change associated with each common phase change is shown in Figure 13.1.5.1.

> *ΔH is positive for any transition from a more ordered to a less ordered state and negative for a transition from a less ordered to a more ordered state.*

Previously, we defined the enthalpy changes associated with various chemical and physical processes. The melting points and molar **enthalpies of fusion** (ΔH_{fus}), the energy required to convert from a solid to a liquid, a process known as fusion (or melting), as well as the normal boiling points and enthalpies of vaporization (ΔH_{vap}) of selected compounds are listed in Table 13.1.5.1.

Table 13.1.5.1: Melting and Boiling Points and Enthalpies of Fusion and Vaporization for Selected Substances. Values given under 1 atm. of external pressure.

Substance	Melting Point (°C)	ΔH_{fus} (kJ/mol)	Boiling Point (°C)	ΔH_{vap} (kJ/mol)

Substance	Melting Point (°C)	ΔH_{fus} (kJ/mol)	Boiling Point (°C)	ΔH_{vap} (kJ/mol)
N_2	−210.0	0.71	−195.8	5.6
HCl	−114.2	2.00	−85.1	16.2
Br_2	−7.2	10.6	58.8	30.0
CCl_4	−22.6	2.56	76.8	29.8
CH_3CH_2OH (ethanol)	−114.1	4.93	78.3	38.6
$CH_3(CH_2)_4CH_3$ (*n*-hexane)	−95.4	13.1	68.7	28.9
H_2O	0	6.01	100	40.7
Na	97.8	2.6	883	97.4
NaF	996	33.4	1704	176.1

The substances with the highest melting points usually have the highest enthalpies of fusion; they tend to be ionic compounds that are held together by very strong electrostatic interactions. Substances with high boiling points are those with strong intermolecular interactions that must be overcome to convert a liquid to a gas, resulting in high enthalpies of vaporization. The enthalpy of vaporization of a given substance is much greater than its enthalpy of fusion because it takes more energy to completely separate molecules (conversion from a liquid to a gas) than to enable them only to move past one another freely (conversion from a solid to a liquid).

> *Less energy is needed to allow molecules to move past each other than to separate them totally.*



Figure 13.1.5.2: The Sublimation of solid iodine. When solid iodine is heated at ordinary atmospheric pressure, it sublimes. When the I_2 vapor comes in contact with a cold surface, it deposits I_2 crystals. Figure used with permission from Wikipedia.

The direct conversion of a solid to a gas, without an intervening liquid phase, is called sublimation. The amount of energy required to sublime 1 mol of a pure solid is the enthalpy of sublimation (ΔH_{sub}). Common substances that sublime at standard temperature and pressure (STP; 0°C, 1 atm) include CO_2 (dry ice); iodine (Figure 13.1.5.2); naphthalene, a substance used to protect woolen clothing against moths; and 1,4-dichlorobenzene. As shown in Figure 13.1.5.1, the enthalpy of sublimation of a substance is the sum of its enthalpies of fusion and vaporization provided all values are at the same *T*; this is an application of Hess's law.

$$\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap} \tag{13.1.5.1}$$

Fusion, vaporization, and sublimation are endothermic processes; they occur only with the absorption of heat. Anyone who has ever stepped out of a swimming pool on a cool, breezy day has felt the heat loss that accompanies the evaporation of water from the skin. Our bodies use this same phenomenon to maintain a constant temperature: we perspire continuously, even when at rest, losing about 600 mL of water daily by evaporation from the skin. We also lose about 400 mL of water as water vapor in the air we exhale, which also contributes to cooling. Refrigerators and air-conditioners operate on a similar principle: heat is absorbed from the object or area to be cooled and used to vaporize a low-boiling-point liquid, such as ammonia or the chlorofluorocarbons (CFCs)

and the hydrofluorocarbons (HCFCs). The vapor is then transported to a different location and compressed, thus releasing and dissipating the heat. Likewise, ice cubes efficiently cool a drink not because of their low temperature but because heat is required to convert ice at 0°C to liquid water at 0°C.

Temperature Curves

The processes on the right side of Figure 13.1.5.1—freezing, condensation, and deposition, which are the reverse of fusion, sublimation, and vaporization—are exothermic. Thus heat pumps that use refrigerants are essentially air-conditioners running in reverse. Heat from the environment is used to vaporize the refrigerant, which is then condensed to a liquid in coils within a house to provide heat. The energy changes that occur during phase changes can be quantified by using a heating or cooling curve.

Heating Curves

Figure 13.1.5.3shows a heating curve, a plot of temperature versus heating time, for a 75 g sample of water. The sample is initially ice at 1 atm and −23°C; as heat is added, the temperature of the ice increases linearly with time. The slope of the line depends on both the mass of the ice and the specific heat (C_s) of ice, which is the number of joules required to raise the temperature of 1 g of ice by 1°C. As the temperature of the ice increases, the water molecules in the ice crystal absorb more and more energy and vibrate more vigorously. At the melting point, they have enough kinetic energy to overcome attractive forces and move with respect to one another. As more heat is added, the temperature of the system does *not* increase further but remains constant at 0°C until all the ice has melted. Once all the ice has been converted to liquid water, the temperature of the water again begins to increase. Now, however, the temperature increases more slowly than before because the specific heat capacity of water is *greater* than that of ice. When the temperature of the water reaches 100°C, the water begins to boil. Here, too, the temperature remains constant at 100°C until all the water has been converted to steam. At this point, the temperature again begins to rise, but at a *faster* rate than seen in the other phases because the heat capacity of steam is *less* than that of ice or water.

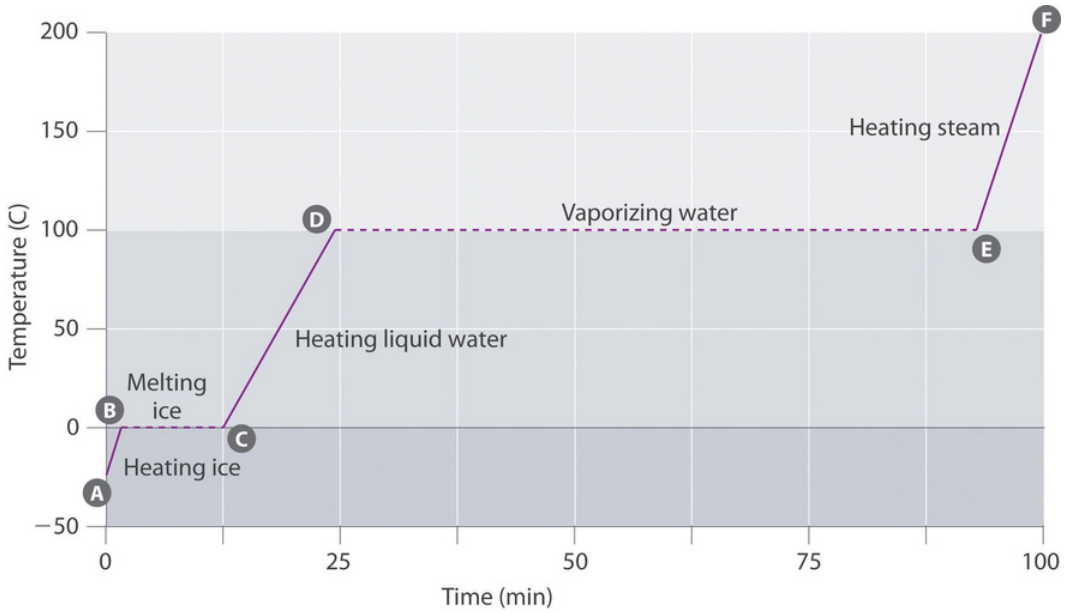


Figure 13.1.5.3: A Heating Curve for Water. This plot of temperature shows what happens to a 75 g sample of ice initially at 1 atm and −23°C as heat is added at a constant rate: A–B: heating solid ice; B–C: melting ice; C–D: heating liquid water; D–E: vaporizing water; E–F: heating steam.

Thus *the temperature of a system does not change during a phase change*. In this example, as long as even a tiny amount of ice is present, the temperature of the system remains at 0°C during the melting process, and as long as even a small amount of liquid water is present, the temperature of the system remains at 100°C during the boiling process. The rate at which heat is added does *not* affect the temperature of the ice/water or water/steam mixture because the added heat is being used exclusively to overcome the attractive forces that hold the more condensed phase together. Many cooks think that food will cook faster if the heat is turned up higher so that the water boils more rapidly. Instead, the pot of water will boil to dryness sooner, but the temperature of the water does not depend on how vigorously it boils.

> *The temperature of a sample does not change during a phase change.*

If heat is added at a constant rate, as in Figure 13.1.5.3, then the length of the horizontal lines, which represents the time during which the temperature does not change, is directly proportional to the magnitude of the enthalpies associated with the phase changes. In Figure 13.1.5.3, the horizontal line at 100°C is much longer than the line at 0°C because the enthalpy of vaporization of water is several times greater than the enthalpy of fusion.

A superheated liquid is a sample of a liquid at the temperature and pressure at which it should be a gas. Superheated liquids are not stable; the liquid will eventually boil, sometimes violently. The phenomenon of superheating causes "bumping" when a liquid is heated in the laboratory. When a test tube containing water is heated over a Bunsen burner, for example, one portion of the liquid can easily become too hot. When the superheated liquid converts to a gas, it can push or "bump" the rest of the liquid out of the test tube. Placing a stirring rod or a small piece of ceramic (a "boiling chip") in the test tube allows bubbles of vapor to form on the surface of the object so the liquid boils instead of becoming superheated. Superheating is the reason a liquid heated in a smooth cup in a microwave oven may not boil until the cup is moved, when the motion of the cup allows bubbles to form.

Cooling Curves

The cooling curve, a plot of temperature versus cooling time, in Figure 13.1.5.4 plots temperature versus time as a 75 g sample of steam, initially at 1 atm and 200°C, is cooled. Although we might expect the cooling curve to be the mirror image of the heating curve in Figure 13.1.5.3, the cooling curve is *not* an identical mirror image. As heat is removed from the steam, the temperature falls until it reaches 100°C. At this temperature, the steam begins to condense to liquid water. No further temperature change occurs until all the steam is converted to the liquid; then the temperature again decreases as the water is cooled. We might expect to reach another plateau at 0°C, where the water is converted to ice; in reality, however, this does not always occur. Instead, the temperature often drops below the freezing point for some time, as shown by the little dip in the cooling curve below 0°C. This region corresponds to an unstable form of the liquid, a supercooled liquid. If the liquid is allowed to stand, if cooling is continued, or if a small crystal of the solid phase is added (a seed crystal), the supercooled liquid will convert to a solid, sometimes quite suddenly. As the water freezes, the temperature increases slightly due to the heat evolved during the freezing process and then holds constant at the melting point as the rest of the water freezes. Subsequently, the temperature of the ice decreases again as more heat is removed from the system.

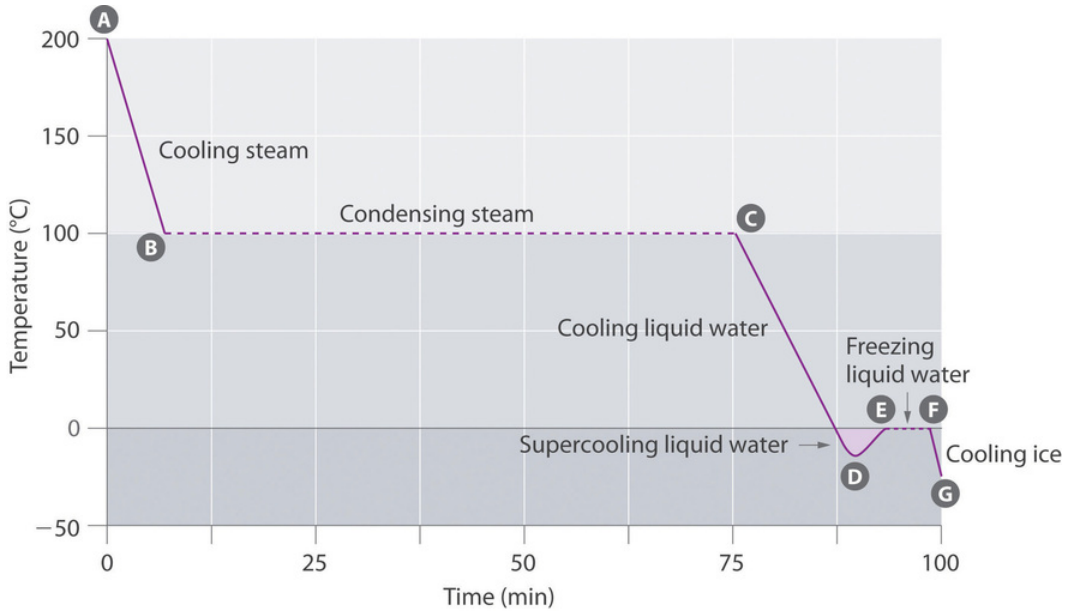


Figure 13.1.5.4: A Cooling Curve for Water. This plot of temperature shows what happens to a 75 g sample of steam initially at 1 atm and 200°C as heat is removed at a constant rate: A–B: cooling steam; B–C: condensing steam; C–D: cooling liquid water to give a supercooled liquid; D–E: warming the liquid as it begins to freeze; E–F: freezing liquid water; F–G: cooling ice.

Supercooling effects have a huge impact on Earth's climate. For example, supercooling of water droplets in clouds can prevent the clouds from releasing precipitation over regions that are persistently arid as a result. Clouds consist of tiny droplets of water, which in principle should be dense enough to fall as rain. In fact, however, the droplets must aggregate to reach a certain size before they can fall to the ground. Usually a small particle (a *nucleus*) is required for the droplets to aggregate; the nucleus can be a dust particle, an ice crystal, or a particle of silver iodide dispersed in a cloud during *seeding* (a method of inducing rain). Unfortunately, the small droplets of water generally remain as a supercooled liquid down to about −10°C, rather than freezing into ice crystals that

are more suitable nuclei for raindrop formation. One approach to producing rainfall from an existing cloud is to cool the water droplets so that they crystallize to provide nuclei around which raindrops can grow. This is best done by dispersing small granules of solid CO_2 (dry ice) into the cloud from an airplane. Solid CO_2 sublimes directly to the gas at pressures of 1 atm or lower, and the enthalpy of sublimation is substantial (25.3 kJ/mol). As the CO_2 sublimes, it absorbs heat from the cloud, often with the desired results.



A Video Discussing the Thermodynamics of Phase Changes. Video Source: The Thermodynamics of Phase Changes, YouTube(opens in new window) [youtu.be]

Example 13.1.5.1: Cooling Tea

If a 50.0 g ice cube at 0.0°C is added to 500 mL of tea at 20.0°C, what is the temperature of the tea when the ice cube has just melted? Assume that no heat is transferred to or from the surroundings. The density of water (and iced tea) is 1.00 g/mL over the range 0°C–20°C, the specific heats of liquid water and ice are 4.184 J/(g•°C) and 2.062 J/(g•°C), respectively, and the enthalpy of fusion of ice is 6.01 kJ/mol.

Given: mass, volume, initial temperature, density, specific heats, and ΔH_{fus}

Asked for: final temperature

Strategy

Substitute the given values into the general equation relating heat gained (by the ice) to heat lost (by the tea) to obtain the final temperature of the mixture.

Solution

When two substances or objects at different temperatures are brought into contact, heat will flow from the warmer one to the cooler. The amount of heat that flows is given by

$$q = mC_s\Delta T$$

where q is heat, m is mass, C_s is the specific heat, and ΔT is the temperature change. Eventually, the temperatures of the two substances will become equal at a value somewhere between their initial temperatures. Calculating the temperature of iced tea after adding an ice cube is slightly more complicated. The general equation relating heat gained and heat lost is still valid, but in this case we also have to take into account the amount of heat required to melt the ice cube from ice at 0.0°C to liquid water at 0.0°C.

The amount of heat gained by the ice cube as it melts is determined by its enthalpy of fusion in kJ/mol:

$$q = n\Delta H_{fus}$$

For our 50.0 g ice cube:

$$q_{ice} = 50.0g \cdot \frac{1\ mol}{18.02\ g} \cdot 6.01\ kJ/mol$$
$$= 16.7\ kJ$$

Thus, when the ice cube has just melted, it has absorbed 16.7 kJ of heat from the tea. We can then substitute this value into the first equation to determine the change in temperature of the tea:

$$q_{tea} = -16,700J = 500mL \cdot \frac{1.00\ g}{1\ mL} \cdot 4.184J/(g \bullet {}^\circ C)\Delta T$$
$$\Delta T = -7.98\,{}^\circ C = T_f - T_i$$
$$= 12.02\,{}^\circ C$$

This would be the temperature of the tea when the ice cube has just finished melting; however, this leaves the melted ice still at 0.0°C. We might more practically want to know what the final temperature of the mixture of tea will be once the melted ice has come to thermal equilibrium with the tea. To determine this, we can add one more step to the calculation by plugging in to the general equation relating heat gained and heat lost again:

$$q_{ice} = -q_{tea}$$
$$q_{ice} = m_{ice}C_s\Delta T = 50.0g \cdot 4.184J/(g \bullet {}^\circ C) \cdot (T_f - 0.0\,{}^\circ C)$$
$$= 209.2J/{}^\circ C \cdot T_f$$
$$q_{tea} = m_{tea}C_s\Delta T = 500g \cdot 4.184J/(g \bullet {}^\circ C) \cdot (T_f - 12.02\,{}^\circ C) = 2092J/{}^\circ C \cdot T_f - 25,150J$$
$$209.2J/{}^\circ C \cdot T_f = -2092J/{}^\circ C \cdot T_f + 25,150J$$
$$2301.2J/{}^\circ C \cdot T_f = 25,150J$$
$$T_f = 10.9\,{}^\circ C$$

The final temperature is in between the initial temperatures of the tea (12.02 °C) and the melted ice (0.0 °C), so this answer makes sense. In this example, the tea loses much more heat in melting the ice than in mixing with the cold water, showing the importance of accounting for the heat of phase changes!

? Exercise 13.1.5.1: Death by Freezing

Suppose you are overtaken by a blizzard while ski touring and you take refuge in a tent. You are thirsty, but you forgot to bring liquid water. You have a choice of eating a few handfuls of snow (say 400 g) at −5.0°C immediately to quench your thirst or setting up your propane stove, melting the snow, and heating the water to body temperature before drinking it. You recall that the survival guide you leafed through at the hotel said something about not eating snow, but you cannot remember why—after all, it's just frozen water. To understand the guide's recommendation, calculate the amount of heat that your body will have to supply to bring 400 g of snow at −5.0°C to your body's internal temperature of 37°C. Use the data in Example 13.1.5.1

Answer

200 kJ (4.1 kJ to bring the ice from −5.0°C to 0.0°C, 133.6 kJ to melt the ice at 0.0°C, and 61.9 kJ to bring the water from 0.0°C to 37°C), which is energy that would not have been expended had you first melted the snow.

Summary

Fusion, vaporization, and sublimation are endothermic processes, whereas freezing, condensation, and deposition are exothermic processes. Changes of state are examples of **phase changes**, or *phase transitions*. All phase changes are accompanied by changes in the energy of a system. Changes from a more-ordered state to a less-ordered state (such as a liquid to a gas) are *endothermic*. Changes from a less-ordered state to a more-ordered state (such as a liquid to a solid) are always *exothermic*. The conversion of a solid to a liquid is called **fusion (or melting)**. The energy required to melt 1 mol of a substance is its enthalpy of fusion (ΔH_{fus}). The energy change required to vaporize 1 mol of a substance is the enthalpy of vaporization (ΔH_{vap}). The direct conversion of a solid to a gas is **sublimation**. The amount of energy needed to sublime 1 mol of a substance is its **enthalpy of sublimation (ΔH_{sub})**

and is the sum of the enthalpies of fusion and vaporization. Plots of the temperature of a substance versus heat added or versus heating time at a constant rate of heating are called **heating curves**. Heating curves relate temperature changes to phase transitions. A **superheated liquid**, a liquid at a temperature and pressure at which it should be a gas, is not stable. A **cooling curve** is not exactly the reverse of the heating curve because many liquids do not freeze at the expected temperature. Instead, they form a **supercooled liquid**, a metastable liquid phase that exists below the normal melting point. Supercooled liquids usually crystallize on standing, or adding a **seed crystal** of the same or another substance can induce crystallization.

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13.1.6: Phase Diagrams

Learning Objectives

- To understand the basics of a one-component phase diagram as a function of temperature and pressure in a closed system.
- To be able to identify the triple point, the critical point, and four regions: solid, liquid, gas, and a supercritical fluid.

The state exhibited by a given sample of matter depends on the identity, temperature, and pressure of the sample. A phase diagram is a graphic summary of the physical state of a substance as a function of temperature and pressure in a closed system.

Introduction

A typical phase diagram consists of discrete regions that represent the different phases exhibited by a substance (Figure 13.1.6.1). Each region corresponds to the range of combinations of temperature and pressure over which that phase is stable. The combination of high pressure and low temperature (upper left of Figure 13.1.6.1) corresponds to the solid phase, whereas the gas phase is favored at high temperature and low pressure (lower right). The combination of high temperature and high pressure (upper right) corresponds to a supercritical fluid.

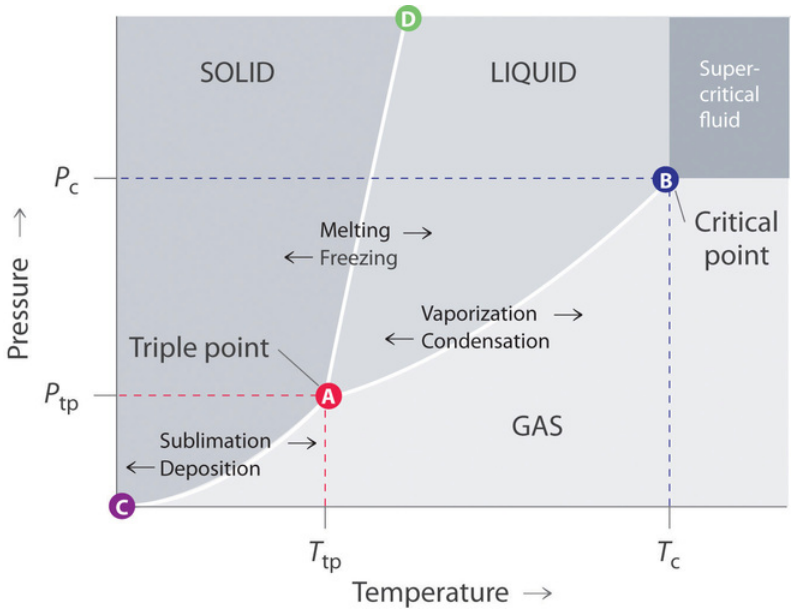


Figure 13.1.6.1: A Typical Phase Diagram for a Substance That Exhibits Three Phases—Solid, Liquid, and Gas—and a Supercritical Region

The solid phase is favored at low temperature and high pressure; the gas phase is favored at high temperature and low pressure.

The lines in a phase diagram correspond to the combinations of temperature and pressure at which two phases can coexist in equilibrium. In Figure 13.1.6.1, the line that connects points A and D separates the solid and liquid phases and shows how the melting point of a solid varies with pressure. The solid and liquid phases are in equilibrium all along this line; crossing the line horizontally corresponds to melting or freezing. The line that connects points A and B is the vapor pressure curve of the liquid, which we discussed in Section 11.5. It ends at the critical point, beyond which the substance exists as a supercritical fluid. The line that connects points A and C is the vapor pressure curve of the *solid* phase. Along this line, the solid is in equilibrium with the vapor phase through sublimation and deposition. Finally, point A, where the solid/liquid, liquid/gas, and solid/gas lines intersect, is the triple point; it is the *only* combination of temperature and pressure at which all three phases (solid, liquid, and gas) are in equilibrium and can therefore exist simultaneously. Because no more than three phases can ever coexist, a phase diagram can never have more than three lines intersecting at a single point.

Remember that a phase diagram, such as the one in Figure 13.1.6.1, is for a single pure substance in a closed system, not for a liquid in an open beaker in contact with air at 1 atm pressure. In practice, however, the conclusions reached about the behavior of a substance in a closed system can usually be extrapolated to an open system without a great deal of error.

The Phase Diagram of Water

Figure 13.1.6.2 shows the phase diagram of water and illustrates that the triple point of water occurs at 0.01°C and 0.00604 atm (4.59 mmHg). Far more reproducible than the melting point of ice, which depends on the amount of dissolved air and the atmospheric pressure, the triple point (273.16 K) is used to define the absolute (Kelvin) temperature scale. The triple point also represents the lowest pressure at which a liquid phase can exist in equilibrium with the solid or vapor. At pressures less than 0.00604 atm, therefore, ice does not melt to a liquid as the temperature increases; the solid sublimes directly to water vapor. Sublimation of water at low temperature and pressure can be used to "freeze-dry" foods and beverages. The food or beverage is first cooled to subzero temperatures and placed in a container in which the pressure is maintained below 0.00604 atm. Then, as the temperature is increased, the water sublimes, leaving the dehydrated food (such as that used by backpackers or astronauts) or the powdered beverage (as with freeze-dried coffee).

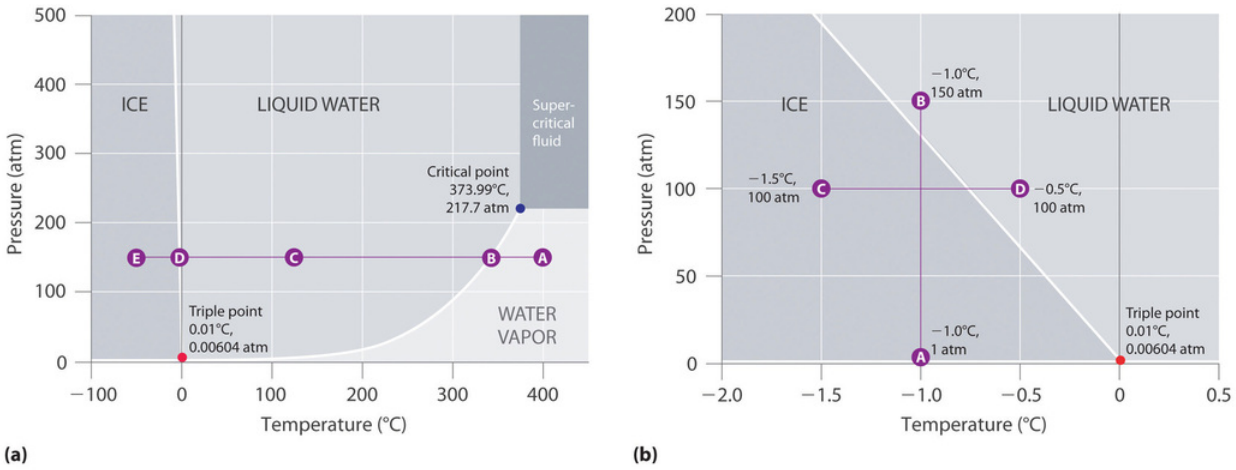


Figure 13.1.6.2: Two Versions of the Phase Diagram of Water. (a) In this graph with linear temperature and pressure axes, the boundary between ice and liquid water is almost vertical. (b) This graph with an expanded scale illustrates the decrease in melting point with increasing pressure. (The letters refer to points discussed in Example 13.1.6.1).

The phase diagram for water illustrated in Figure 13.1.6.2*b* shows the boundary between ice and water on an expanded scale. The melting curve of ice slopes up and slightly to the left rather than up and to the right as in Figure 13.1.6.1; that is, the melting point of ice *decreases* with increasing pressure; at 100 MPa (987 atm), ice melts at −9°C. Water behaves this way because it is one of the few known substances for which the crystalline solid is *less dense* than the liquid (others include antimony and bismuth). Increasing the pressure of ice that is in equilibrium with water at 0°C and 1 atm tends to push some of the molecules closer together, thus decreasing the volume of the sample. The decrease in volume (and corresponding increase in density) is smaller for a solid or a liquid than for a gas, but it is sufficient to melt some of the ice.

In Figure 13.1.6.2*b* point A is located at P = 1 atm and T = −1.0°C, within the solid (ice) region of the phase diagram. As the pressure increases to 150 atm while the temperature remains the same, the line from point A crosses the ice/water boundary to point B, which lies in the liquid water region. Consequently, applying a pressure of 150 atm will melt ice at −1.0°C. We have already indicated that the pressure dependence of the melting point of water is of vital importance. If the solid/liquid boundary in the phase diagram of water were to slant up and to the right rather than to the left, ice would be denser than water, ice cubes would sink, water pipes would not burst when they freeze, and antifreeze would be unnecessary in automobile engines.

Ice Skating: An Incorrect Hypothesis of Phase Transitions

Until recently, many textbooks described ice skating as being possible because the pressure generated by the skater's blade is high enough to melt the ice under the blade, thereby creating a lubricating layer of liquid water that enables the blade to slide across the ice. Although this explanation is intuitively satisfying, it is incorrect, as we can show by a simple calculation.



Pressure from ice skates on ice. from wikihow.com.

Recall that pressure (*P*) is the force (*F*) applied per unit area (*A*):

$$P = \frac{F}{A}$$

To calculate the pressure an ice skater exerts on the ice, we need to calculate only the force exerted and the area of the skate blade. If we assume a 75.0 kg (165 lb) skater, then the force exerted by the skater on the ice due to gravity is

$$F = mg$$

where *m* is the mass and *g* is the acceleration due to Earth's gravity (9.81 m/s^2). Thus the force is

$$F = (75.0\ kg)(9.81\ m/s^2) = 736\ (kg \bullet m)/s^2 = 736N$$

If we assume that the skate blades are 2.0 mm wide and 25 cm long, then the area of the bottom of each blade is

$$A = (2.0 \times 10^{-3}\ m)(25 \times 10^{-2}\ m) = 5.0 \times 10^{-4} m^2$$

If the skater is gliding on one foot, the pressure exerted on the ice is

$$P = \frac{736\ N}{5.0 \times 10^{-4}\ m^2} = 1.5 \times 10^6\ N/m^2 = 1.5 \times 10^6\ Pa = 15\ atm$$

The pressure is much lower than the pressure needed to decrease the melting point of ice by even 1°C, and experience indicates that it is possible to skate even when the temperature is well below freezing. Thus pressure-induced melting of the ice cannot explain the low friction that enables skaters (and hockey pucks) to glide. Recent research indicates that the surface of ice, where the ordered array of water molecules meets the air, consists of one or more layers of almost liquid water. These layers, together with melting induced by friction as a skater pushes forward, appear to account for both the ease with which a skater glides and the fact that skating becomes more difficult below about −7°C, when the number of lubricating surface water layers decreases.

✔ Example 13.1.6.1: Water

Referring to the phase diagram of water in Figure 13.1.6.2

a. predict the physical form of a sample of water at 400°C and 150 atm.
b. describe the changes that occur as the sample in part (a) is slowly allowed to cool to −50°C at a constant pressure of 150 atm.

Given: phase diagram, temperature, and pressure

Asked for: physical form and physical changes

Strategy:

A. Identify the region of the phase diagram corresponding to the initial conditions and identify the phase that exists in this region.
B. Draw a line corresponding to the given pressure. Move along that line in the appropriate direction (in this case cooling) and describe the phase changes.

Solution:

a. **A** Locate the starting point on the phase diagram in part (a) in Figure 13.1.6.2 The initial conditions correspond to point A, which lies in the region of the phase diagram representing water vapor. Thus water at *T* = 400°C and *P* = 150 atm is a gas.

b. **B** Cooling the sample at constant pressure corresponds to moving left along the horizontal line in part (a) in Figure 13.1.6.2 At about 340°C (point B), we cross the vapor pressure curve, at which point water vapor will begin to condense and the sample will consist of a mixture of vapor and liquid. When all of the vapor has condensed, the temperature drops further, and we enter the region corresponding to liquid water (indicated by point C). Further cooling brings us to the melting curve, the line that separates the liquid and solid phases at a little below 0°C (point D), at which point the sample will consist of a mixture of liquid and solid water (ice). When all of the water has frozen, cooling the sample to −50°C takes us along the horizontal line to point E, which lies within the region corresponding to solid water. At P = 150 atm and T = −50°C, therefore, the sample is solid ice.

? Exercise 13.1.6.2

Referring to the phase diagram of water in Figure 13.1.6.2, predict the physical form of a sample of water at −0.0050°C as the pressure is gradually increased from 1.0 mmHg to 218 atm.

Answer

The sample is initially a gas, condenses to a solid as the pressure increases, and then melts when the pressure is increased further to give a liquid.

The Phase Diagram of Carbon Dioxide

In contrast to the phase diagram of water, the phase diagram of CO_2 (Figure 13.1.6.3) has a more typical melting curve, sloping up and to the right. The triple point is −56.6°C and 5.11 atm, which means that liquid CO_2 cannot exist at pressures lower than 5.11 atm. At 1 atm, therefore, solid CO_2 sublimes directly to the vapor while maintaining a temperature of −78.5°C, the normal sublimation temperature. Solid CO_2 is generally known as dry ice because it is a cold solid with no liquid phase observed when it is warmed.



Dry ice ($CO_2(s)$) sublimed in air under room temperature and pressure. from Wikipedia.

Also notice the critical point at 30.98°C and 72.79 atm. Supercritical carbon dioxide is emerging as a natural refrigerant, making it a low carbon (and thus a more environmentally friendly) solution for domestic heat pumps.

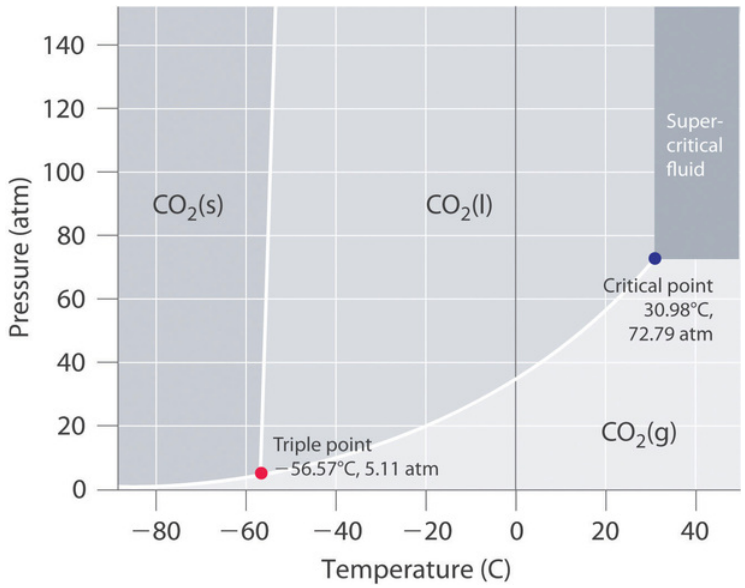


Figure 13.1.6.3: The Phase Diagram of Carbon Dioxide. Note the critical point, the triple point, and the normal sublimation temperature in this diagram.

The triple point is at -57.57 degrees C and 5.11 atm. The critical point is at 30.98 degree C and 72.79 atm.

The Critical Point

As the phase diagrams above demonstrate, a combination of high pressure and low temperature allows gases to be liquefied. As we increase the temperature of a gas, liquefaction becomes more and more difficult because higher and higher pressures are required to overcome the increased kinetic energy of the molecules. In fact, for every substance, there is some temperature above which the gas can no longer be liquefied, regardless of pressure. This temperature is the critical temperature (T_c), the highest temperature at which a substance can exist as a liquid. Above the critical temperature, the molecules have too much kinetic energy for the intermolecular attractive forces to hold them together in a separate liquid phase. Instead, the substance forms a single phase that completely occupies the volume of the container. Substances with strong intermolecular forces tend to form a liquid phase over a very large temperature range and therefore have high critical temperatures. Conversely, substances with weak intermolecular interactions have relatively low critical temperatures. Each substance also has a critical pressure (P_c), the minimum pressure needed to liquefy it at the critical temperature. The combination of critical temperature and critical pressure is called the critical point. The critical temperatures and pressures of several common substances are listed in Figure 13.1.6.1.

Figure 13.1.6.1: Critical Temperatures and Pressures of Some Simple Substances

Substance	T_c (°C)	P_c (atm)
NH_3	132.4	113.5
CO_2	31.0	73.8
CH_3CH_2OH (ethanol)	240.9	61.4
He	−267.96	2.27
Hg	1477	1587
CH_4	−82.6	46.0
N_2	−146.9	33.9
H_2O	374.0	217.7

High-boiling-point, nonvolatile liquids have high critical temperatures and vice versa.



A Video Discussing Phase Diagrams. Video Source: Phase Diagrams(opens in new window) [youtu.be]

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13.1.E: Solids, Liquids, and Phase Transitions (Exercises)

These are homework exercises to accompany the Textmap created for "Principles of Modern Chemistry" by Oxtoby et al. Complementary General Chemistry question banks can be found for other Textmaps and can be accessed here.

Q.1

If a substance has relatively strong intermolecular forces, a high melting point, and is not easily compressed, will this substance be a solid, liquid, or gas?

Solution

The substance is a solid because solids have relatively stronger intermolecular forces than liquids or gases. These strong intermolecular forces strongly hold the molecules in the solid together which makes it hard to compress a solid. Solids also have higher melting points because you need to put a lot more energy into solids to break apart the intermolecular forces to make the solid change phases.

Q.3

An unknown sample at 25^oC had a volume of $3.00 \times 10^{14} \mu m^3$ and a mass of $3.20 \times 10^3\ g$.

a. Is this sample most likely in a gaseous state or a condensed one? Why? (HINT: The density of water is $1.000 \frac{g}{mL}$).
b. After completing mass spectroscopy the molar mass of the material was found to be 127 g mol^{-1}, what is the molar volume at 25^oC from using the answer in part (a).

Solution

We need to compute the density of the liquid first:

$$\left(\frac{3.2 \times 10^3 g}{3.0 \times 10^{14}\ \mu\cancel{m^3}}\right)\left(\frac{1.0 \times 10^{12}\ \mu\cancel{m^3}}{1\ \text{cm}^3}\right) = 1.07 \times 10^1 \text{g cm}^{-3}$$

This material is known to be condensed because its density is higher than that of water.

Calculate the molar volume by:

$$\left(\frac{1\ \text{cm}^3}{10.7\ \cancel{g}}\right)\left(\frac{127\ \cancel{g}}{1\ \text{mol}}\right) = 1.19 \times 10^1 \text{cm}^3 mol^{-1}$$

Q.6A

If the volume of a substance changes from 300 cm^3 to 313 cm^3 when it is heated from 25^oC to 40^oC, is the substance ideal gas, nearly ideal gas, or condensed?

Solution

Temperature change = 15^oC

$$\text{Volume change ratio:} \frac{(313-300)}{300} = \frac{13}{300}$$

Hence, change percentage per ^oC is

$$\frac{13}{300} \times \frac{1}{15} \times 100\% = \frac{13}{1500}\% = 0.288\%$$

Since $0.288\%$is close to the ideal gas percentage of 0.366%, it is a nearly ideal gas.

Q.6B

Cooling a sample of matter from 130° to 50° at a constant pressure causes its volume to increase from 769.1 to 930.1 cm^3. Classify the material as nearly ideal gas, a non ideal gas, or condensed.

Solution

Charles' Law - Ideal Gases

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$0.00191 \frac{L}{K} = 0.00288 \frac{L}{K}$$

The material is a non-ideal gas.

Q.7

The molar volume of a substance is the volume occupied by one mole of the substance. The molar volume of a typical solid or liquid is $10 \frac{cm^3}{mol}$ to $100 \frac{cm^3}{mol}$, while the molar volume of a gas under the same conditions is about $24,000 \frac{cm^3}{mol}$. What does the similarity of the molar volumes of solid and liquid forms of the same substance suggest? What does the great difference of the the molar volumes of solid/liquid and gas forms of the same substance suggest?

Solution

The similarity of the molar volumes of solid and liquid forms of the same substance suggests that the distance between neighboring molecules of the substance in solid phase is approximately the same as the distance between neighboring molecules in liquid phase. The great difference of the molar volumes of solid/liquid and gas forms of the same substance suggests that the distance between neighboring molecules of the substance in gas phase is greater the distance between neighboring molecules in solid/liquid phase. This would explain why solids and liquids are called condensed states of matter, because the particles in these two phases are very close together, hence, solids and liquids have definite volumes. While the particles in the gas phase are so far away from each other that they can move freely at high speed, allowing the gas substance to assume the shape and volume of its container.

Q.9

Suppose you have to choose between solid $\mathrm{I_2}$ and solid $\mathrm{NH_4Cl}$ to fill your cushion and you prefer softer cushions, which one would you choose and why?

Solution

Non-directional ion-ion interaction is the dominant intermolecular interaction solid $\mathrm{NH_4Cl}$ has, and weaker London dispersion forces are the main intermolecular interaction $\mathrm{I_2}$ has, while the feeling of softness (indentation that breaks bonds in the solid) of the two solids depends on their strength of intermolecular interactions; in this case $\mathrm{I_2}$ has weaker intermolecular interactions and will feel softer.

Q.11

The diffusion constant is defined as the amount of substance that when diffusing from a region of high concentration to that of a low concentration goes through each unit of cross section per unit time. What happens to the diffusion constant, at constant temperature, as density of a liquid decreases, as the density of a solid increases, and as the density of a gas decreases? Explain the phenomena.

Solution

As the density of a liquid decreases, the diffusion constant will increase. This is because as density of the liquid decreases, there is more space in between the liquid molecules, and hence more movement is possible for the liquid molecules.

As density of a solid increases, diffusion constant will decrease. Similarly, in concept for the liquid molecules, if the density of a solid increases, there is even less space between the solid molecules than there was before. This further restricts the movements of the solid molecules and decreases diffusion. Note: solids also undergo diffusion; however, it occurs at an extremely slow rate.

As the density of gas decreases, diffusion constant will increase. As the density of a gas decreases, collision between gas molecules will occur less frequently, thus increasing freedom of movement for gas molecules and increasing the diffusion

constant.

Q.15

For the following chemicals list attractive intermolecular forces that you expect to see with each chemical. Of the forces you listed for each example, rank the intermolecular forces from strongest to weakest.

a. He
b. $\mathrm{H_2O}$
c. NaCl
d. $\mathrm{CH_4}$
e. CO
f. $\mathrm{O_2}$

Solution

a. London dispersion forces
b. Hydrogen bonding > dispersion forces
c. Ionic bonding > dispersion forces
d. London dispersion forces
e. Dipole-dipole forces > dispersion forces
f. London dispersion forces

Q.17

Which of the the following will be most strongly attracted to a lithium ion:

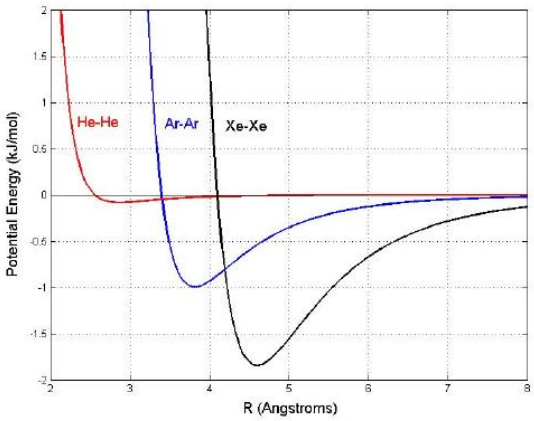
a. fluoride ion
b. a molecule of hydrogen fluoride
c. atom of Argon

Solution

A fluoride ion will be most strongly attracted to a lithium ion. The attraction between unlike charges such as lithium and fluoride are much stronger than the ion dipole attraction between $\mathrm{Li^+}$ and HF and the ion-induced dipole attraction between $\mathrm{Li^+}$ and Ar.

Q.19

Estimate the bond length of $\mathrm{He_2}$, $\mathrm{Ar_2}$, and $\mathrm{Xe_2}$ from the potential energy curves below. For each interacting pair, identify the attractive and repulsive distances. What are the intermolecular forces exist in each of the pair of molecules? Order the potential interactions in term of strength of intermolecular forces.



Solution

- $He_2 \approx 2.7 Å$
- $Ar_2 \approx 3.8 Å$
- $Xe_2 \approx 4.5 Å$

Repulsion is when R less than R at equilibrium. Attraction is when R is bigger than R at equilibrium.

Increasing order of intermolecular forces: He_2 < Ar_2 < Xe_2. The intermolecular force that the molecules have is London Dispersion Force (Van der Waals force). Larger molecules tend to have greater polarizability because they have more electrons and their electrons are further away from the nucleus. Therefore, LDF tend to get stronger when the molecule becomes larger. Based on the graph, the higher the potential energy, the stronger the interaction is.

Q.23

Arrange the following substances in order of decreasing normal boiling points and explain the rationale.

a. $CH_3CH_2CH_2CH_2CH_3$
b. $CH_3CH_2CH_2CH_2OH$
c. CH_4
d. $CH_3CH(CH_3)CH_2CH_3$

Solution

$$CH_3CH_2CH_2CH_2OH > CH_3CH_2CH_2CH_2CH_3 > CH_3CH(CH_3)CH_2CH_3 > CH_4$$

1-Butanol has the greatest boiling point due to strong hydrogen bonding with the alcohol group. Pentane has the second strongest boiling point due to its systematical structure and large London Dispersion force. Although 2-methylbutane has the same molecular mass as pentane, its geometrical structure hinders stacking which leads to lower intermolecular force. Therefore, 2-methylbutane has the lowest boiling point.

Q.24

You are given four beakers A, B, C, and D with four different chemicals. You forgot to label the beakers, so to identify them you boiled them to find their normal boiling points. The order of the boiling points came out to be B>D>A>C. If the chemicals in the beakers were HF (Hydrogen Fluoride), Ar (Argon), Cesium Chloride $CsCl$ and Hydrochloric Acid HCl, assign the chemicals to their respective beakers and give the reasoning behind your answer.

Solution

The primary intermolecular forces in the compounds are

- HF → Hydrogen Bonding
- Ar → Dispersion Forces
- $CsCl$ → Ionic Bonding
- HCl → Dipole-Dipole Interactions

Ionic Bonding > Hydrogen Bonding > Dipole-Dipole Interactions > Dispersion Forces

The stronger the intermolecular forces, the lower the vapor pressure, hence the boiling point would be higher.

Hence the beakers contain

- A = HCl
- B = $CsCl$
- C = Ar
- D = HF

Q.25

Like a normal human being, Kris enjoys breathing. But unfortunately for Kris, she is clinically paranoid, and feels as though she's breathing in a little too much ethanol. To calm Kris down, you say that as a vapor, ethanol exists, to an extent, as a dimer, ($(CH_3CH_2OH)_2$), in which two CH_3CH_2OH molecules are held together by hydrogen bonds. Propose and draw a reasonable structure for this dimer to help Kris deal with her problems.

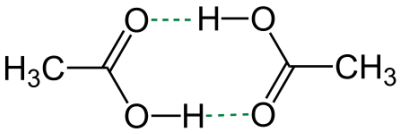
Solution

Hydrogen bonds are a type of intermolecular forces. It is the bond between a hydrogen atom and a high electronegative atom such as N, O, and F. The only hydrogen bonding which can take place between the ethanol molecules is between one's oxygen and the other's hydrogen bonded onto the other's oxygen. So any two membered structure of two ethanol molecukes with this criteria indicated is acceptable.

Q.25

Acetic acid (CH_3COOH) forms a dimer in the gas phase, where two acetic acid molecules are held together by hydrogen bonds. Draw a reasonable structure for this dimer.

Solution

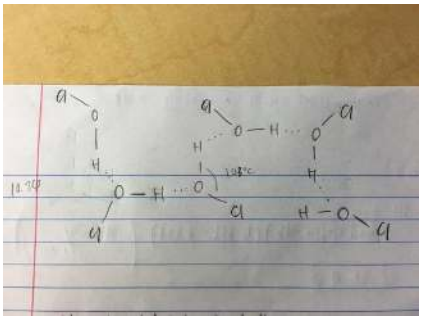


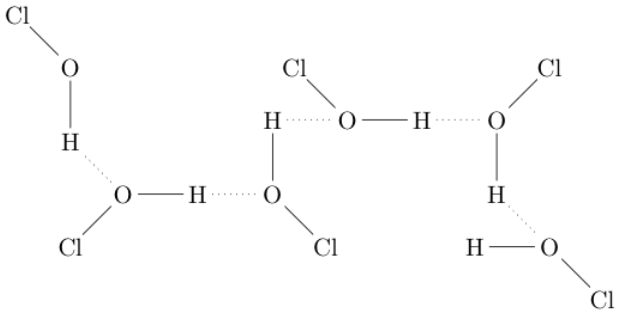
The diagram above shows a reasonable structure of a acetic acid dimer, where the dash lines represent hydrogen bonds.

Q.26

Hypochlorous acid ($HOCl$) is a similar compound to HOF, which is the simplest possible compound that allows comparison between fluoride and oxygen in their abilities to form hydrogen bonds. Although Cl attracts electrons more strongly than O, solid $HOCl$ cannot form $H-Cl$ bonds. Draw the proposed structure for chains of $HOCl$ molecules in the crystalline state. The bond angle for $HOCl$ is 103°.

Solution





Q.27

How do the boiling points of hydrogen halides differ from that of hydrogen fluoride (HF). Explain your reasoning. Answer: HF has a much higher boiling point (20^oC) compared to the other hydrogen halides. This is because HF is capable of forming hydrogen bonding within its compounds.

Solution

Fluorine is capable of doing hydrogen bonding as opposed to the other halogens in the periodic table. Since fluorine is the element with the highest electronegativity, the hydrogen-fluorine bond in hydrogen fluoride is highly polarized, creating a partial positive charge (δ+) on the hydrogen and, a negative charge (δ-) on the fluorine atom. Furthermore, the lone pairs situated on the fluorine atom are in the second energy level, thus they are very close and the negative charge on the atom is very concentrated, thus it has a strong attraction force. Hydrogen bonds form between the positively charged H atoms and the lone pair of the F atom. The other halogens are not capable of hydrogen bonding because they are not as electronegative as fluorine and they are larger in size. Thus the bond within the molecule is not as polarized and the lone pairs on the halogen atom are not as concentrated. Thus, the stronger the intermolecular forcers of the liquid, the harder it is for a molecule to gain enough energy to overcome the intermolecular forces that bond it in a liquid. The more energy is required to enter the gas phase. The higher the boiling point. Fluorine has higher intermolecular forces, thus it has a higher boiling point compared to the other hydrogen halides.

Q.31

Oxygen is stored at a temperature of 105 K and a pressure of 3.356 atm. If the volume of the container is 2.5 L, calculate the number of moles of oxygen in the container. Compare this number of moles to the number of moles in the same container at standard pressure and 298 K. Is it fewer, more, or unchanged?

Solution

This is an ideal gas law problem, so the formula $PV = nRT$ should be used.

$$P = 3.356\,\text{atm} \quad V = 2.5\,\text{L} \quad n = ? \quad R = 0.0821\,\frac{\text{L atm}}{\text{mol K}} \quad T = 105K$$

$$n = \frac{3.356 \times 2.5}{0.0821 \times 105}\,\text{mol}$$

$$n = 0.9733\,\text{mol}$$

Standard pressure = 1 atm

$$n = \frac{1 \times 2.5}{0.0821 \times 298}$$

$$n = 0.102\,\text{mol} < 0.9733\,\text{mol}$$

Therefore, under standard conditions, there are fewer moles of oxygen in the container.

Q.35

Consider the reaction at 25ºC.

$$\text{CaC}_2(\text{s}) + 2\,\text{H}_2\text{O}(\text{l}) \longrightarrow \text{C}_2\text{H}_2(\text{g}) + \text{Ca(OH)}_2(\text{s})$$

If the total pressure is 0.9124 atm and the vapor pressure of water at this temperature is 0.0313 atm. What is the mass of acetylene (C_2H_2) per liter of "wet" acetylene collected by this reaction (i.e., collected over a pool of water)? Assume all gases behave ideally.

Solution

Partial pressures in gases are additive via Dalton's Law.

- $P_T = 0.9124atm$
- $P_{\text{H}_2\text{O}} = 0.0313atm$

$$P_T - P_{\text{H}_2\text{O}} = P_{\text{C}_2\text{H}_2} = 0.8811atm$$

Using the Ideal Gas Law, moles per liter of acetylene can be found by rearranging the equation:

$$\frac{n}{V} = \frac{P_{\text{C}_2\text{H}_2}}{RT}$$

$$\frac{0.8811}{0.082057 \times 298.15} = \frac{0.036mol}{1L}$$

The question asks for grams per liter, so:

$$\left(\frac{0.036\ \cancel{mol\ C_2H_2}}{1L}\right)\left(\frac{26.036\ gC_2H_2}{1\ \cancel{mol\ C_2H_2}}\right) = 0.9376\ \frac{g}{L}$$

Q.39

The highest value of sea-level pressure on Earth occurs in Siberia where the Siberian High often allows water to boil at 80°C. Using chart 10.16 on page 431 of the text book, what can the fraction of pressure be in this location?

Solution

According to the graph, a location where the boiling temperature is 80°C correlates approximately to a fraction of 0.5 atm pressure.

Q.41

Water (H_2O) has a melting point of $0.00^\circ C$ and a boiling point of $100.0^\circ C$. Benzene (C_6H_6) has a melting point of $5.5^\circ C$ and a boiling point of $80.1^\circ C$. At $20.0^\circ C$, which of the two substances would be expected to have a greater surface tension? Explain?

Solution

At $20.0^\circ C$, water H_2O has a greater surface tension ($72.86\frac{mN}{m}$) than benzene, (C_6H_6), ($28.88\frac{mN}{m}$) because the intermolecular forces between water molecules are stronger than the intermolecular forces between benzene molecules. Water is capable of forming hydrogen-bonds, whereas the only forces that act in benzene are London dispersion forces.

Surface tension is the energy/work required to increase the surface area of a liquid. Molecules at the surface of a liquid do not experience any intermolecular interactions on one interface with air and therefore experience a net attractive force towards the center of the liquid. For surface molecules, the stronger the intermolecular forces between the molecules of the liquid, the stronger the net attractive force towards the center of the liquid will be. Compared to benzene, water possesses stronger intermolecular forces, therefore its surface molecules exhibit a stronger net attractive force towards the center of the liquid. As a result, more energy/work is required to counteract the net attractive force in order to increase the surface area. This indicates that for any liquid, stronger intermolecular forces allow for stronger surface tensions.

Q.43

At gallium's melting point of $302.91K$, its density is $6.095\frac{g}{cm^3}$. The density of solid gallium under standard conditions is $5.91\frac{g}{cm^3}$. When Ga is at $301.91K$ and pressure is strongly increased, will Ga undergo a phase change?

Solution

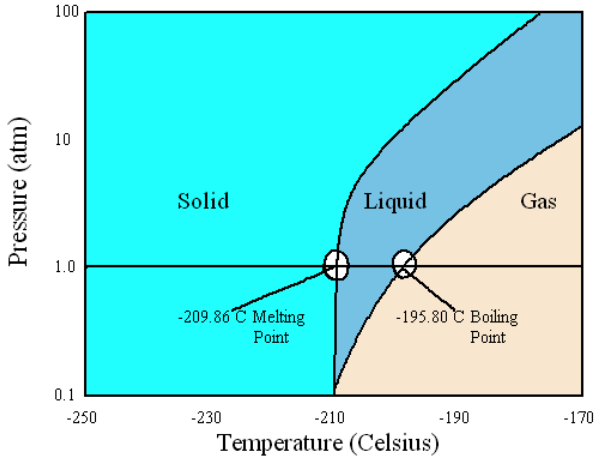
Compression favors the denser phase. Since Ga is a solid at $301.9K$, then it will undergo a phase change to become a liquid.

Q.45

Given the information below, sketch the phase diagram of Nitrogen:

- Triple point: 0.1252 bar, -210°C
- Normal boiling point: 1 bar, -195.8°C
- Normal melting point: 1 bar, -210°C

Solution



Normally, phase diagrams show pressures below that of the critical point.

Q.47

Use the phase diagram of water to determine whether water is a solid, a liquid, or a gas at each of the following combinations of temperature and pressure.

a. 1 atm and 20^oC
b. 0.006 atm and 100^oC
c. 210 atm and 100^oC
d. 10 atm and 50^oC

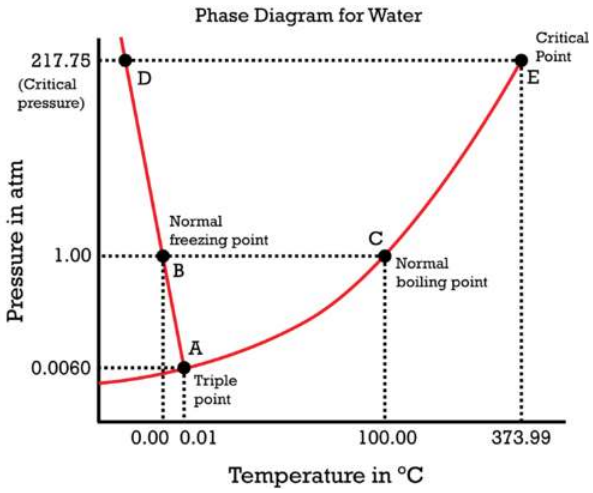


Figure used with permission (CK-12 Foundation – Christopher Auyeung)

Solution

Using the phase diagram of water,

1. Liquid
2. Gaseous
3. Liquid
4. Liquid

Q.53

What phase does candle wax exist in? How about butter?

Solution

Matter can exist in different phases depending on the temperature of the substance. For example, candle wax and butter can exist as a solid at room temperature, but when enough heat is applied to these substances, they can exist in a liquid or a gaseous phase.

Q.59

The equilibrium vapor pressure of water at 19^oC is $0.02168\,atm$ A humidifier is placed in a room with a volume of $180m^3$ and operates until the the room becomes saturated with water vapor. Initially there is no water vapor in water vapor in the air. Assuming that the room is closed completely from the outside such that water vapor cannot escape, calculate the mass of water that has passed into the air.

Solution

The air in the room becomes saturated once the vapor pressure of water in the room is equivalent to the equilibrium vapor pressure of water. Plug in given values into the ideal gas law to find the number of moles of water in the room when it is saturated, and then convert to grams.

$$PV = nRT$$

$$(0.02168atm)(180m^3)(\frac{1000L}{m^3}) = (n)(0.08206\frac{L\,atm}{mol\,K})(292.15K)$$

$$n = 162.77mols$$

$$m = 162.77mols \times \frac{18.02g}{mol} = 2930g$$

Q.65

A cooling bath is a mixture that is primarily liquid which is kept at a constant, low temperature. While in the lab, Po'lah accidently severed its hand after trying to make some mac and cheese. As a result it had to immediately transfer its hand to a cooling bath to sufficiently preserve it but not so that it could be of some use later on. In order to achieve this, the cooling bath had to be kept at around $0^\circ C$. The only liquids it had access to were water and methanol, both at room temperature, and the only cooling agents that it had were liquid nitrogen and dry ice (solid carbon dioxide). What combination did Po'lah use and why?

Relevant Information:

- Carbon Dioxide: sublimes at $-78.5^\circ C$
- Nitrogen: boils at $-195.8^\circ C$
- Water: freezes at $0^\circ C$
- Ethanol: freezes at $-143.7^\circ C$

Solution

This question is a bit tricky. The coolants Liquid Nitrogen and Dry ice, ($CO_2(s)$), both turn into gasses at very low temperatures. After they turn into gaseous, they are no longer "useful", since they cannot be added into the bath. Therefore, after adding sufficient amounts of either of the coolants to either of the liquids, the temperature of the bath would decrease way past the freezing point of either liquid, resulting in a cooling "block" rather than a bath. So what is the deal? Is this problem unsolvable?

Fortunately, it isn't. Think about a glass of ice water. If enough ice is put into the water, then eventually the water and ice would equilibrate at $0^\circ C$ which is the equilibrium point of the water where both its solid and liquid states can exit. Unfortunately, while the ice is not available at this time, the same concept can be applied. Remember, if enough of either coolant is used, then the entire cup of water will freeze over. However, if just enough of either coolant is put in so that the cooling bath remains at $0^\circ C$, a cooling bath that is somewhat solid and somewhat liquid will form, giving an adequate place for Po'lah to put its hand. Water is perfect for this because it remains a liquid at $0^\circ C$, and cannot exist as such at any lower temperature. Since Ethanol freezes at $-143.7^\circ C$, adding dry ice or liquid nitrogen would bring the cooling bath much lower than $0^\circ C$, which would destroy Po'lah's hand

Thus, it doesn't matter what cooling agent is used, either can bring water down to $0^\circ C$. However, methane cannot be used.

Abstract: Add a little of either coolant to bring the water down to $0^{\circ}C$, and it will remain at both a liquid and a solid which creates a $0^{\circ}C$ cooling bath. Methanol cannot be used.

Q.71

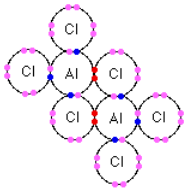
The melting points of the chlorides of third period elements are: $NaCl = 1074\,K$, $MgCl_2 = 987\,K$, $AlCl_3 = 465\,K$, $SiCl_4 = 204.4\,K$, $PCl_3 = 179\,K$. Based on the applicable intermolecular forces present in each compound, explain this trend in melting points.

Solution

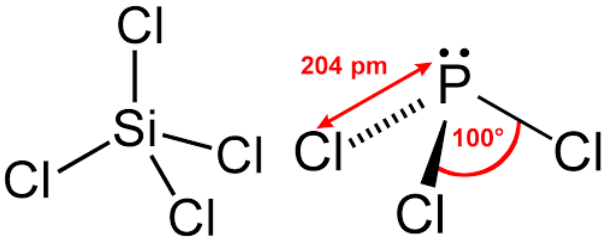
Experimentally, as the chloride compounds make their way across the third period elements, the melting points gradually decrease. This may appear an easy question to address since the melting points are a also measure of the magnitude of the intermolecular forces as play in the specific system, however it a quite complicated and to answer properly require knowledge of the chloride compounds.

Both ($NaCl$ and $MgCl_2$) are both "ionic solids" with strong ion-ion bonding and hence have the highest melting temperatures in the comparative series. We would expect the Na^+ ions in ($NaCl$ to have weaker Coulombic interactions than the Mg^{2+} ions in $MgCl_2$ since the latter are smaller and double the charge (i.e., a higher charge density). That would make the lattice energy higher because it would generate stronger ionic bonds (lattice energy of $NaCl$ and $MgCl_2$ are 876 and 2526 kJ/mol). However, this ionic perspective is insufficient to explain the observed melting points with ($NaCl > MgCl_2$), which we ascribe to bonding never being 100% ionic. As expected for teh difference in electronegativity of chlorine, magnesium, and sodium, the percent ionic character of the $Na-Cl$ bond is 71% and for $Mg-Cl$ is even lower, at 58%. Hence, the $Na-Cl$ bond is 29% covalent and the $Mg-Cl$ bond is 42% covalent. The covalent character reduces the melting point of $MgCl_2$, even though Mg^+ has a higher charge-to-size ratio than Na^+.

$AlCl_3$ is a molecular framework solid which means the solid is an extended covalent molecule and not individual $AlCl_3$ molecules bound by intermolecular forces.



Both $SiCl_4$ and PCl_4 solids are molecular in nature. To understand the strength of intermolecular forces as play this properly, we need to apply basic VESPR rules to identify the structures of these molecules.



$SiCl_4$ is a tetrahedral molecule with no dipole moment (nor quadrupole moment either). PCl_4 is trigonal pyramidal and since P has a different electronegativity than Cl, it has a dipole moment (0.97D). From this argument, we would think that PCl_4 would have a higher melting point, however both molecules have dispersive forces (London) too. Since the magnitude of dispersive forces increased wtih larger molecules (with more electrons to shift around), this is higher in PCl_4, which beats out the weak dipole-dipole interactions in PCl_4.

Q.71

Why are the melting points of $NaCl$ (801 °C) and $MgCl_2$ (714 °C) so much higher than the melting points of SCl_2 (-122 °C) and Cl_2 (-101.5 °C)? Explain answer in terms of intermolecular forces and identify any potential forces involved.

Solution

As with all bulk properties, the melting points are a measure of the magnitude of the intermolecular forces as play in the specific system (geometric structures also affects bulk properties like the nature of the crystal lattice, but that is a secondary issue). From inspection, it is clear that the $NaCl$ and $MgCl_2$ are ionic held together the strongest permanent electrostatic interaction (charge-charge or monopole-monopole); these are ionic solids. For SCl_2 and Cl_2, the solid is a molecular solid wtih constituent molecules that lack charge and even dipole (easy to tell for Cl_2 and requires a little VSEPR effort for SCl_2. Hence, the next higher permanent electrostatic interactions are active in these molecules (i.e. quadrupole-quadrupole) along with dispersion and repulsive interactions; all of which are much weaker than the charge-charge interactions in $NaCl$ and $MgCl_2$. The weaker the interactions, the lower the boiling point since less thermal energy is needed to break those interactions.

Now, a more advanced question is to explain the origin of the differences in the melting points of $NaCl$ vs. $MgCl_2$. Also to explain the origin of the differences in the melting points of SCl_2 vs. Cl_2. No answer given.

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SECTION OVERVIEW

13.2: Solutions

An General Chemistry Libretexts Textmap organized around the textbook

Principles of Modern Chemistry

by Oxtoby, Gillis, and Campion

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A solution is a **homogeneous** mixture composed of two or more substances. In such a mixture, a solute is a substance dissolved in another substance, known as a solvent.

13.2.1: Composition of Solutions

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13.2.1: Composition of Solutions

Learning Objectives

- To describe the concentration of a solution in the way that is most appropriate for a particular problem or application.
- To be familiar with the different units used to express the concentrations of a solution.

There are several different ways to quantitatively describe the concentration of a solution. For example, molarity is a useful way to describe solution concentrations for reactions that are carried out in solution. Mole fractions are used not only to describe gas concentrations but also to determine the vapor pressures of mixtures of similar liquids. Example 13.2.1.1reviews the methods for calculating the molarity and mole fraction of a solution when the masses of its components are known.

Example 13.2.1.1: Molarity and Mole Fraction

Commercial vinegar is essentially a solution of acetic acid in water. A bottle of vinegar has 3.78 g of acetic acid per 100.0 g of solution. Assume that the density of the solution is 1.00 g/mL.

a. What is its molarity?
b. What is its mole fraction?

Given: mass of substance and mass and density of solution

Asked for: molarity and mole fraction

Strategy:

A. Calculate the number of moles of acetic acid in the sample. Then calculate the number of liters of solution from its mass and density. Use these results to determine the molarity of the solution.
B. Determine the mass of the water in the sample and calculate the number of moles of water. Then determine the mole fraction of acetic acid by dividing the number of moles of acetic acid by the total number of moles of substances in the sample.

Solution:

A: The molarity is the number of moles of acetic acid per liter of solution. We can calculate the number of moles of acetic acid as its mass divided by its molar mass.

$$\text{moles } CH_3CO_2H = \frac{3.78 \text{ g } CH_3CO_2H}{60.05 \text{ g/mol}}$$

$$= 0.0629 \text{ mol}$$

The volume of the solution equals its mass divided by its density.

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

$$= \frac{100.0 \text{ g solution}}{1.00 \text{ g/mL}} = 100 \ mL$$

Then calculate the molarity directly.

$$\text{molarity of } CH_3CO_2H = \frac{\text{moles } CH_3CO_2H}{\text{liter solution}}$$

$$= \frac{0.0629 \ mol \ CH_3CO_2H}{(100 \text{ mL})(1 \ L/1000 \text{ mL})} = 0.629 \ M \ CH_3CO_2H$$

This result makes intuitive sense. If 100.0 g of aqueous solution (equal to 100 mL) contains 3.78 g of acetic acid, then 1 L of solution will contain 37.8 g of acetic acid, which is a little more than $\frac{1}{2}$ mole. Keep in mind, though, that the mass and volume of a solution are related by its density; concentrated aqueous solutions often have densities greater than 1.00 g/mL.

B: To calculate the mole fraction of acetic acid in the solution, we need to know the number of moles of both acetic acid and water. The number of moles of acetic acid is 0.0629 mol, as calculated in part (a). We know that 100.0 g of vinegar contains 3.78 g of acetic acid; hence the solution also contains (100.0 g − 3.78 g) = 96.2 g of water. We have

$$moles\ \mathrm{H_2O} = \frac{96.2\ \cancel{\mathrm{g}}\ \mathrm{H_2O}}{18.02\ \cancel{\mathrm{g}}/mol} = 5.34\ mol\ \mathrm{H_2O}$$

The mole fraction χ of acetic acid is the ratio of the number of moles of acetic acid to the total number of moles of substances present:

$$\begin{aligned}\chi_{\mathrm{CH_3CO_2H}} &= \frac{moles\ \mathrm{CH_3CO_2H}}{moles\ \mathrm{CH_3CO_2H} + moles\ \mathrm{H_2O}} \\ &= \frac{0.0629\ mol}{0.0629\ mol + 5.34\ mol} \\ &= 0.0116 = 1.16 \times 10^{-2}\end{aligned}$$

This answer makes sense, too. There are approximately 100 times as many moles of water as moles of acetic acid, so the ratio should be approximately 0.01.

? Exercise 13.2.1.1: Molarity and Mole Fraction

A solution of HCl gas dissolved in water (sold commercially as “muriatic acid,” a solution used to clean masonry surfaces) has 20.22 g of HCl per 100.0 g of solution, and its density is 1.10 g/mL.

a. What is its molarity?
b. What is its mole fraction?

Answer a

6.10 M HCl

Answer b

$\chi_{HCl} = 0.111$

The concentration of a solution can also be described by its molality (m), the number of moles of solute per kilogram of solvent:

$$\text{molality (m)} = \frac{\text{moles solute}}{\text{kilogram solvent}} \tag{13.2.1.1}$$

Molality, therefore, has the same numerator as molarity (the number of moles of solute) but a different denominator (kilogram of solvent rather than liter of solution). For dilute aqueous solutions, the molality and molarity are nearly the same because dilute solutions are mostly solvent. Thus because the density of water under standard conditions is very close to 1.0 g/mL, the volume of 1.0 kg of H_2O under these conditions is very close to 1.0 L, and a 0.50 M solution of KBr in water, for example, has approximately the same concentration as a 0.50 m solution.

Another common way of describing concentration is as the ratio of the mass of the solute to the total mass of the solution. The result can be expressed as mass percentage, parts per million (ppm), or parts per billion (ppb):

$$\text{mass percentage} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100 \tag{13.2.1.2}$$

$$\text{parts per million (ppm)} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6 \tag{13.2.1.3}$$

$$\text{parts per billion (ppb)} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^9 \tag{13.2.1.4}$$

In the health sciences, the concentration of a solution is often expressed as parts per thousand (ppt), indicated as a proportion. For example, adrenalin, the hormone produced in high-stress situations, is available in a 1:1000 solution, or one gram of adrenalin per

1000 g of solution.

The labels on bottles of commercial reagents often describe the contents in terms of mass percentage. Sulfuric acid, for example, is sold as a 95% aqueous solution, or 95 g of H_2SO_4 per 100 g of solution. Parts per million and parts per billion are used to describe concentrations of highly dilute solutions. These measurements correspond to milligrams and micrograms of solute per kilogram of solution, respectively. For dilute aqueous solutions, this is equal to milligrams and micrograms of solute per liter of solution (assuming a density of 1.0 g/mL).

✔ Example 13.2.1.2: Molarity and Mass

Several years ago, millions of bottles of mineral water were contaminated with benzene at ppm levels. This incident received a great deal of attention because the lethal concentration of benzene in rats is 3.8 ppm. A 250 mL sample of mineral water has 12.7 ppm of benzene. Because the contaminated mineral water is a very dilute aqueous solution, we can assume that its density is approximately 1.00 g/mL.

a. What is the molarity of the solution?
b. What is the mass of benzene in the sample?

Given: volume of sample, solute concentration, and density of solution

Asked for: molarity of solute and mass of solute in 250 mL

Strategy:

A. Use the concentration of the solute in parts per million to calculate the molarity.
B. Use the concentration of the solute in parts per million to calculate the mass of the solute in the specified volume of solution.

Solution:

a. A To calculate the molarity of benzene, we need to determine the number of moles of benzene in 1 L of solution. We know that the solution contains 12.7 ppm of benzene. Because 12.7 ppm is equivalent to 12.7 mg/1000 g of solution and the density of the solution is 1.00 g/mL, the solution contains 12.7 mg of benzene per liter (1000 mL). The molarity is therefore

$$\begin{aligned}\text{molarity} &= \frac{\text{moles}}{\text{liter solution}} \\ &= \frac{(12.7\ \cancel{mg})\left(\frac{1\ \cancel{g}}{1000\ \cancel{mg}}\right)\left(\frac{1\ mol}{78.114\ \cancel{g}}\right)}{1.00\ L} \\ &= 1.63 \times 10^{-4} M\end{aligned}$$

b. B We are given that there are 12.7 mg of benzene per 1000 g of solution, which is equal to 12.7 mg/L of solution. Hence the mass of benzene in 250 mL (250 g) of solution is

$$\begin{aligned}\text{mass of benzene} &= \frac{(12.7\ mg\ \text{benzene})(250\ \cancel{mL})}{1000\ \cancel{mL}} \\ &= 3.18\ mg \\ &= 3.18 \times 10^{-3}\ g\ \text{benzene}\end{aligned}$$

? Exercise 13.2.1.2: Molarity of Lead Solution

The maximum allowable concentration of lead in drinking water is 9.0 ppb.

a. What is the molarity of Pb^{2+} in a 9.0 ppb aqueous solution?
b. Use your calculated concentration to determine how many grams of Pb^{2+} are in an 8 oz glass of water.

Answer a

4.3×10^{-8} M

Answer b

2×10^{-6} g

How do chemists decide which units of concentration to use for a particular application? Although molarity is commonly used to express concentrations for reactions in solution or for titrations, it does have one drawback—molarity is the number of moles of solute divided by the volume of the solution, and the volume of a solution depends on its density, which is a function of temperature. Because volumetric glassware is calibrated at a particular temperature, typically 20°C, the molarity may differ from the original value by several percent if a solution is prepared or used at a significantly different temperature, such as 40°C or 0°C. For many applications this may not be a problem, but for precise work these errors can become important. In contrast, mole fraction, molality, and mass percentage depend on only the masses of the solute and solvent, which are independent of temperature.

Mole fraction is not very useful for experiments that involve quantitative reactions, but it is convenient for calculating the partial pressure of gases in mixtures, as discussed previously. Mole fractions are also useful for calculating the vapor pressures of certain types of solutions. Molality is particularly useful for determining how properties such as the freezing or boiling point of a solution vary with solute concentration. Because mass percentage and parts per million or billion are simply different ways of expressing the ratio of the mass of a solute to the mass of the solution, they enable us to express the concentration of a substance even when the molecular mass of the substance is unknown. Units of ppb or ppm are also used to express very low concentrations, such as those of residual impurities in foods or of pollutants in environmental studies.

Table 13.2.1.1summarizes the different units of concentration and typical applications for each. When the molar mass of the solute and the density of the solution are known, it becomes relatively easy with practice to convert among the units of concentration we have discussed, as illustrated in Example 13.2.1.3

Table 13.2.1.1: Different Units for Expressing the Concentrations of Solutions*

Unit	Definition	Application
molarity (M)	moles of solute/liter of solution (mol/L)	Used for quantitative reactions in solution and titrations; mass and molecular mass of solute and volume of solution are known.
mole fraction (χ)	moles of solute/total moles present (mol/mol)	Used for partial pressures of gases and vapor pressures of some solutions; mass and molecular mass of each component are known.
molality (m)	moles of solute/kg of solvent (mol/kg)	Used in determining how colligative properties vary with solute concentration; masses and molecular mass of solute are known.
mass percentage (%)	[mass of solute (g)/mass of solution (g)] × 100	Useful when masses are known but molecular masses are unknown.
parts per thousand (ppt)	[mass of solute/mass of solution] × 10^3 (g solute/kg solution)	Used in the health sciences, ratio solutions are typically expressed as a proportion, such as 1:1000.
parts per million (ppm)	[mass of solute/mass of solution] × 10^6 (mg solute/kg solution)	Used for trace quantities; masses are known but molecular masses may be unknown.
parts per billion (ppb)	[mass of solute/mass of solution] × 10^9 (µg solute/kg solution)	Used for trace quantities; masses are known but molecular masses may be unknown.

*The molarity of a solution is temperature dependent, but the other units shown in this table are independent of temperature.

Example 13.2.1.3: Vodka

Vodka is essentially a solution of ethanol in water. Typical vodka is sold as “80 proof,” which means that it contains 40.0% ethanol by volume. The density of pure ethanol is 0.789 g/mL at 20°C. If we assume that the volume of the solution is the sum of the volumes of the components (which is not strictly correct), calculate the following for the ethanol in 80-proof vodka.

a. the mass percentage
b. the mole fraction
c. the molarity
d. the molality

Given: volume percent and density

Asked for: mass percentage, mole fraction, molarity, and molality

Strategy:

A. Use the density of the solute to calculate the mass of the solute in 100.0 mL of solution. Calculate the mass of water in 100.0 mL of solution.
B. Determine the mass percentage of solute by dividing the mass of ethanol by the mass of the solution and multiplying by 100.
C. Convert grams of solute and solvent to moles of solute and solvent. Calculate the mole fraction of solute by dividing the moles of solute by the total number of moles of substances present in solution.
D. Calculate the molarity of the solution: moles of solute per liter of solution. Determine the molality of the solution by dividing the number of moles of solute by the kilograms of solvent.

Solution:

The key to this problem is to use the density of pure ethanol to determine the mass of ethanol (CH_3CH_2OH), abbreviated as EtOH, in a given volume of solution. We can then calculate the number of moles of ethanol and the concentration of ethanol in any of the required units. A Because we are given a percentage by volume, we assume that we have 100.0 mL of solution. The volume of ethanol will thus be 40.0% of 100.0 mL, or 40.0 mL of ethanol, and the volume of water will be 60.0% of 100.0 mL, or 60.0 mL of water. The mass of ethanol is obtained from its density:

$$mass\ of\ EtOH = (40.0\ \cancel{mL}) \left(\frac{0.789\ g}{\cancel{mL}} \right) = 31.6\ g\ EtOH$$

If we assume the density of water is 1.00 g/mL, the mass of water is 60.0 g. We now have all the information we need to calculate the concentration of ethanol in the solution.

B The mass percentage of ethanol is the ratio of the mass of ethanol to the total mass of the solution, expressed as a percentage:

$$\begin{aligned} \%EtOH &= \left(\frac{mass\ of\ EtOH}{mass\ of\ solution} \right) (100) \\ &= \left(\frac{31.6\ \cancel{g}\ EtOH}{31.6\ \cancel{g}\ EtOH + 60.0\ \cancel{g}\ H_2O} \right) (100) \\ &= 34.5\% \end{aligned}$$

C The mole fraction of ethanol is the ratio of the number of moles of ethanol to the total number of moles of substances in the solution. Because 40.0 mL of ethanol has a mass of 31.6 g, we can use the molar mass of ethanol (46.07 g/mol) to determine the number of moles of ethanol in 40.0 mL:

$$\begin{aligned} moles\ CH_3CH_2OH &= (31.6\ \ g\ \cancel{CH_3CH_2OH}) \left(\frac{1\ mol}{46.07\ \ g\ \cancel{CH_3CH_2OH}} \right) \\ &= 0.686\ mol\ CH_3CH_2OH \end{aligned}$$

Similarly, the number of moles of water is

$$moles\ H_2O = (60.0\ \ g\ H_2O)\left(\frac{1\ mol\ H_2O}{18.02\ \ g\ H_2O}\right) = 3.33\ mol\ H_2O$$

The mole fraction of ethanol is thus

$$\chi_{CH_3CH_2OH} = \frac{0.686\ \ mol}{0.686\ \ mol + 3.33\ \ mol} = 0.171$$

D The molarity of the solution is the number of moles of ethanol per liter of solution. We already know the number of moles of ethanol per 100.0 mL of solution, so the molarity is

$$M_{CH_3CH_2OH} = \left(\frac{0.686\ mol}{100\ \ mL}\right)\left(\frac{1000\ \ mL}{L}\right) = 6.86\ M$$

The molality of the solution is the number of moles of ethanol per kilogram of solvent. Because we know the number of moles of ethanol in 60.0 g of water, the calculation is again straightforward:

$$m_{CH_3CH_2OH} = \left(\frac{0.686\ mol\ EtOH}{60.0\ \ g\ H_2O}\right)\left(\frac{1000\ \ g}{kg}\right) = \frac{11.4\ mol\ EtOH}{kg\ H_2O} = 11.4\ m$$

? Exercise 13.2.1.3: Toluene/Benzene Solution

A solution is prepared by mixing 100.0 mL of toluene with 300.0 mL of benzene. The densities of toluene and benzene are 0.867 g/mL and 0.874 g/mL, respectively. Assume that the volume of the solution is the sum of the volumes of the components. Calculate the following for toluene.

a. mass percentage
b. mole fraction
c. molarity
d. molality

Answer a

mass percentage toluene = 24.8%

Answer b

$\chi_{toluene} = 0.219$

Answer c

2.35 M toluene

Answer d

3.59 m toluene



A Video Discussing Different Measures of Concentration. Video Link: Measures of Concentration, YouTube (opens in new window) [youtu.be]



A Video Discussing how to Convert Measures of Concentration. Video Link: Converting Units of Concentration, YouTube(opens in new window) [youtu.be]

Summary

Different units are used to express the concentrations of a solution depending on the application. The concentration of a solution is the quantity of solute in a given quantity of solution. It can be expressed in several ways: molarity (moles of solute per liter of solution); mole fraction, the ratio of the number of moles of solute to the total number of moles of substances present; mass percentage, the ratio of the mass of the solute to the mass of the solution times 100; parts per thousand (ppt), grams of solute per kilogram of solution; parts per million (ppm), milligrams of solute per kilogram of solution; parts per billion (ppb), micrograms of solute per kilogram of solution; and molality (m), the number of moles of solute per kilogram of solvent.

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13.2.2: Nature of Dissolved Species

Learning Objectives

- To understand how enthalpy and entropy changes affect solution formation.
- To use the magnitude of the changes in both enthalpy and entropy to predict whether a given solute–solvent combination will spontaneously form a solution.

In all solutions, whether gaseous, liquid, or solid, the substance present in the greatest amount is the solvent, and the substance or substances present in lesser amounts are the solute(s). The solute does not have to be in the same physical state as the solvent, but the physical state of the solvent usually determines the state of the solution. As long as the solute and solvent combine to give a homogeneous solution, the solute is said to be soluble in the solvent. Table 13.2.2.1 lists some common examples of gaseous, liquid, and solid solutions and identifies the physical states of the solute and solvent in each.

Table 13.2.2.1: Types of Solutions

Solution	Solute	Solvent	Examples
gas	gas	gas	air, natural gas
liquid	gas	liquid	seltzer water (CO_2 gas in water)
liquid	liquid	liquid	alcoholic beverage (ethanol in water), gasoline
liquid	solid	liquid	tea, salt water
solid	gas	solid	H_2 in Pd (used for H_2 storage)
solid	solid	liquid	mercury in silver or gold (amalgam often used in dentistry)
solid	solid	solid	alloys and other "solid solutions"

Forming a Solution

The formation of a solution from a solute and a solvent is a physical process, not a chemical one. That is, both solute and solvent can be recovered in chemically unchanged forms using appropriate separation methods. For example, solid zinc nitrate dissolves in water to form an aqueous solution of zinc nitrate:

$$\mathrm{Zn(NO_3)_2(s) + H_2O(l) \rightarrow Zn^{2+}(aq) + 2\,NO_3^-(aq)} \tag{13.2.2.1}$$

Because $Zn(NO_3)_2$ can be recovered easily by evaporating the water, this is a physical process. In contrast, metallic zinc appears to dissolve in aqueous hydrochloric acid. In fact, the two substances undergo a chemical reaction to form an aqueous solution of zinc chloride with evolution of hydrogen gas:

$$\mathrm{Zn(s) + 2\,H^+(aq) + 2\,Cl^-(aq) \rightarrow Zn^{2+}(aq) + 2\,Cl^-(aq) + H_2(g)} \tag{13.2.2.2}$$

When the solution evaporates, we do not recover metallic zinc, so we cannot say that metallic zinc is soluble in aqueous hydrochloric acid because it is chemically transformed when it dissolves. The dissolution of a solute in a solvent to form a solution does not involve a chemical transformation (that it is a physical change).

> *Dissolution of a solute in a solvent to form a solution does not involve a chemical transformation.*

Substances that form a single homogeneous phase in all proportions are said to be completely *miscible* in one another. Ethanol and water are miscible, just as mixtures of gases are miscible. If two substances are essentially insoluble in each other, such as oil and water, they are *immiscible*. Examples of gaseous solutions that we have already discussed include Earth's atmosphere.

The Role of Enthalpy in Solution Formation

Energy is required to overcome the intermolecular interactions in a solute, which can be supplied only by the new interactions that occur in the solution, when each solute particle is surrounded by particles of the solvent in a process called solvation (or hydration when the solvent is water). Thus all of the solute–solute interactions and many of the solvent–solvent interactions must be disrupted for a solution to form. In this section, we describe the role of enthalpy in this process.

Because enthalpy is a state function, we can use a thermochemical cycle to analyze the energetics of solution formation. The process occurs in three discrete steps, indicated by ΔH_1, ΔH_2, and ΔH_3 in Figure 13.2.2.2 The overall enthalpy change in the formation of the solution (ΔH_{soln}) is the sum of the enthalpy changes in the three steps:

$$\Delta H_{soln} = \Delta H_1 + \Delta H_2 + \Delta H_3 \tag{13.2.2.3}$$

When a solvent is added to a solution, steps 1 and 2 are both endothermic because energy is required to overcome the intermolecular interactions in the solvent (ΔH_1) and the solute (ΔH_2). Because ΔH is positive for both steps 1 and 2, the solute–solvent interactions (ΔH_3) must be stronger than the solute–solute and solvent–solvent interactions they replace in order for the dissolution process to be exothermic ($\Delta H_{soln} < 0$). When the solute is an ionic solid, ΔH_2 corresponds to the lattice energy that must be overcome to form a solution. The higher the charge of the ions in an ionic solid, the higher the lattice energy. Consequently, solids that have very high lattice energies, such as MgO (−3791 kJ/mol), are generally insoluble in all solvents.

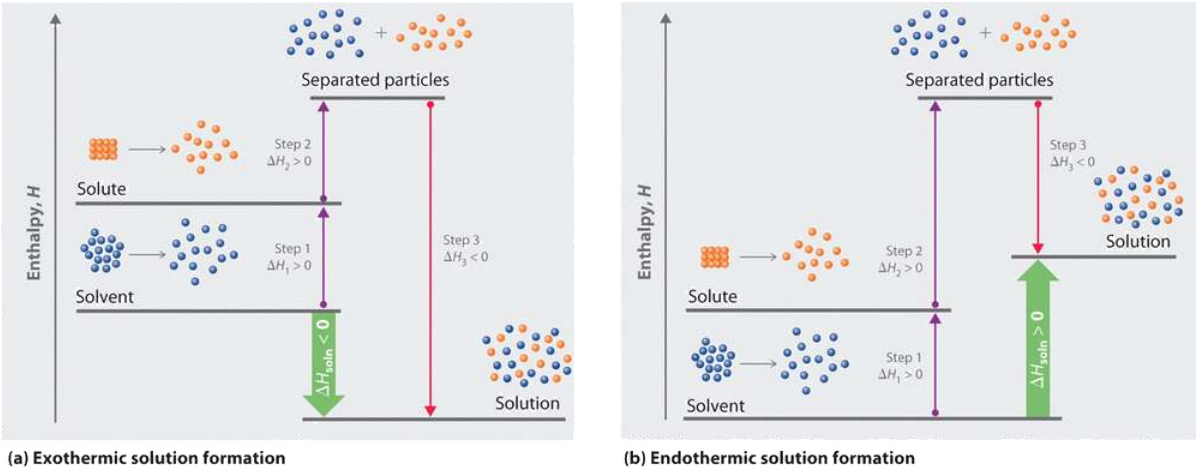


Figure 13.2.2.2: Enthalpy Changes That Accompany the Formation of a Solution. Solvation can be an exothermic or endothermic process depending on the nature of the solute and solvent. In both cases, step 1, separation of the solvent particles, is energetically uphill ($\Delta H_1 > 0$), as is step 2, separation of the solute particles ($\Delta H_2 > 0$). In contrast, energy is released in step 3 ($\Delta H_3 < 0$) because of interactions between the solute and solvent. (a) When ΔH_3 is larger in magnitude than the sum of ΔH_1 and ΔH_2, the overall process is exothermic ($\Delta H_{soln} < 0$), as shown in the thermochemical cycle. (b) When ΔH_3 is smaller in magnitude than the sum of ΔH_1 and ΔH_2, the overall process is endothermic ($\Delta H_{soln} > 0$).

A positive value for ΔH_{soln} does not mean that a solution will not form. Whether a given process, including formation of a solution, occurs spontaneously depends on whether the total energy of the system is lowered as a result. Enthalpy is only one of the contributing factors. A high ΔH_{soln} is usually an indication that the substance is not very soluble. Instant cold packs used to treat athletic injuries, for example, take advantage of the large positive ΔH_{soln} of ammonium nitrate during dissolution (+25.7 kJ/mol), which produces temperatures less than 0°C (Figure 13.2.2.3).



Figure 13.2.2.3: Commercial Cold Packs for Treating Injuries. These packs contain solid NH_4NO_3 and water in separate compartments. When the seal between the compartments is broken, the NH_4NO_3 dissolves in the water. Because ΔH_{soln} for NH_4NO_3 is much greater than zero, heat is absorbed by the cold pack during the dissolution process, producing local temperatures less than 0°C.

Entropy and Solution Formation

The enthalpy change that accompanies a process is important because processes that release substantial amounts of energy tend to occur spontaneously. A second property of any system, its entropy, is also important in helping us determine whether a given process occurs spontaneously. We will discuss entropy in more detail elsewhere, but for now we can state that entropy (S) is a thermodynamic property of all substances that is proportional to their degree of disorder. A perfect crystal at 0 K, whose atoms are regularly arranged in a perfect lattice and are motionless, has an entropy of zero. In contrast, gases have large positive entropies because their molecules are highly disordered and in constant motion at high speeds.

The formation of a solution disperses molecules, atoms, or ions of one kind throughout a second substance, which generally increases the disorder and results in an increase in the entropy of the system. Thus entropic factors almost always favor formation of a solution. In contrast, a change in enthalpy may or may not favor solution formation. The London dispersion forces that hold cyclohexane and n-hexane together in pure liquids, for example, are similar in nature and strength. Consequently, ΔH_{soln} should be approximately zero, as is observed experimentally. Mixing equal amounts of the two liquids, however, produces a solution in which the n-hexane and cyclohexane molecules are uniformly distributed over approximately twice the initial volume. In this case, the driving force for solution formation is not a negative ΔH_{soln} but rather the increase in entropy due to the increased disorder in the mixture. All spontaneous processes with $\Delta H \geq 0$ are characterized by an *increase* in entropy. In other cases, such as mixing oil with water, salt with gasoline, or sugar with hexane, the enthalpy of solution is large and positive, and the increase in entropy resulting from solution formation is not enough to overcome it. Thus in these cases a solution does not form.

> *All spontaneous processes with ΔH ≥ 0 are characterized by an increase in entropy.*

Table 13.2.2.2summarizes how enthalpic factors affect solution formation for four general cases. The column on the far right uses the relative magnitudes of the enthalpic contributions to predict whether a solution will form from each of the four. Keep in mind that in each case entropy favors solution formation. In two of the cases the enthalpy of solution is expected to be relatively small and can be either positive or negative. Thus the entropic contribution dominates, and we expect a solution to form readily. In the other two cases the enthalpy of solution is expected to be large and positive. The entropic contribution, though favorable, is usually too small to overcome the unfavorable enthalpy term. Hence we expect that a solution will not form readily.

Table 13.2.2.2: Relative Changes in Enthalpies for Different Solute–Solvent Combinations*

ΔH_1 (separation of solvent molecules)	ΔH_2 (separation of solute particles)	ΔH_3 (solute–solvent interactions)	ΔH_{soln} (ΔH_1 + ΔH_2 +ΔH_3)	Result of Mixing Solute and Solvent†
large; positive	large; positive	large; negative	small; positive or negative	solution will usually form
small; positive	large; positive	small; negative	large; positive	solution will not form
large; positive	small; positive	small; negative	large; positive	solution will not form

ΔH_1 (separation of solvent molecules)	ΔH_2 (separation of solute particles)	ΔH_3 (solute–solvent interactions)	ΔH_{soln} (ΔH_1 + ΔH_2 +ΔH_3)	Result of Mixing Solute and Solvent†
small; positive	small; positive	small; negative	small; positive or negative	solution will usually form

*ΔH_1, ΔH_2, and ΔH_3 refer to the processes indicated in the thermochemical cycle shown in Figure 13.2.2.2
†In all four cases, entropy increases.

In contrast to liquid solutions, the intermolecular interactions in gases are weak (they are considered to be nonexistent in ideal gases). Hence mixing gases is usually a thermally neutral process ($\Delta H_{soln} \approx 0$), and the entropic factor due to the increase in disorder is dominant (Figure 13.2.2.4). Consequently, all gases dissolve readily in one another in all proportions to form solutions.

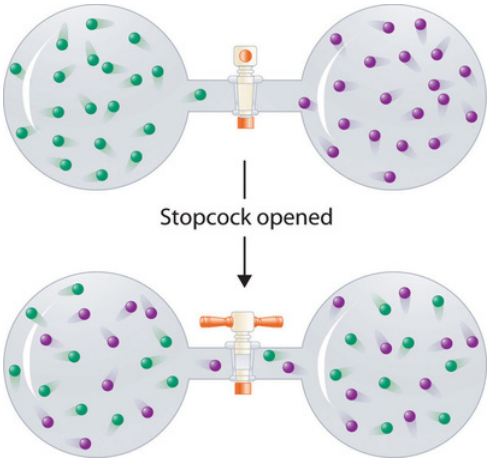
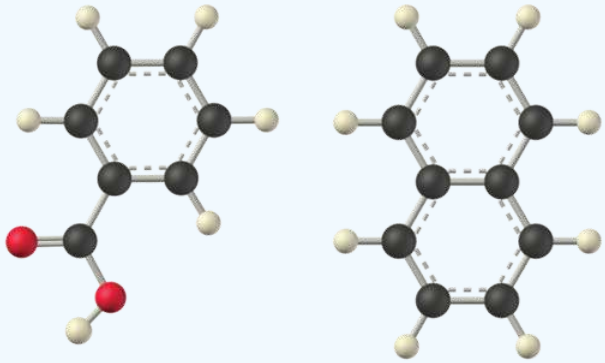


Figure 13.2.2.4: Formation of a Solution of Two Gases. (top) Pure samples of two different gases are in separate bulbs. (bottom) When the connecting stopcock is opened, diffusion causes the two gases to mix together and form a solution. Even though ΔH_{soln} is zero for the process, the increased entropy of the solution (the increased disorder) versus that of the separate gases favors solution formation.

Example 13.2.2.1

Considering $LiCl$, benzoic acid ($C_6H_5CO_2H$), and naphthalene, which will be most soluble and which will be least soluble in water?



Given: three compounds

Asked for: relative solubilities in water

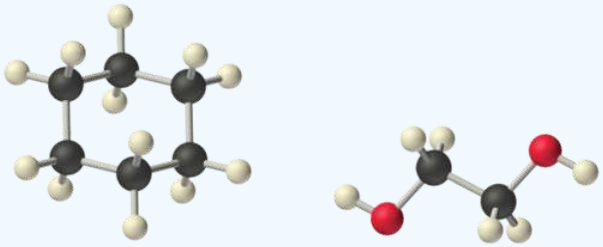
Strategy: Assess the relative magnitude of the enthalpy change for each step in the process shown in Figure 13.2.2.2 Then use Table 13.2.2.2to predict the solubility of each compound in water and arrange them in order of decreasing solubility.

Solution:

The first substance, LiCl, is an ionic compound, so a great deal of energy is required to separate its anions and cations and overcome the lattice energy (ΔH_2 is far greater than zero in Equation 13.2.2.1). Because water is a polar substance, the interactions between both Li^+ and Cl^- ions and water should be favorable and strong. Thus we expect ΔH_3 to be far less than zero, making LiCl soluble in water. In contrast, naphthalene is a nonpolar compound, with only London dispersion forces holding the molecules together in the solid state. We therefore expect ΔH_2 to be small and positive. We also expect the interaction between polar water molecules and nonpolar naphthalene molecules to be weak $\Delta H_3 \approx 0$. Hence we do not expect naphthalene to be very soluble in water, if at all. Benzoic acid has a polar carboxylic acid group and a nonpolar aromatic ring. We therefore expect that the energy required to separate solute molecules (ΔH_2) will be greater than for naphthalene and less than for LiCl. The strength of the interaction of benzoic acid with water should also be intermediate between those of LiCl and naphthalene. Hence benzoic acid is expected to be more soluble in water than naphthalene but less soluble than LiCl. We thus predict LiCl to be the most soluble in water and naphthalene to be the least soluble.

? Exercise 13.2.2.1

Considering ammonium chloride, cyclohexane, and ethylene glycol ($HOCH_2CH_2OH$), which will be most soluble and which will be least soluble in benzene?



Cyclohexane

Ethylene glycol

Answer

The most soluble is cyclohexane; the least soluble is ammonium chloride.

Summary

Solutions are homogeneous mixtures of two or more substances whose components are uniformly distributed on a microscopic scale. The component present in the greatest amount is the solvent, and the components present in lesser amounts are the solute(s). The formation of a solution from a solute and a solvent is a physical process, not a chemical one. Substances that are miscible, such as gases, form a single phase in all proportions when mixed. Substances that form separate phases are immiscible. Solvation is the process in which solute particles are surrounded by solvent molecules. When the solvent is water, the process is called hydration. The overall enthalpy change that accompanies the formation of a solution, ΔH_{soln}, is the sum of the enthalpy change for breaking the intermolecular interactions in both the solvent and the solute and the enthalpy change for the formation of new solute–solvent interactions. Exothermic ($\Delta H_{soln} < 0$) processes favor solution formation. In addition, the change in entropy, the degree of disorder of the system, must be considered when predicting whether a solution will form. An increase in entropy (a decrease in order) favors dissolution.

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13.2.3: Phase Equilibrium in Solutions - Nonvolatile Solutes

Learning Objectives

- To describe the relationship between solute concentration and the physical properties of a solution.
- To understand that the total number of nonvolatile solute particles determines the decrease in vapor pressure, increase in boiling point, and decrease in freezing point of a solution versus the pure solvent.

Many of the physical properties of solutions differ significantly from those of the pure substances discussed in earlier chapters, and these differences have important consequences. For example, the limited temperature range of liquid water (0°C–100°C) severely limits its use. Aqueous solutions have both a lower freezing point and a higher boiling point than pure water. Probably one of the most familiar applications of this phenomenon is the addition of ethylene glycol ("antifreeze") to the water in an automobile radiator. This solute lowers the freezing point of the water, preventing the engine from cracking in very cold weather from the expansion of pure water on freezing. Antifreeze also enables the cooling system to operate at temperatures greater than 100°C without generating enough pressure to explode.

Changes in the freezing point and boiling point of a solution depend primarily on the number of solute particles present rather than the kind of particles. Such properties of solutions are called colligative properties (from the Latin *colligatus*, meaning "bound together" as in a quantity). As we will see, the vapor pressure and osmotic pressure of solutions are also colligative properties.

Counting Concentrations and Effective Concentrations

When we determine the number of particles in a solution, it is important to remember that not all solutions with the same molarity contain the same concentration of solute particles. Consider, for example, 0.01 M aqueous solutions of sucrose, NaCl, and $\mathrm{CaCl_2}$. Because sucrose dissolves to give a solution of neutral molecules, the concentration of solute particles in a 0.01 M sucrose solution is 0.01 M. In contrast, both NaCl and $\mathrm{CaCl_2}$ are ionic compounds that dissociate in water to yield solvated ions. As a result, a 0.01 M aqueous solution of NaCl contains 0.01 M $\mathrm{Na^+}$ ions and 0.01 M $\mathrm{Cl^-}$ ions, for a total particle concentration of 0.02 M. Similarly, the $\mathrm{CaCl_2}$ solution contains 0.01 M $\mathrm{Ca^{2+}}$ ions and 0.02 M $\mathrm{Cl^-}$ ions, for a total particle concentration of 0.03 M. These values are correct for dilute solutions, where the dissociation of the compounds to form separately solvated ions is complete.

At **higher concentrations** (typically >1 M), especially with salts of small, highly charged ions (such as $\mathrm{Mg^{2+}}$ or $\mathrm{Al^{3+}}$), or in solutions with less polar solvents, dissociation to give separate ions is often incomplete. The sum of the concentrations of the dissolved solute particles dictates the physical properties of a solution. In the following discussion, we must therefore keep the chemical nature of the solute firmly in mind. A greater discussion of this is below.

Vapor Pressure of Solutions and Raoult's Law For Nonvolatile Solutes

Adding a nonvolatile solute, one whose vapor pressure is too low to measure readily, to a volatile solvent decreases the vapor pressure of the solvent. We can understand this phenomenon qualitatively by examining Figure 13.2.3.1, which is a schematic diagram of the surface of a solution of glucose in water. In an aqueous solution of glucose, a portion of the surface area is occupied by nonvolatile glucose molecules rather than by volatile water molecules. As a result, fewer water molecules can enter the vapor phase per unit time, even though the surface water molecules have the same kinetic energy distribution as they would in pure water. At the same time, the rate at which water molecules in the vapor phase collide with the surface and reenter the solution is unaffected. The net effect is to shift the dynamic equilibrium between water in the vapor and the liquid phases, decreasing the vapor pressure of the solution compared with the vapor pressure of the pure solvent.

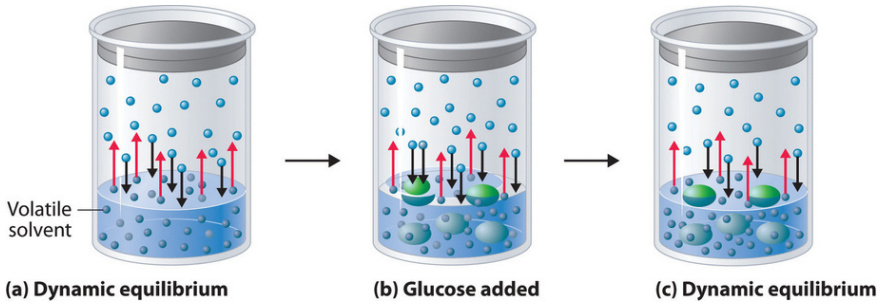


Figure 13.2.3.1: A Model Depicting Why the Vapor Pressure of a Solution of Glucose Is Less Than the Vapor Pressure of Pure Water. (a) When water or any volatile solvent is in a closed container, water molecules move into and out of the liquid phase at the same rate in a dynamic equilibrium. (b) If a nonvolatile solute such as glucose is added, some fraction of the surface area is occupied by solvated solute molecules. As a result, the rate at which water molecules evaporate is decreased, although initially their rate of condensation is unchanged. (c) When the glucose solution reaches equilibrium, the concentration of water molecules in the vapor phase, and hence the vapor pressure, is less than that of pure water. (CC BY-NC-SA; anonymous)

Figure 13.2.3.2 shows two beakers, one containing pure water and one containing an aqueous glucose solution, in a sealed chamber. We can view the system as having two competing equilibria: water vapor will condense in both beakers at the same rate, but water molecules will evaporate more slowly from the glucose solution because fewer water molecules are at the surface. Eventually all of the water will evaporate from the beaker containing the liquid with the higher vapor pressure (pure water) and condense in the beaker containing the liquid with the lower vapor pressure (the glucose solution). If the system consisted of only a beaker of water inside a sealed container, equilibrium between the liquid and vapor would be achieved rather rapidly, and the amount of liquid water in the beaker would remain constant.

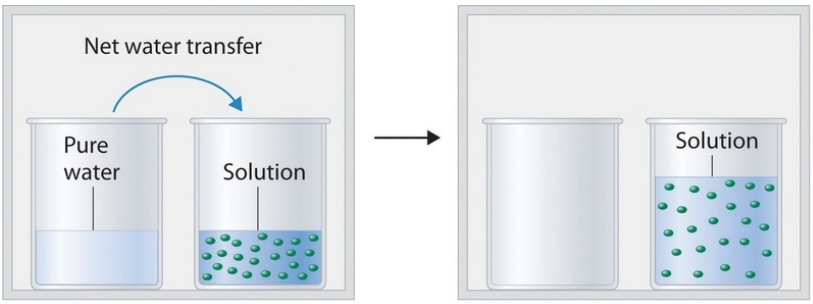


Figure 13.2.3.2: Transfer of Water to a Beaker Containing a Glucose Solution. (top) One beaker contains an aqueous solution of glucose, and the other contains pure water. If they are placed in a sealed chamber, the lower vapor pressure of water in the glucose solution results in a net transfer of water from the beaker containing pure water to the beaker containing the glucose solution. (bottom) Eventually, all of the water is transferred to the beaker that has the glucose solution. (CC BY-NC-SA; anonymous)

If the particles of a solute are essentially the same size as those of the solvent and both solute and solvent have roughly equal probabilities of being at the surface of the solution, then the effect of a solute on the vapor pressure of the solvent is proportional to the number of sites occupied by solute particles at the surface of the solution. Doubling the concentration of a given solute causes twice as many surface sites to be occupied by solute molecules, resulting in twice the decrease in vapor pressure. The relationship between solution composition and vapor pressure is therefore

$$P_A = \chi_A P_A^0 \tag{13.2.3.1}$$

where P_A is the vapor pressure of component A of the solution (in this case the solvent), χ_A is the mole fraction of A in solution, and P_A^0 is the vapor pressure of pure A. Equation 13.2.3.1 is known as **Raoult's law**, after the French chemist who developed it. If the solution contains only a single nonvolatile solute (B), then we can relate the mole fraction of the solvent to the solute

$$\chi_A + \chi_B = 1$$

and we can substitute $\chi_A = 1 - \chi_B$ into Equation 13.2.3.1 to obtain

$$\begin{aligned} P_A &= (1 - \chi_B) P_A^0 \\ &= P_A^0 - \chi_B P_A^0 \end{aligned}$$

Rearranging and defining $\Delta P_A = P_A^0 - P_A$, we obtain a relationship between the decrease in vapor pressure and the mole fraction of nonvolatile solute:

$$P_A^0 - P_A = \Delta P_A \tag{13.2.3.2}$$

$$= \chi_B P_A^0 \tag{13.2.3.3}$$

We can solve vapor pressure problems in either of two ways: by using Equation 13.2.3.1 to calculate the actual vapor pressure above a solution of a nonvolatile solute, or by using Equation 13.2.3.3 to calculate the decrease in vapor pressure caused by a specified amount of a nonvolatile solute.

Example 13.2.3.1: Anti-Freeze

Ethylene glycol ($HOCH_2CH_2OH$), the major ingredient in commercial automotive antifreeze, increases the boiling point of radiator fluid by lowering its vapor pressure. At 100°C, the vapor pressure of pure water is 760 mmHg. Calculate the vapor pressure of an aqueous solution containing 30.2% ethylene glycol by mass, a concentration commonly used in climates that do not get extremely cold in winter.

Given: identity of solute, percentage by mass, and vapor pressure of pure solvent

Asked for: vapor pressure of solution

Strategy:

A. Calculate the number of moles of ethylene glycol in an arbitrary quantity of water, and then calculate the mole fraction of water.
B. Use Raoult's law (Equation 13.2.3.1) to calculate the vapor pressure of the solution.

Solution:

A A 30.2% solution of ethylene glycol contains 302 g of ethylene glycol per kilogram of solution; the remainder (698 g) is water. To use Raoult's law to calculate the vapor pressure of the solution, we must know the mole fraction of water. Thus we must first calculate the number of moles of both ethylene glycol (EG) and water present:

$$moles\ EG = (302\ \cancel{g}) \left(\frac{1\ mol}{62.07\ \cancel{g}} \right) = 4.87\ mol\ EG$$

$$moles\ H_2O = (698\ \cancel{g}) \left(\frac{1\ mol}{18.02\ \cancel{g}} \right) = 38.7\ mol\ H_2O$$

The mole fraction of water is thus

$$\chi_{H_2O} = \frac{38.7\ \cancel{mol}\ H_2O}{38.7\ \cancel{mol}\ H_2O + 4.87\ \cancel{mol}\ EG} = 0.888$$

B From Raoult's law (Equation 13.2.3.1), the vapor pressure of the solution is

$$P_{H_2O} = (\chi_{H_2O})(P^0_{H_2O})$$

$$= (0.888)(760\ mmHg) = 675\ mmHg$$

Alternatively, we could solve this problem by calculating the mole fraction of ethylene glycol and then using Equation 13.2.3.3 to calculate the resulting decrease in vapor pressure:

$$\chi_{EG} = \frac{4.87\ mol\ EG}{4.87\ mol\ EG + 38.7\ mol\ H_2O}$$

$$= 0.112$$

$$\Delta P_{H_2O} = (\chi_{EG})(P^0_{H_2O})$$

$$= (0.112)(760\ mmHg) = 85.1\ mmHg$$

$$P_{H_2O} = P^0_{H_2O} - \Delta P_{H_2O} = 760\ mmHg - 85.1\ mmHg = 675\ mmHg$$

The same result is obtained using either method.

? Exercise 13.2.3.1

Seawater is an approximately 3.0% aqueous solution of NaCl by mass with about 0.5% of other salts by mass. Calculate the decrease in the vapor pressure of water at 25°C caused by this concentration of NaCl, remembering that 1 mol of NaCl produces 2 mol of solute particles. The vapor pressure of pure water at 25°C is 23.8 mmHg.

Answer

0.45 mmHg. This may seem like a small amount, but it constitutes about a 2% decrease in the vapor pressure of water and accounts in part for the higher humidity in the north-central United States near the Great Lakes, which are freshwater lakes. The decrease therefore has important implications for climate modeling.

Boiling Point Elevation

Recall that the normal boiling point of a substance is the temperature at which the vapor pressure equals 1 atm. If a nonvolatile solute lowers the vapor pressure of a solvent, it must also affect the boiling point. Because the vapor pressure of the solution at a given temperature is less than the vapor pressure of the pure solvent, achieving a vapor pressure of 1 atm for the solution requires a higher temperature than the normal boiling point of the solvent. Thus the boiling point of a solution is always greater than that of the pure solvent. We can see why this must be true by comparing the phase diagram for an aqueous solution with the phase diagram for pure water (Figure 13.2.3.4). The vapor pressure of the solution is less than that of pure water at all temperatures. Consequently, the liquid–vapor curve for the solution crosses the horizontal line corresponding to $P = 1\,atm$ at a higher temperature than does the curve for pure water.

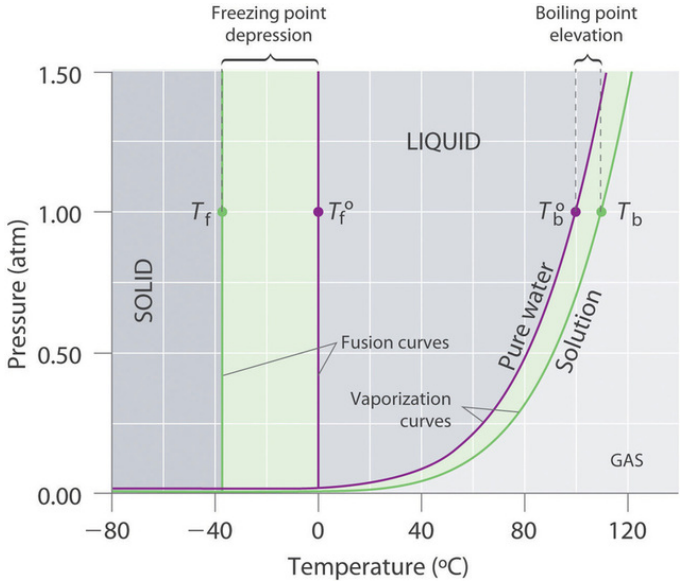


Figure 13.2.3.4: Phase Diagrams of Pure Water and an Aqueous Solution of a Nonvolatile Solute. The vaporization curve for the solution lies below the curve for pure water at all temperatures, which results in an increase in the boiling point and a decrease in the freezing point of the solution. (CC BY-NC-SA; anonymous)

> *The boiling point of a solution with a nonvolatile solute is **always** greater than the boiling point of the pure solvent.*

The magnitude of the increase in the boiling point is related to the magnitude of the decrease in the vapor pressure. As we have just discussed, the decrease in the vapor pressure is proportional to the concentration of the solute in the solution. Hence the magnitude of the increase in the boiling point must also be proportional to the concentration of the solute (Figure 13.2.3.5).

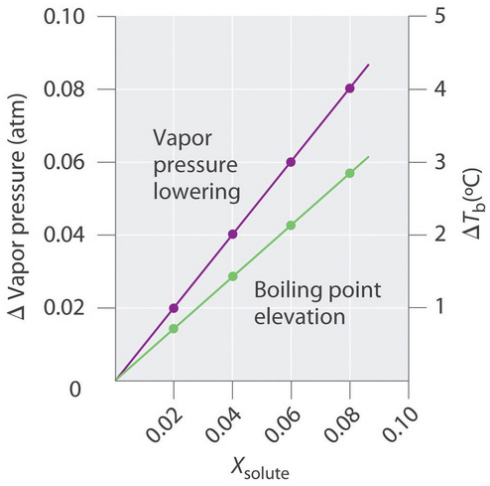


Figure 13.2.3.5: Vapor Pressure Decrease and Boiling Point Increase as Functions of the Mole Fraction of a Nonvolatile Solute. (CC BY-NC-SA; anonymous)

We can define the boiling point elevation (ΔT_b) as the difference between the boiling points of the solution and the pure solvent:

$$\Delta T_b = T_b - T_b^0 \tag{13.2.3.4}$$

where T_b is the boiling point of the solution and T_b^0 is the boiling point of the pure solvent. We can express the relationship between ΔT_b and concentration as follows

$$\Delta T_b = mK_b \tag{13.2.3.5}$$

where m is the concentration of the solute expressed in molality, and K_b is the **molal boiling point elevation constant** of the solvent, which has units of °C/m. Table 13.2.3.1 lists characteristic K_b values for several commonly used solvents. For relatively dilute solutions, the magnitude of both properties is proportional to the solute concentration.

Table 13.2.3.1: Boiling Point Elevation Constants (K_b) and Freezing Point Depression Constants (K_f) for Some Solvents

Solvent	Boiling Point (°C)	K_b (°C/m)	Freezing Point (°C)	K_f (°C/m)
acetic acid	117.90	3.22	16.64	3.63
benzene	80.09	2.64	5.49	5.07
d-(+)-camphor	207.4	4.91	178.8	37.8
carbon disulfide	46.2	2.42	−112.1	3.74
carbon tetrachloride	76.8	5.26	−22.62	31.4
chloroform	61.17	3.80	−63.41	4.60
nitrobenzene	210.8	5.24	5.70	6.87
water	100.00	0.51	0.00	1.86

The concentration of the solute is typically expressed as molality rather than mole fraction or molarity for two reasons. First, because the density of a solution changes with temperature, the value of molarity also varies with temperature. If the boiling point depends on the solute concentration, then by definition the system is not maintained at a constant temperature. Second, molality and mole fraction are proportional for relatively dilute solutions, but molality has a larger numerical value (a mole fraction can be only between zero and one). Using molality allows us to eliminate nonsignificant zeros.

According to Table 13.2.3.1, the molal boiling point elevation constant for water is 0.51°C/m. Thus a 1.00 m aqueous solution of a nonvolatile molecular solute such as glucose or sucrose will have an increase in boiling point of 0.51°C, to give a boiling point of 100.51°C at 1.00 atm. The increase in the boiling point of a 1.00 m aqueous NaCl solution will be approximately twice as large as that of the glucose or sucrose solution because 1 mol of NaCl produces 2 mol of dissolved ions. Hence a 1.00 m NaCl solution will have a boiling point of about 101.02°C.

Example 13.2.3.3

In Example 13.2.3.1, we calculated that the vapor pressure of a 30.2% aqueous solution of ethylene glycol at 100°C is 85.1 mmHg less than the vapor pressure of pure water. We stated (without offering proof) that this should result in a higher boiling point for the solution compared with pure water. Now that we have seen why this assertion is correct, calculate the boiling point of the aqueous ethylene glycol solution.

Given: composition of solution

Asked for: boiling point

Strategy:

Calculate the molality of ethylene glycol in the 30.2% solution. Then use Equation 13.2.3.5 to calculate the increase in boiling point.

Solution:

From Example 13.2.3.1, we know that a 30.2% solution of ethylene glycol in water contains 302 g of ethylene glycol (4.87 mol) per 698 g of water. The molality of the solution is thus

$$\text{molality of ethylene glycol} = \left(\frac{4.87\ mol}{698\ \cancel{g}\ H_2O}\right)\left(\frac{1000\ \cancel{g}}{1\ kg}\right)$$
$$= 6.98\,m$$

From Equation 13.2.3.5, the increase in boiling point is therefore

$$\Delta T_b = mK_b$$
$$= (6.98\ \cancel{m})(0.51^\circ C/\ \cancel{m})$$
$$= 3.6^\circ C$$

The boiling point of the solution is thus predicted to be 104°C. With a solute concentration of almost 7 m, however, the assumption of a dilute solution used to obtain Equation 13.2.3.5 may not be valid.

Exercise 13.2.3.3

Assume that a tablespoon (5.00 g) of NaCl is added to 2.00 L of water at 20.0°C, which is then brought to a boil to cook spaghetti. At what temperature will the water boil?

Answer

100.04°C, or 100°C to three significant figures. (Recall that 1 mol of NaCl produces 2 mol of dissolved particles. The small increase in temperature means that adding salt to the water used to cook pasta has essentially no effect on the cooking time.)

Freezing Point Depression

The phase diagram in Figure 13.2.3.4 shows that dissolving a nonvolatile solute in water not only raises the boiling point of the water but also lowers its freezing point. The solid–liquid curve for the solution crosses the line corresponding to $P = 1\ atm$ at a lower temperature than the curve for pure water.

We can understand this result by imagining that we have a sample of water at the normal freezing point temperature, where there is a dynamic equilibrium between solid and liquid. Water molecules are continuously colliding with the ice surface and entering the solid phase at the same rate that water molecules are leaving the surface of the ice and entering the liquid phase. If we dissolve a nonvolatile solute such as glucose in the liquid, the dissolved glucose molecules will reduce the number of collisions per unit time between water molecules and the ice surface because some of the molecules colliding with the ice will be glucose. Glucose, though, has a very different structure than water, and it cannot fit into the ice lattice. Consequently, the presence of glucose molecules in the solution can only decrease the rate at which water molecules in the liquid collide with the ice surface and solidify. Meanwhile, the rate at which the water molecules leave the surface of the ice and enter the liquid phase is unchanged. The net

effect is to cause the ice to melt. The only way to reestablish a dynamic equilibrium between solid and liquid water is to lower the temperature of the system, which decreases the rate at which water molecules leave the surface of the ice crystals until it equals the rate at which water molecules in the solution collide with the ice.

By analogy to our treatment of boiling point elevation,the freezing point depression (ΔT_f) is defined as the difference between the freezing point of the pure solvent and the freezing point of the solution:

$$\Delta T_f = T_f^0 - T_f \tag{13.2.3.6}$$

where T_f^0 is the freezing point of the pure solvent and T_f is the freezing point of the solution.

The order of the terms is reversed compared with Equation 13.2.3.4to express the freezing point depression as a positive number. The relationship between ΔT_f and the solute concentration is given by an equation analogous to Equation 13.2.3.5:

$$\Delta T_f = mK_f \tag{13.2.3.7}$$

where m is the molality of the solution and K_f is the molal freezing point depression constant for the solvent (in units of °C/m).

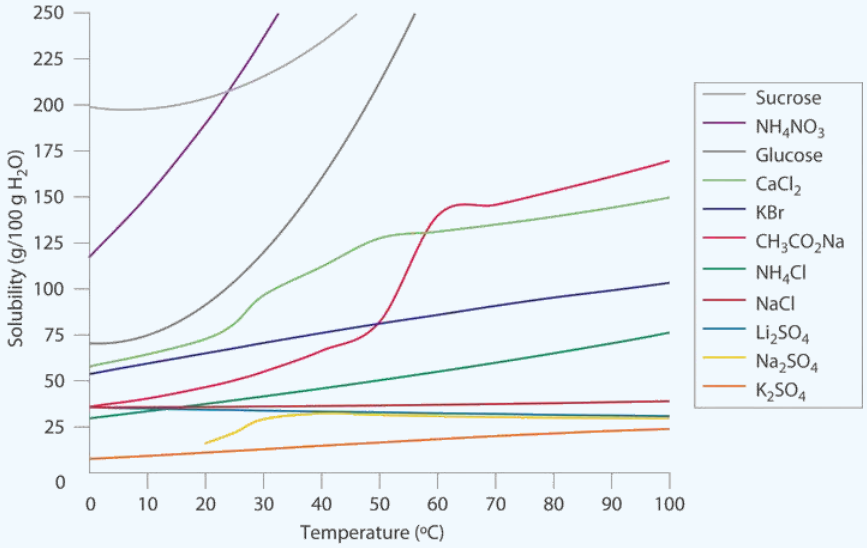
Like K_b, each solvent has a characteristic value of K_f (see Table 13.2.3.1). Freezing point depression depends on the total number of dissolved nonvolatile solute particles, just as with boiling point elevation. Thus an aqueous NaCl solution has twice as large a freezing point depression as a glucose solution of the same molality.

People who live in cold climates use freezing point depression to their advantage in many ways. For example, salt is used to melt ice and snow on roads and sidewalks, ethylene glycol is added to engine coolant water to prevent an automobile engine from being destroyed, and methanol is added to windshield washer fluid to prevent the fluid from freezing.

> The decrease in vapor pressure, increase in boiling point, and decrease in freezing point of a solution versus a pure liquid all depend on the total number of dissolved nonvolatile solute particles.

Example 13.2.3.4: Salting the Roads

In colder regions of the United States, NaCl or $\mathrm{CaCl_2}$ is often sprinkled on icy roads in winter to melt the ice and make driving safer. Use the data in the Figure below to estimate the concentrations of two saturated solutions at 0°C, one of NaCl and one of $\mathrm{CaCl_2}$, and calculate the freezing points of both solutions to see which salt is likely to be more effective at melting ice.



Solubilities of Several Inorganic and Organic Solids in Water as a Function of Temperature. Solubility may increase or decrease with temperature; the magnitude of this temperature dependence varies widely among compounds. (CC BY-NC-SA; anonymous)

Given: solubilities of two compounds

Asked for: concentrations and freezing points

Strategy:

A. Estimate the solubility of each salt in 100 g of water from the figure. Determine the number of moles of each in 100 g and calculate the molalities.
B. Determine the concentrations of the dissolved salts in the solutions. Substitute these values into Equation 13.2.3.7to calculate the freezing point depressions of the solutions.

Solution:

A. From Figure above, we can estimate the solubilities of NaCl and $\mathrm{CaCl_2}$ to be about 36 g and 60 g, respectively, per 100 g of water at 0°C. The corresponding concentrations in molality are

$$m_{NaCl} = \left(\frac{36\ \cancel{g\ NaCl}}{100\ \cancel{g}\ H_2O}\right)\left(\frac{1\ mol\ NaCl}{58.44\ \cancel{g\ NaCl}}\right)\left(\frac{1000\ \cancel{g}}{1\ kg}\right) = 6.2\ m$$

$$m_{CaCl_2} = \left(\frac{60\ \cancel{g\ CaCl_2}}{100\ \cancel{g}\ H_2O}\right)\left(\frac{1\ mol\ CaCl_2}{110.98\ \cancel{g\ CaCl_2}}\right)\left(\frac{1000\ \cancel{g}}{1kg}\right) = 5.4\ m$$

The lower formula mass of NaCl more than compensates for its lower solubility, resulting in a saturated solution that has a slightly higher concentration than $\mathrm{CaCl_2}$.

B. Because these salts are ionic compounds that dissociate in water to yield two and three ions per formula unit of NaCl and $\mathrm{CaCl_2}$, respectively, the actual concentrations of the dissolved species in the two saturated solutions are 2 × 6.2 m = 12 m for NaCl and 3 × 5.4 m = 16 m for $\mathrm{CaCl_2}$. The resulting freezing point depressions can be calculated using Equation 13.2.3.7:

$$\mathrm{NaCl}: \Delta T_f = mK_f = (12\ \cancel{m})(1.86^\circ C/\ \cancel{m}) = 22^\circ C$$

$$\mathrm{CaCl_2}: \Delta T_f = mK_f = (16\ \cancel{m})(1.86^\circ C/\ \cancel{m}) = 30^\circ C$$

Because the freezing point of pure water is 0°C, the actual freezing points of the solutions are −22°C and −30°C, respectively. Note that $\mathrm{CaCl_2}$ is substantially more effective at lowering the freezing point of water because its solutions contain three ions per formula unit. In fact, $\mathrm{CaCl_2}$ is the salt usually sold for home use, and it is also often used on highways.

Because the solubilities of both salts decrease with decreasing temperature, the freezing point can be depressed by only a certain amount, regardless of how much salt is spread on an icy road. If the temperature is significantly below the minimum temperature at which one of these salts will cause ice to melt (say −35°C), there is no point in using salt until it gets warmer

? Exercise 13.2.3.4

Calculate the freezing point of the 30.2% solution of ethylene glycol in water whose vapor pressure and boiling point we calculated in Examples 13.2.3.1and 13.2.3.3

Answer

−13.0°C

✔ Example 13.2.3.5

Arrange these aqueous solutions in order of decreasing freezing points: 0.1 m KCl, 0.1 m glucose, 0.1 m $\mathrm{SrCl_2}$, 0.1 m ethylene glycol, 0.1 m benzoic acid, and 0.1 m HCl.

Given: molalities of six solutions

Asked for: relative freezing points

Strategy:

A. Identify each solute as a strong, weak, or nonelectrolyte, and use this information to determine the number of solute particles produced.

B. Multiply this number by the concentration of the solution to obtain the effective concentration of solute particles. The solution with the highest effective concentration of solute particles has the largest freezing point depression.

Solution:

A Because the molal concentrations of all six solutions are the same, we must focus on which of the substances are strong electrolytes, which are weak electrolytes, and which are nonelectrolytes to determine the actual numbers of particles in solution. KCl, $SrCl_2$, and HCl are **strong electrolytes**, producing two, three, and two ions per formula unit, respectively. Benzoic acid is a weak electrolyte (approximately one particle per molecule), and glucose and ethylene glycol are both nonelectrolytes (one particle per molecule).

B The molalities of the solutions in terms of the total particles of solute are: KCl and HCl, 0.2 m; $SrCl_2$, 0.3 m; glucose and ethylene glycol, 0.1 m; and benzoic acid, 0.1–0.2 m. Because the magnitude of the decrease in freezing point is proportional to the concentration of dissolved particles, the order of freezing points of the solutions is: glucose and ethylene glycol (highest freezing point, smallest freezing point depression) > benzoic acid > HCl = KCl > $SrCl_2$.

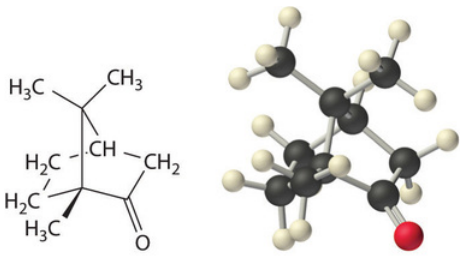
? Exercise 13.2.3.5

Arrange these aqueous solutions in order of increasing freezing points: 0.2 m NaCl, 0.3 m acetic acid, 0.1 m $CaCl_2$, and 0.2 m sucrose.

Answer

0.2 m NaCl (lowest freezing point) < 0.3 m acetic acid ≈ 0.1 m $CaCl_2$ < 0.2 m sucrose (highest freezing point)

Colligative properties can also be used to determine the molar mass of an unknown compound. One method that can be carried out in the laboratory with minimal equipment is to measure the freezing point of a solution with a known mass of solute. This method is accurate for dilute solutions (≤1% by mass) because changes in the freezing point are usually large enough to measure accurately and precisely. By comparing K_b and K_f values in Table 13.2.3.1, we see that changes in the boiling point are smaller than changes in the freezing point for a given solvent. Boiling point elevations are thus more difficult to measure precisely. For this reason, freezing point depression is more commonly used to determine molar mass than is boiling point elevation. Because of its very large value of K_f (37.8°C/m), d-(+)-camphor (Table 13.2.3.1) is often used to determine the molar mass of organic compounds by this method.



d-(+)-Camphor

✓ Example 13.2.3.6: Sulfur

A 7.08 g sample of elemental sulfur is dissolved in 75.0 g of CS_2 to create a solution whose freezing point is −113.5°C. Use these data to calculate the molar mass of elemental sulfur and thus the formula of the dissolved Sn molecules (i.e., what is the value of n?).

Given: masses of solute and solvent and freezing point

Asked for: molar mass and number of S atoms per molecule

Strategy:

A. Use Equation 13.2.3.6, the measured freezing point of the solution, and the freezing point of CS_2 from Table 13.2.3.1 to calculate the freezing point depression. Then use Equation 13.2.3.7 and the value of K_f from Table 13.2.3.1 to calculate the molality of the solution.

B. From the calculated molality, determine the number of moles of solute present.
C. Use the mass and number of moles of the solute to calculate the molar mass of sulfur in solution. Divide the result by the molar mass of atomic sulfur to obtain n, the number of sulfur atoms per mole of dissolved sulfur.

Solution:

A The first step is to calculate the freezing point depression using Equation 13.2.3.6:

$$\Delta T_f = T_f^0 - T_f = -112.1^\circ C - (-113.5^\circ C) = 1.4^\circ C$$

Then Equation 13.2.3.7 gives

$$m = \frac{\Delta T_f}{K_f} = \frac{1.4^\circ \cancel{C}}{3.74^\circ \cancel{C}/m} = 0.37\ m$$

B The total number of moles of solute present in the solution is

$$\text{moles solute} = \left(\frac{0.37 mol}{\cancel{kg}}\right)(75.0\ g)\left(\frac{1 kg}{1000\ g}\right) = 0.028\ mol$$

C We now know that 0.708 g of elemental sulfur corresponds to 0.028 mol of solute. The molar mass of dissolved sulfur is thus

$$\text{molar mass} = \frac{7.08\ g}{0.028\ mol} = 260\ g/mol$$

The molar mass of atomic sulfur is 32 g/mol, so there must be 260/32 = 8.1 sulfur atoms per mole, corresponding to a formula of S_8.

? Exercise 13.2.3.6

One of the byproducts formed during the synthesis of C_{60} is a deep red solid containing only carbon. A solution of 205 mg of this compound in 10.0 g of CCl_4 has a freezing point of −23.38°C. What are the molar mass and most probable formula of the substance?

Answer

847 g/mol; C_{70}

Osmotic Pressure

Osmotic pressure is a colligative property of solutions that is observed using a semipermeable membrane, a barrier with pores small enough to allow solvent molecules to pass through but not solute molecules or ions. The net flow of solvent through a semipermeable membrane is called osmosis (from the Greek osmós, meaning “push”). The direction of net solvent flow is always from the side with the lower concentration of solute to the side with the higher concentration.

Osmosis can be demonstrated using a U-tube like the one shown in Figure 13.2.3.6, which contains pure water in the left arm and a dilute aqueous solution of glucose in the right arm. A net flow of water through the membrane occurs until the levels in the arms eventually stop changing, which indicates that equilibrium has been reached. The osmotic pressure (Π) of the glucose solution is the difference in the pressure between the two sides, in this case the heights of the two columns. Although the semipermeable membrane allows water molecules to flow through in either direction, the rate of flow is not the same in both directions because the concentration of water is not the same in the two arms. The net flow of water through the membrane can be prevented by applying a pressure to the right arm that is equal to the osmotic pressure of the glucose solution.

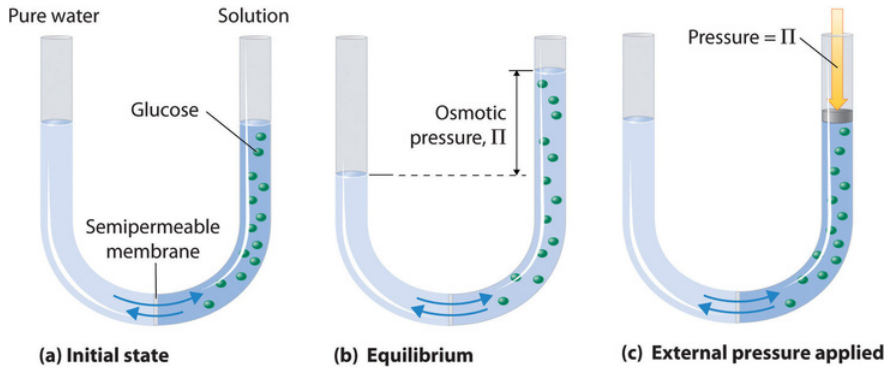


Figure 13.2.3.6: Osmotic Pressure. (a) A dilute solution of glucose in water is placed in the right arm of a U-tube, and the left arm is filled to the same height with pure water; a semipermeable membrane separates the two arms. Because the flow of pure solvent through the membrane from left to right (from pure water to the solution) is greater than the flow of solvent in the reverse direction, the level of liquid in the right tube rises. (b) At equilibrium, the pressure differential, equal to the osmotic pressure of the solution (Π_{soln}), equalizes the flow rate of solvent in both directions. (c) Applying an external pressure equal to the osmotic pressure of the original glucose solution to the liquid in the right arm reverses the flow of solvent and restores the original situation. (CC BY-NC-SA; anonymous)

Just as with any other colligative property, the osmotic pressure of a solution depends on the concentration of dissolved solute particles. Osmotic pressure obeys a law that resembles the ideal gas equation:

$$\Pi = \frac{nRT}{V} = MRT \tag{13.2.3.8}$$

where M is the number of moles of solute per unit volume of solution (i.e., the molarity of the solution), R is the ideal gas constant, and T is the absolute temperature.

As shown in Example 13.2.3.7, osmotic pressures tend to be quite high, even for rather dilute solutions.

Example 13.2.3.7

When placed in a concentrated salt solution, certain yeasts are able to produce high internal concentrations of glycerol to counteract the osmotic pressure of the surrounding medium. Suppose that the yeast cells are placed in an aqueous solution containing 4.0% NaCl by mass; the solution density is 1.02 g/mL at 25°C.

a. Calculate the osmotic pressure of a 4.0% aqueous NaCl solution at 25°C.
b. If the normal osmotic pressure inside a yeast cell is 7.3 atm, corresponding to a total concentration of dissolved particles of 0.30 M, what concentration of glycerol must the cells synthesize to exactly balance the external osmotic pressure at 25°C?

Given: concentration, density, and temperature of NaCl solution; internal osmotic pressure of cell

Asked for: osmotic pressure of NaCl solution and concentration of glycerol needed

Strategy:

A. Calculate the molarity of the NaCl solution using the formula mass of the solute and the density of the solution. Then calculate the total concentration of dissolved particles.
B. Use Equation 13.2.3.8to calculate the osmotic pressure of the solution.
C. Subtract the normal osmotic pressure of the cells from the osmotic pressure of the salt solution to obtain the additional pressure needed to balance the two. Use Equation 13.2.3.8to calculate the molarity of glycerol needed to create this osmotic pressure.

Solution:

A The solution contains 4.0 g of NaCl per 100 g of solution. Using the formula mass of NaCl (58.44 g/mol) and the density of the solution (1.02 g/mL), we can calculate the molarity:

$$M_{NaCl} = \frac{moles\ NaCl}{\text{liter solution}}$$

$$= \left(\frac{4.0\ \cancel{g}\ NaCl}{58.44\ \cancel{g}/mol\ NaCl}\right)\left(\frac{1}{100\ \cancel{g\ solution}}\right)\left(\frac{1.02\ \cancel{g\ solution}}{1.00\ \cancel{mL}\ solution}\right)\left(\frac{1000\ \cancel{mL}}{1\ L}\right)$$

$$= 0.70\ M\ \text{NaCl}$$

Because 1 mol of NaCl produces 2 mol of particles in solution, the total concentration of dissolved particles in the solution is (2)(0.70 M) = 1.4 M.

B Now we can use Equation 13.2.3.8to calculate the osmotic pressure of the solution:

$$\Pi = MRT$$

$$= (1.4\ mol/L)\,[0.0821\ (L\cdot atm)/(K\cdot mol)]\,(298\ K)$$

$$= 34\ atm$$

C If the yeast cells are to exactly balance the external osmotic pressure, they must produce enough glycerol to give an additional internal pressure of (34 atm − 7.3 atm) = 27 atm. Glycerol is a nonelectrolyte, so we can solve Equation 13.2.3.8for the molarity corresponding to this osmotic pressure:

$$M = \frac{\Pi}{RT}$$

$$= \frac{27\ \cancel{atm}}{[0.0821(L\cdot\ \cancel{atm})/(\ \cancel{K}\cdot mol)](298\ \cancel{K})}$$

$$= 1.1\ M\ \text{glycerol}$$

In solving this problem, we could also have recognized that the only way the osmotic pressures can be the same inside the cells and in the solution is if the concentrations of dissolved particles are the same. We are given that the normal concentration of dissolved particles in the cells is 0.3 M, and we have calculated that the NaCl solution is effectively 1.4 M in dissolved particles. The yeast cells must therefore synthesize enough glycerol to increase the internal concentration of dissolved particles from 0.3 M to 1.4 M—that is, an additional 1.1 M concentration of glycerol.

? Exercise 13.2.3.7

Assume that the fluids inside a sausage are approximately 0.80 M in dissolved particles due to the salt and sodium nitrite used to prepare them. Calculate the osmotic pressure inside the sausage at 100°C to learn why experienced cooks pierce the semipermeable skin of sausages before boiling them.

Answer

24 atm

Because of the large magnitude of osmotic pressures, osmosis is extraordinarily important in biochemistry, biology, and medicine. Virtually every barrier that separates an organism or cell from its environment acts like a semipermeable membrane, permitting the flow of water but not solutes. The same is true of the compartments inside an organism or cell. Some specialized barriers, such as those in your kidneys, are slightly more permeable and use a related process called dialysis, which permits both water and small molecules to pass through but not large molecules such as proteins.

The same principle has long been used to preserve fruits and their essential vitamins over the long winter. High concentrations of sugar are used in jams and jellies not for sweetness alone but because they greatly increase the osmotic pressure. Thus any bacteria not killed in the cooking process are dehydrated, which keeps them from multiplying in an otherwise rich medium for bacterial growth. A similar process using salt prevents bacteria from growing in ham, bacon, salt pork, salt cod, and other preserved meats. The effect of osmotic pressure is dramatically illustrated in Figure 13.2.3.7, which shows what happens when red blood cells are placed in a solution whose osmotic pressure is much lower or much higher than the internal pressure of the cells.

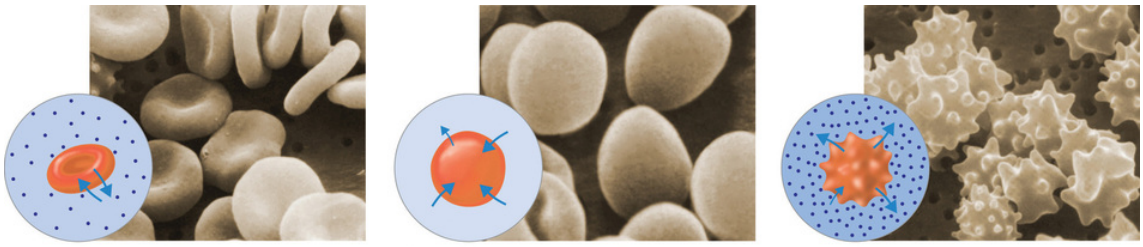


Figure 13.2.3.7: Effect on Red Blood Cells of the Surrounding Solution's Osmotic Pressure. (a) When red blood cells are placed in a dilute salt solution having the same osmotic pressure as the intracellular fluid, the rate of flow of water into and out of the cells is the same and their shape does not change. (b) When cells are placed in distilled water whose osmotic pressure is less than that of the intracellular fluid, the rate of flow of water into the cells is greater than the rate of flow out of the cells. The cells swell and eventually burst. (c) When cells are placed in a concentrated salt solution with an osmotic pressure greater than that of the intracellular fluid, the rate of flow of water out of the cells is greater than the rate of flow into the cells. The cells shrivel and become so deformed that they cannot function. (CC BY-NC-SA; anonymous)

In addition to capillary action, trees use osmotic pressure to transport water and other nutrients from the roots to the upper branches. Evaporation of water from the leaves results in a local increase in the salt concentration, which generates an osmotic pressure that pulls water up the trunk of the tree to the leaves.

Finally, a process called reverse osmosis can be used to produce pure water from seawater. As shown schematically in Figure 13.2.3.8, applying high pressure to seawater forces water molecules to flow through a semipermeable membrane that separates pure water from the solution, leaving the dissolved salt behind. Large-scale desalinization plants that can produce hundreds of thousands of gallons of freshwater per day are common in the desert lands of the Middle East, where they supply a large proportion of the freshwater needed by the population. Similar facilities are now being used to supply freshwater in southern California. Small, hand-operated reverse osmosis units can produce approximately 5 L of freshwater per hour, enough to keep 25 people alive, and are now standard equipment on US Navy lifeboats.

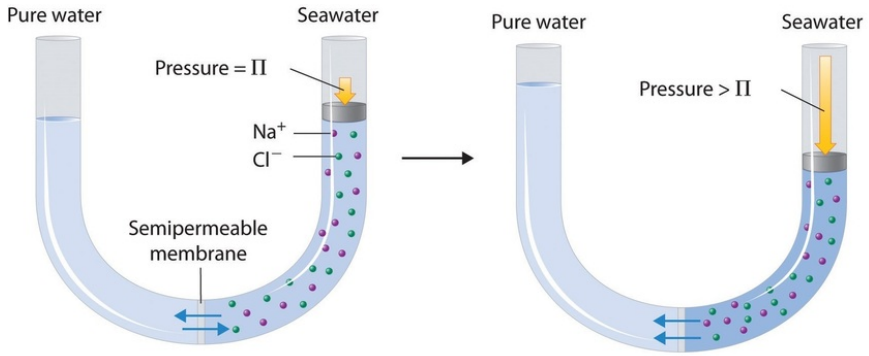


Figure 13.2.3.8: Desalinization of Seawater by Reverse Osmosis. (top) When the pressure applied to seawater equals its osmotic pressure (Π_{soln}), there is no net flow of water across the semipermeable membrane. (bottom) The application of pressure greater than the osmotic pressure of seawater forces water molecules to flow through the membrane, leaving behind a concentrated salt solution. In desalinization plants, seawater is continuously introduced under pressure and pure water is collected, so the process continues indefinitely. (CC BY-NC-SA; anonymous)

Colligative Properties of Electrolyte Solutions

Thus far we have assumed that we could simply multiply the molar concentration of a solute by the number of ions per formula unit to obtain the actual concentration of dissolved particles in an electrolyte solution. We have used this simple model to predict such properties as freezing points, melting points, vapor pressure, and osmotic pressure. If this model were perfectly correct, we would expect the freezing point depression of a 0.10 m solution of sodium chloride, with 2 mol of ions per mole of NaCl in solution, to be exactly twice that of a 0.10 m solution of glucose, with only 1 mol of molecules per mole of glucose in solution. In reality, this is not always the case. Instead, the observed change in freezing points for 0.10 m aqueous solutions of NaCl and KCl are significantly less than expected (−0.348°C and −0.344°C, respectively, rather than −0.372°C), which suggests that fewer particles than we expected are present in solution.

The relationship between the actual number of moles of solute added to form a solution and the apparent number as determined by colligative properties is called the van 't Hoff factor (i) and is defined as follows:

$$i = \frac{\text{apparent number of particles in solution}}{\text{number of moles of solute dissolved}} \tag{13.2.3.9}$$

Named for Jacobus Hendricus van 't Hoff (1852–1911), a Dutch chemistry professor at the University of Amsterdam who won the first Nobel Prize in Chemistry (1901) for his work on thermodynamics and solutions.

> *As the solute concentration increases, the van 't Hoff factor decreases.*

The van 't Hoff factor is therefore **a measure of a deviation from ideal behavior**. The lower the van 't Hoff factor, the greater the deviation. As the data in Table 13.2.3.2show, the van 't Hoff factors for ionic compounds are somewhat lower than expected; that is, their solutions apparently contain fewer particles than predicted by the number of ions per formula unit. As the concentration of the solute increases, the van 't Hoff factor decreases because ionic compounds generally do not totally dissociate in aqueous solution.

Table 13.2.3.2: van 't Hoff Factors for 0.0500 M Aqueous Solutions of Selected Compounds at 25°C

Compound	i (measured)	i (ideal)
glucose	1.0	1.0
sucrose	1.0	1.0
$NaCl$	1.9	2.0
HCl	1.9	2.0
$MgCl_2$	2.7	3.0
$FeCl_3$	3.4	4.0
$Ca(NO_3)_2$	2.5	3.0
$AlCl_3$	3.2	4.0
$MgSO_4$	1.4	2.0

Instead, some of the ions exist as ion pairs, a cation and an anion that for a brief time are associated with each other without an intervening shell of water molecules (Figure 13.2.3.9). Each of these temporary units behaves like a single dissolved particle until it dissociates. Highly charged ions such as Mg^{2+}, Al^{3+}, SO_4^{2-}, and PO_4^{3-} have a greater tendency to form ion pairs because of their strong electrostatic interactions. The actual number of solvated ions present in a solution can be determined by measuring a colligative property at several solute concentrations.

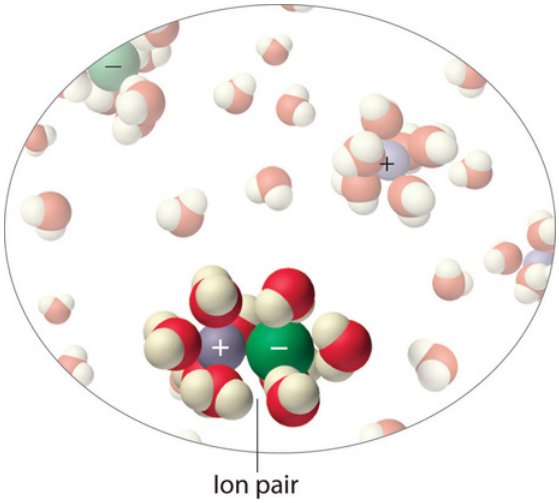


Figure 13.2.3.9: Ion Pairs. In concentrated solutions of electrolytes like $NaCl$, some of the ions form neutral ion pairs that are not separated by solvent and diffuse as single particles.

Example 13.2.3.8: Iron Chloride in Water

A 0.0500 M aqueous solution of $\mathrm{FeCl_3}$ has an osmotic pressure of 4.15 atm at 25°C. Calculate the van 't Hoff factor i for the solution.

Given: solute concentration, osmotic pressure, and temperature

Asked for: van 't Hoff factor

Strategy:

A. Use Equation 13.2.3.8to calculate the expected osmotic pressure of the solution based on the effective concentration of dissolved particles in the solvent.
B. Calculate the ratio of the observed osmotic pressure to the expected value. Multiply this number by the number of ions of solute per formula unit, and then use Equation 13.2.3.9to calculate the van 't Hoff factor.

Solution:

A If $\mathrm{FeCl_3}$ dissociated completely in aqueous solution, it would produce four ions per formula unit (one $\mathrm{Fe^{3+}(aq)}$ and three \(\ce{Cl^{-}(aq)} ions) for an effective concentration of dissolved particles of 4 × 0.0500 M = 0.200 M. The osmotic pressure would be

$$\begin{aligned}\Pi &= MRT \\ &= (0.200\ mol/L)\,[0.0821\ (L\cdot atm)/(K\cdot mol)]\,(298\ K) = 4.89\ atm\end{aligned}$$

B The observed osmotic pressure is only 4.15 atm, presumably due to ion pair formation. The ratio of the observed osmotic pressure to the calculated value is 4.15 atm/4.89 atm = 0.849, which indicates that the solution contains (0.849)(4) = 3.40 moles of particles per mole of $\mathrm{FeCl_3}$ dissolved. Alternatively, we can calculate the observed particle concentration from the osmotic pressure of 4.15 atm:

$$4.15\ atm = M\left(\frac{0.0821\ (L\cdot atm)}{(K\cdot mol)}\right)(298\ K)$$

or after rearranging

$$M = 0.170 mol$$

The ratio of this value to the expected value of 0.200 M is 0.170 M/0.200 M = 0.850, which again gives us (0.850)(4) = 3.40 mole of particles per mole of $\mathrm{FeCl_3}$ dissolved. From Equation 13.2.3.9, the van 't Hoff factor for the solution is

$$i = \frac{3.40\ \text{particles observed}}{1\ \text{formula unit}\ \mathrm{FeCl_3}} = 3.40$$

Exercise 13.2.3.8: Magnesium Chloride in Water

Calculate the van 't Hoff factor for a 0.050 m aqueous solution of $\mathrm{MgCl_2}$ that has a measured freezing point of −0.25°C.

Answer

2.7 (versus an ideal value of 3).

Summary

The colligative properties of a solution depend on only the total number of dissolved particles in solution, not on their chemical identity. Colligative properties include vapor pressure, boiling point, freezing point, and osmotic pressure. The addition of a nonvolatile solute (one without a measurable vapor pressure) decreases the vapor pressure of the solvent. The vapor pressure of the solution is proportional to the mole fraction of solvent in the solution, a relationship known as **Raoult's law**. The boiling point elevation (ΔT_b) and freezing point depression (ΔT_f) of a solution are defined as the differences between the boiling and freezing points, respectively, of the solution and the pure solvent. Both are proportional to the molality of the solute. When a solution and a pure solvent are separated by a semipermeable membrane, a barrier that allows solvent molecules but not solute molecules to pass

through, the flow of solvent in opposing directions is unequal and produces an osmotic pressure, which is the difference in pressure between the two sides of the membrane. Osmosis is the net flow of solvent through such a membrane due to different solute concentrations. Dialysis uses a semipermeable membrane with pores that allow only small solute molecules and solvent molecules to pass through. In more concentrated solutions, or in solutions of salts with highly charged ions, the cations and anions can associate to form ion pairs, which decreases their effect on the colligative properties of the solution. The extent of ion pair formation is given by the van ’t Hoff factor (i), the ratio of the apparent number of particles in solution to the number predicted by the stoichiometry of the salt.

- **Henry’s law:**

$$C = kP$$

- **Raoult’s law**:

$$P_A = \chi_A P_A^0$$

- **vapor pressure lowering**:

$$P_A^0 - P_A = \Delta P_A = \chi_B P_A^0$$

- **vapor pressure of a system containing two volatile components**:

$$P_{tot} = \chi_A P_A^0 + (1 - \chi_A) P_B^0$$

- **boiling point elevation**:

$$\Delta T_b = m K_b$$

- **freezing point depression:**

$$\Delta T_f = m K_f$$

- **osmotic pressure**:

$$\Pi = \frac{n}{V} RT = MRT$$

- **van ’t Hoff factor**:

$$i = \frac{\text{apparent number of particles in solution}}{\text{number of moles of solute dissolved}}$$

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13.2.4: Phase Equilibrium in Solutions - Volatile Solutes

Learning Objectives

- To understand the relationship among temperature, pressure, and solubility.
- The understand that the solubility of a solid may increase or decrease with increasing temperature,
- To understand that the solubility of a gas decreases with an increase in temperature and a decrease in pressure.

Effect of Pressure on the Solubility of Gases: Henry's Law

External pressure has very little effect on the solubility of liquids and solids. In contrast, the solubility of gases increases as the partial pressure of the gas above a solution increases. This point is illustrated in Figure 13.2.4.1, which shows the effect of increased pressure on the dynamic equilibrium that is established between the dissolved gas molecules in solution and the molecules in the gas phase above the solution. Because the concentration of molecules in the gas phase increases with increasing pressure, the concentration of dissolved gas molecules in the solution at equilibrium is also higher at higher pressures.

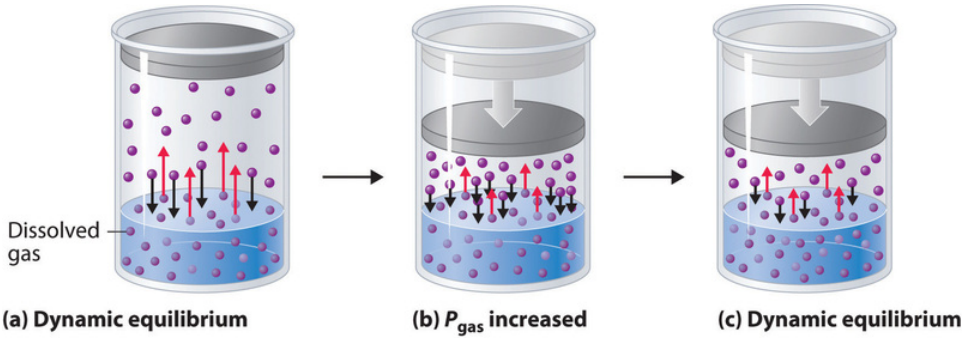


Figure 13.2.4.1: A Model Depicting Why the Solubility of a Gas Increases as the Partial Pressure Increases at Constant Temperature. (a) When a gas comes in contact with a pure liquid, some of the gas molecules (purple spheres) collide with the surface of the liquid and dissolve. When the concentration of dissolved gas molecules has increased so that the rate at which gas molecules escape into the gas phase is the same as the rate at which they dissolve, a dynamic equilibrium has been established, as depicted here. This equilibrium is entirely analogous to the one that maintains the vapor pressure of a liquid. (b) Increasing the pressure of the gas increases the number of molecules of gas per unit volume, which increases the rate at which gas molecules collide with the surface of the liquid and dissolve. (c) As additional gas molecules dissolve at the higher pressure, the concentration of dissolved gas increases until a new dynamic equilibrium is established.

The relationship between pressure and the solubility of a gas is described quantitatively by Henry's law, which is named for its discoverer, the English physician and chemist, William Henry (1775–1836):

$$C = k_H P \tag{13.2.4.1}$$

where C is the concentration of dissolved gas at equilibrium, P is the partial pressure of the gas, and k_H is the Henry's law constant, which must be determined experimentally for each combination of gas, solvent, and temperature.

Although the gas concentration may be expressed in any convenient units, we will use molarity exclusively. The units of the Henry's law constant are therefore mol/(L·atm) = M/atm. Values of the Henry's law constants for solutions of several gases in water at 20°C are listed in Table 13.2.4.1.

As the data in Table 13.2.4.1 demonstrate, the concentration of a dissolved gas in water at a given pressure depends strongly on its physical properties. For a series of related substances, London dispersion forces increase as molecular mass increases. Thus among the elements of Group 18, the Henry's law constants increase smoothly from He to Ne to Ar. The table also shows that O_2 is almost twice as soluble as N_2. Although London dispersion forces are too weak to explain such a large difference, O_2 is paramagnetic and hence more polarizable than N_2, which explains its high solubility.

Table 13.2.4.1: Henry's Law Constants for Selected Gases in Water at 20°C

Gas	Henry's Law Constant [mol/(L·atm)] × 10^{-4}
Ar	15
CO_2	392

Gas	Henry's Law Constant [mol/(L·atm)] × 10^{-4}
H_2	8.1
He	3.9
N_2	7.1
Ne	4.7
O_2	14

Gases that react with the solvent do not obey Henry's law

Gases that react chemically with water, such as HCl and the other hydrogen halides, H_2S, and NH_3, do not obey Henry's law; all of these gases are much more soluble than predicted by Henry's law. For example, HCl reacts with water to give $H^+(aq)$ and $Cl^-(aq)$, not dissolved HCl molecules,

$$HCl(g) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$

The dissociation of HCl into ions results in a much higher effective "solubility" than expected for a neutral molecule.

Jan 3, 2019, 5:36 PM

https://en.Wikipedia.org/wiki/Henry%...constants_Heff

https://www.sciencedirect.com/scienc...0469818690079X

https://www.atmos-chem-phys.net/15/4...-4399-2015.pdf

Henry's law has important applications. For example, bubbles of CO_2 form as soon as a carbonated beverage is opened because the drink was bottled under CO_2 at a pressure greater than 1 atm. When the bottle is opened, the pressure of CO_2 above the solution drops rapidly, and some of the dissolved gas escapes from the solution as bubbles. Henry's law also explains why scuba divers have to be careful to ascend to the surface slowly after a dive if they are breathing compressed air. At the higher pressures under water, more N_2 from the air dissolves in the diver's internal fluids. If the diver ascends too quickly, the rapid pressure change causes small bubbles of N_2 to form throughout the body, a condition known as "the bends." These bubbles can block the flow of blood through the small blood vessels, causing great pain and even proving fatal in some cases.

Due to the low Henry's law constant for O_2 in water, the levels of dissolved oxygen in water are too low to support the energy needs of multicellular organisms, including humans. To increase the O_2 concentration in internal fluids, organisms synthesize highly soluble carrier molecules that bind O_2 reversibly. For example, human red blood cells contain a protein called hemoglobin that specifically binds O_2 and facilitates its transport from the lungs to the tissues, where it is used to oxidize food molecules to provide energy. The concentration of hemoglobin in normal blood is about 2.2 mM, and each hemoglobin molecule can bind four O_2 molecules. Although the concentration of dissolved O_2 in blood serum at 37°C (normal body temperature) is only 0.010 mM, the total dissolved O_2 concentration is 8.8 mM, almost a thousand times greater than would be possible without hemoglobin. Synthetic oxygen carriers based on fluorinated alkanes have been developed for use as an emergency replacement for whole blood. Unlike donated blood, these "blood substitutes" do not require refrigeration and have a long shelf life. Their very high Henry's law constants for O_2 result in dissolved oxygen concentrations comparable to those in normal blood.

Example 13.2.4.1: Oxygen in Water

The Henry's law constant for O_2 in water at 25°C is $1.27 \times 10^{-3} M/atm$, and the mole fraction of O_2 in the atmosphere is 0.21. Calculate the solubility of O_2 in water at 25°C at an atmospheric pressure of 1.00 atm.

Given: Henry's law constant, mole fraction of O_2, and pressure

Asked for: solubility

Strategy:

A. Use Dalton's law of partial pressures to calculate the partial pressure of oxygen.
B. Use Henry's law (Equation 13.2.4.1) to calculate the solubility, expressed as the concentration of dissolved gas.

Solution:

A According to Dalton's law, the partial pressure of O_2 is proportional to the mole fraction of O_2:

$$P_A = \chi_A P_t = (0.21)(1.00\ atm) = 0.21\ atm$$

B From Henry's law, the concentration of dissolved oxygen under these conditions is

$$CO_2 = k_H P_{O_2} = (1.27 \times 10^{-3}\ M/\ \cancel{atm})(0.21\ \ \cancel{atm}) = 2.7 \times 10^{-4}\ M$$

Exercise 13.2.4.1: Carbon Dioxide in Water

To understand why soft drinks "fizz" and then go "flat" after being opened, calculate the concentration of dissolved CO_2 in a soft drink:

a. bottled under a pressure of 5.0 atm of CO_2
b. in equilibrium with the normal partial pressure of CO_2 in the atmosphere (approximately $3 \times 10^{-4}\ atm$). The Henry's law constant for CO_2 in water at 25°C is $3.4 \times 10^{-2}\ M/atm$.

Answer a

0.17 M

Answer b

$1 \times 10^{-5} M$

Summary

The solubility of most substances depends strongly on the temperature and, in the case of gases, on the pressure. The solubility of most solid or liquid solutes increases with increasing temperature. The components of a mixture can often be separated using fractional crystallization, which separates compounds according to their solubilities. The solubility of a gas decreases with increasing temperature. Henry's law describes the relationship between the pressure and the solubility of a gas.

13.2.4: Phase Equilibrium in Solutions - Volatile Solutes is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

13.2.5: Colloidal Suspensions

Learning Objectives

- To distinguish between true solutions and solutions with aggregate particles.

Suspensions and colloids are two common types of mixtures whose properties are in many ways intermediate between those of true solutions and heterogeneous mixtures. A suspension is a heterogeneous mixture of particles with diameters of about 1 µm (1000 nm) that are distributed throughout a second phase. Common suspensions include paint, blood, and hot chocolate, which are solid particles in a liquid, and aerosol sprays, which are liquid particles in a gas. If the suspension is allowed to stand, the two phases will separate, which is why paints must be thoroughly stirred or shaken before use. A colloid is also a heterogeneous mixture, but the particles of a colloid are typically smaller than those of a suspension, generally in the range of 2 to about 500 nm in diameter. Colloids include fog and clouds (liquid particles in a gas), milk (solid particles in a liquid), and butter (solid particles in a solid). Other colloids are used industrially as catalysts. Unlike in a suspension, the particles in a colloid do not separate into two phases on standing. The only combination of substances that cannot produce a suspension or a colloid is a mixture of two gases because their particles are so small that they always form true solutions. The properties of suspensions, colloids, and solutions are summarized in Table 13.2.5.1

Table 13.2.5.1: Properties of Liquid Solutions, Colloids, and Suspensions

Type of Mixture	Approximate Size of Particles (nm)	Characteristic Properties	Examples
solution	< 2	not filterable; does not separate on standing; does not scatter visible light	air, white wine, gasoline, salt water
colloid	2–500	scatters visible light; translucent or opaque; not filterable; does not separate on standing	smoke, fog, ink, milk, butter, cheese
suspension	500–1000	cloudy or opaque; filterable; separates on standing	muddy water, hot cocoa, blood, paint

Colloids and Suspensions

Colloids were first characterized in about 1860 by Thomas Graham, who also gave us Graham's law of diffusion and effusion. Although some substances, such as starch, gelatin, and glue, appear to dissolve in water to produce solutions, Graham found that they diffuse very slowly or not at all compared with solutions of substances such as salt and sugar. Graham coined the word colloid (from the Greek kólla, meaning "glue") to describe these substances, as well as the words sol and gel to describe certain types of colloids in which all of the solvent has been absorbed by the solid particles, thus preventing the mixture from flowing readily, as we see in Jell-O. Two other important types of colloids are aerosols, which are dispersions of solid or liquid particles in a gas, and emulsions, which are dispersions of one liquid in another liquid with which it is immiscible.

Colloids share many properties with solutions. For example, the particles in both are invisible without a powerful microscope, do not settle on standing, and pass through most filters. However, the particles in a colloid scatter a beam of visible light, a phenomenon known as the Tyndall effect,The effect is named after its discoverer, John Tyndall, an English physicist (1820–1893). whereas the particles of a solution do not. The Tyndall effect is responsible for the way the beams from automobile headlights are clearly visible from the side on a foggy night but cannot be seen from the side on a clear night. It is also responsible for the colored rays of light seen in many sunsets, where the sun's light is scattered by water droplets and dust particles high in the atmosphere. An example of the Tyndall effect is shown in Figure 13.2.5.1



Figure 13.2.5.1: Tyndall Effect, the Scattering of Light by Colloids (CC BY; LibreTexts)

Although colloids and suspensions can have particles similar in size, the two differ in stability: the particles of a colloid remain dispersed indefinitely unless the temperature or chemical composition of the dispersing medium is changed. The chemical explanation for the stability of colloids depends on whether the colloidal particles are hydrophilic or hydrophobic.

Most proteins, including those responsible for the properties of gelatin and glue, are hydrophilic because their exterior surface is largely covered with polar or charged groups. Starch, a long-branched polymer of glucose molecules, is also hydrophilic. A hydrophilic colloid particle interacts strongly with water, resulting in a shell of tightly bound water molecules that prevents the particles from aggregating when they collide. Heating such a colloid can cause aggregation because the particles collide with greater energy and disrupt the protective shell of solvent. Moreover, heat causes protein structures to unfold, exposing previously buried hydrophobic groups that can now interact with other hydrophobic groups and cause the particles to aggregate and precipitate from solution. When an egg is boiled, for example, the egg white, which is primarily a colloidal suspension of a protein called albumin, unfolds and exposes its hydrophobic groups, which aggregate and cause the albumin to precipitate as a white solid.

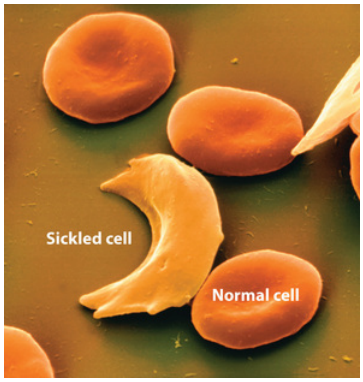


Figure 13.2.5.2: Sickle-Cell Anemia The characteristic shape of sickled red blood cells is the result of fibrous aggregation of hemoglobin molecules inside the cell.

A normal blood cell is circular in shape with a dimple in the middle, a sickled cell is banana shaped.

In some cases, a stable colloid can be transformed to an aggregated suspension by a minor chemical modification. Consider, for example, the behavior of hemoglobin, a major component of red blood cells. Hemoglobin molecules normally form a colloidal suspension inside red blood cells, which typically have a “donut” shape and are easily deformed, allowing them to squeeze through the capillaries to deliver oxygen to tissues. In a common inherited disease called sickle-cell anemia, one of the amino acids in hemoglobin that has a hydrophilic carboxylic acid side chain (glutamate) is replaced by another amino acid that has a hydrophobic side chain (valine). Under some conditions, the abnormal hemoglobin molecules can aggregate to form long, rigid fibers that cause the red blood cells to deform, adopting a characteristic sickle shape that prevents them from passing through the capillaries (Figure 13.2.5.2). The reduction in blood flow results in severe cramps, swollen joints, and liver damage. Until recently, many patients with sickle-cell anemia died before the age of 30 from infection, blood clots, or heart or kidney failure, although individuals with the sickle-cell genetic trait are more resistant to malaria than are those with “normal” hemoglobin.

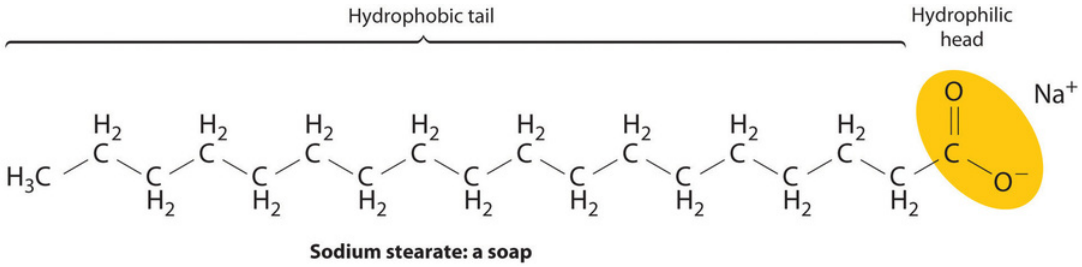


Figure 13.2.5.3: Formation of New Land by the Destabilization of a Colloid Suspension. This satellite photograph shows the Mississippi River delta from New Orleans (top) to the Gulf of Mexico (bottom). Where seawater mixes with freshwater from the Mississippi River, colloidal clay particles in the river water precipitate (tan area).

Aggregation and precipitation can also result when the outer, charged layer of a particle is neutralized by ions with the opposite charge. In inland waterways, clay particles, which have a charged surface, form a colloidal suspension. High salt concentrations in seawater neutralize the charge on the particles, causing them to precipitate and form land at the mouths of large rivers, as seen in the satellite view in Figure 13.2.5.3 Charge neutralization is also an important strategy for precipitating solid particles from gaseous colloids such as smoke, and it is widely used to reduce particulate emissions from power plants that burn fossil fuels.

Emulsions

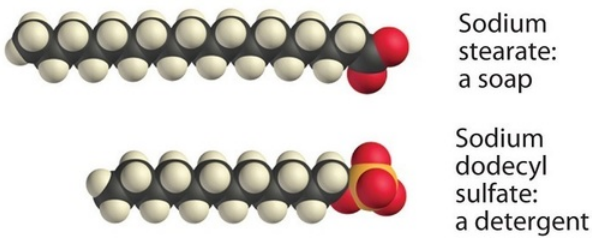
Emulsions are colloids formed by the dispersion of a hydrophobic liquid in water, thereby bringing two mutually insoluble liquids, such as oil and water, in close contact. Various agents have been developed to stabilize emulsions, the most successful being molecules that combine a relatively long hydrophobic "tail" with a hydrophilic "head":



Sodium stearate: a soap

Bond line drawing of soap, The hydrophobic tail is a long hydrocarbon chain. The hydrophilic heat is a carbon double bonded to an oxygen and single bonded to a negatively charged oxygen.

Examples of such emulsifying agents include soaps, which are salts of long-chain carboxylic acids, such as sodium stearate $[CH_3(CH_2)_{16}CO_2 - Na^+]$, and detergents, such as sodium dodecyl sulfate $[CH_3(CH_2)_{11}OSO_3 - Na^+]$, whose structures are as follows:



When you wash your laundry, the hydrophobic tails of soaps and detergents interact with hydrophobic particles of dirt or grease through dispersion forces, dissolving in the interior of the hydrophobic particle. The hydrophilic group is then exposed at the

surface of the particle, which enables it to interact with water through ion–dipole forces and hydrogen bonding. This causes the particles of dirt or grease to disperse in the wash water and allows them to be removed by rinsing. Similar agents are used in the food industry to stabilize emulsions such as mayonnaise.

A related mechanism allows us to absorb and digest the fats in buttered popcorn and French fries. To solubilize the fats so that they can be absorbed, the gall bladder secretes a fluid called bile into the small intestine. Bile contains a variety of bile salts, detergent-like molecules that emulsify the fats.

Micelles

Detergents and soaps are surprisingly soluble in water in spite of their hydrophobic tails. The reason for their solubility is that they do not, in fact, form simple solutions. Instead, above a certain concentration they spontaneously form micelles, which are spherical or cylindrical aggregates that minimize contact between the hydrophobic tails and water. In a micelle, only the hydrophilic heads are in direct contact with water, and the hydrophobic tails are in the interior of the aggregate (Figure 13.2.5.4*a*).

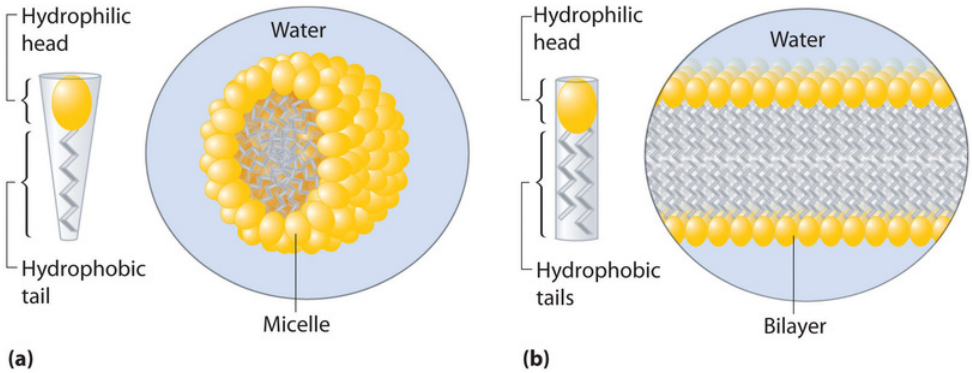
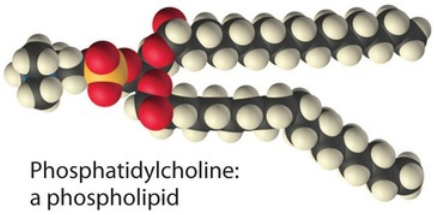


Figure 13.2.5.4: Micelles and a Phospholipid Bilayer. (a) Soaps and detergents, which contain a single hydrophobic tail on each molecule, form spherical micelles with the intertwined tails in the interior and the hydrophilic head groups on the exterior. (b) Phospholipids, which have two hydrophobic tails, tend to form extended double layers in which the hydrophobic tails are sandwiched between the hydrophilic head groups.

A large class of biological molecules called phospholipids consists of detergent-like molecules with a hydrophilic head and two hydrophobic tails, as can be seen in the molecule of phosphatidylcholine. The additional tail results in a cylindrical shape that prevents phospholipids from forming a spherical micelle. Consequently, phospholipids form bilayers, extended sheets consisting of a double layer of molecules. As shown in Figure 13.2.5.4*b* the hydrophobic tails are in the center of the bilayer, where they are not in contact with water, and the hydrophilic heads are on the two surfaces, in contact with the surrounding aqueous solution.



A cell membrane is essentially a mixture of phospholipids that form a phospholipid bilayer. One definition of a cell is a collection of molecules surrounded by a phospholipid bilayer that is capable of reproducing itself. The simplest cells are bacteria, which consist of only a single compartment surrounded by a single membrane. Animal and plant cells are much more complex, however, and contain many different kinds of compartments, each surrounded by a membrane and able to carry out specialized tasks.

Summary

A suspension is a heterogeneous mixture of particles of one substance distributed throughout a second phase; the dispersed particles separate from the dispersing phase on standing. In contrast, the particles in a colloid are smaller and do not separate on standing. A colloid can be classified as a sol, a dispersion of solid particles in a liquid or solid; a gel, a semisolid sol in which all of the liquid phase has been absorbed by the solid particles; an aerosol, a dispersion of solid or liquid particles in a gas; or an emulsion, a dispersion of one liquid phase in another. A colloid can be distinguished from a true solution by its ability to scatter a beam of light, known as the Tyndall effect. Hydrophilic colloids contain an outer shell of groups that interact favorably with water,

whereas hydrophobic colloids have an outer surface with little affinity for water. Emulsions are prepared by dispersing a hydrophobic liquid in water. In the absence of a dispersed hydrophobic liquid phase, solutions of detergents in water form organized spherical aggregates called micelles. Phospholipids are a class of detergent-like molecules that have two hydrophobic tails attached to a hydrophilic head. A bilayer is a two-dimensional sheet consisting of a double layer of phospholipid molecules arranged tail to tail with a hydrophobic interior and a hydrophilic exterior. Cells are collections of molecules that are surrounded by a phospholipid bilayer called a cell membrane and are able to reproduce themselves.

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13.2.E: Solutions (Exercises)

These are homework exercises to accompany the Textmap created for "Principles of Modern Chemistry" by Oxtoby et al. Complementary General Chemistry question banks can be found for other Textmaps and can be accessed here.

Q.1

A student goes to the hospital and has blood work done and the results state that he has a bromide count of $3.17\,\frac{mg}{dL}$.

a. What is the molar concentration of the students blood?
b. What is the molality of the student's blood if the density of his blood was found to be $1.06\,\frac{g}{mL}$?
c. How much of the students blood would be require to get $3g$ of bromide?

Solution

The molar mass of bromide is $79.90\,\frac{g}{mol}$ $1L = 10dL$, $1g = 1000mg$

$$\left(\frac{3.17\ \cancel{mg}}{1\ \cancel{dL}}\right)\left(\frac{1\ \cancel{g}}{1000\ \cancel{mg}}\right)\left(\frac{10\ \cancel{dL}}{1\text{L}}\right)\left(\frac{1\text{mol}}{79.90\ \cancel{g}}\right) = 3.97\times10^{-4}\ \frac{mol}{L}$$

Assume there is 1L of solution. Modality (m) is calculated by:

$$3.17\text{ x }10^{-2}\ \cancel{g}\left(\frac{1\text{ mol}}{79.90\ \cancel{g}}\right)\left(\frac{1}{1.06\text{ kg}}\right) = 3.74\times10^{-4}\,\frac{mol}{kg}$$

If we know that there is $3.17\times10^{-2}g$ of bromide in $1L$ of blood, so all that needs to be done is divide $3g$ by $3.17\times10^{-2}\ \frac{g}{L}$:
Volume of Blood = 94.64 L

Q.5

Given a 3.1416 M aqueous solution of sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ with a density of $1.5986\ \frac{\text{g}}{\text{mL}}$. Calculate the molality of this solution, remember that the molar mass of sucrose is $342.297\frac{\text{g}}{\text{mol}}$

Solution

Before we calculate the molality of this solution, don't forget that molarity is just mol/L so we will multiply the molarity of the solution by 1 L to isolate the moles.

$$1.00\ \cancel{L}\ \text{Water} = \frac{3.1416\ mol\ \text{Sucrose}}{1.00\ \cancel{L}\ \text{Water}} = 3.1416\ mol\ \text{Sucrose}$$

Once we have the moles of Sucrose we will multiply it by the molar mass of sucrose in order to find the number of sucrose grams present in the solution:

$$3.1416\ \cancel{mol}\ \text{Sucrose} = \frac{342.297\ g\ \text{Sucrose}}{1.00\ \cancel{mol}\ \text{Sucrose}} = 1075.4\ g\ \text{Sucrose}$$

We next will multiply the density by 1000 mL so as get the number of grams per liter, this way we can find the total grams of the solution and can subtract the sucrose grams from the solution grams to find the grams of water.

$$1000\ \cancel{mL}\ = \frac{1.5986\ g\ \text{SucroseSoln}}{1.00\ \cancel{mL}\ \text{SucroseSoln}} = 1598.6\ g/L\ \text{SucroseSoln}$$

$$\text{Water grams} = [1598.6g\ \text{Sucrose Soln.}] - [1075.4g\ \text{Sucrose}] = 523.2g\ \text{Water}\ = 0.5232\ kg\ \text{Water}$$

Lastly we divide the moles of Sucrose by the kg of water in order to get molality.

$$\frac{3.1416\ mol\ \text{Sucrose}}{0.5232\ kg\ \text{Water}} = 6.005\ molal$$

Q.9

A solution contains 75% of ethanol (C_2H_6O) by mass and the rest is water.

a. What is the density of the solution if there is 15 mol of ethanol per liter of solution?
b. To prepare a 3.5L of 2M ethanol, how many milliliters of the solution is needed?

Solution

a) For easy calculation, assume that there is 1 L of the solution. Using:

$$\text{mol} = \text{molarity} \times \text{volume} \tag{13.2.E.1}$$

The mol of 15M ethanol in 1L is 15 mol. The molar mass of ethanol is $46.068 \frac{g}{mol}$ Using the equation below:

$$\text{ethanol mol} = \frac{\text{mass ethanol}}{\text{ethanol molar mass}} \tag{13.2.E.2}$$

$$\text{ethanol mass in the solution} = \text{ethanol mol} \times \text{molar mass} = (15mol)(46.068 \frac{g}{mol}) = 691.02g \tag{13.2.E.3}$$

Ethanol is 75% of the solution by mass, therefore:

$$\text{mass of solution} \times 0.75 = \text{mass of ethanol} \tag{13.2.E.4}$$

$$\text{mass of solution} \times 0.75 = 691.02g \tag{13.2.E.5}$$

$$\text{mass of solution} = \frac{691.02g}{0.75} = 921.36g \tag{13.2.E.6}$$

The equation to calculate density is:

$$\text{Density} = \frac{\text{mass}}{\text{volume}} \tag{13.2.E.7}$$

$$\text{Density} = \frac{921.36g}{1L} = 0.921 \frac{g}{ml} \tag{13.2.E.8}$$

b)To prepare a 3.5L of 2M ethanol;

$$\text{ethanol mol needed} = \text{molarity} \times \text{volume} = (2\,\text{M})(3.5\,\text{L}) = 7\,\text{mol} \tag{13.2.E.9}$$

$$V_{\text{ethanol needed}} = \frac{\text{mol needed}}{\text{molarity}} = \frac{7\,\text{mol}}{15\,\text{mol}} \times 1\,\text{L} = 0.467\,\text{L} \tag{13.2.E.10}$$

0.467L of the solution is needed, which is 467mL.

Q.14

Rewrite the following balanced equations as net ionic equations.

a. $H_2SO_4(aq) + 2\,NaOH(aq) \rightarrow 2\,H_2O(l) + Na_2SO_4(aq)$
b. $2\,Na_3PO_4(aq) + 3\,CaCl_2(aq) \rightarrow 6\,NaCl(aq) + Ca_3(PO_4)_2(s)$
c. $BaCl_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2\,NaCl(aq)$
d. $2\,AgNO_3(aq) + ZnCl_2(aq) \rightarrow 2\,AgCl(s) + Zn(NO_3)_2(aq)$

Solution

a. $2\,H^+(aq) + 2\,OH^-(aq) \longrightarrow 2\,H_2O(l)$
b. $2\,PO_4^{3-}(aq) + 3\,Ca^{2+}(aq) \longrightarrow Ca_3(PO_4)_2(s)$
c. $Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s)$
d. $2\,Ag^{2+}(aq) + Cl^-(aq) \longrightarrow 2\,AgCl(s)$

Q.15

Write the balanced chemical equation for the titration of H_2SO_4 with KOH, then find the volume of a 5.49 M KOH solution needed to neutralize 36.2 g of H_2SO_4 .

Solution

The balanced equation of H_2SO_4 with KOH is:

$$H_2SO_4(aq) + 2\,KOH(aq) \longrightarrow K_2SO_4(aq) + 2\,H_2O(l)$$

Calculate the amount of moles of H_2SO_4 being neutralized:

$$n_{H_2SO_4} = 36.2\text{ g } H_2SO_4 \times \frac{1\text{ mol } H_2SO_4}{98.079\text{ g } H_2SO_4} = 0.369\text{ mol } H_2SO_4$$

Using stoichiometry to find the amount of moles of KOH needed to neutralize the amount of H_2SO_4 present:

$$n_{KOH} = 0.369\text{ mol } H_2SO_4 \times \frac{2\text{ mol KOH}}{1\text{ mol } H_2SO_4} = 0.738\text{ mol KOH}$$

Calculate the volume of the 5.49 M KOH solution needed to neutralize the amount of H_2SO_4 present:

$$V_{KOH} = 0.738\text{ mol KOH} \times \frac{1\text{ L}}{5.49\text{ mol KOH}} = 0.134\text{ L} = 134\text{ mL}$$

Therefore, approximately 134 mL of the 5.49 M KOH solution is needed to neutralize 36.2 g H_2SO_4.

Q.16

Phosphoric acid is made industrially as a by-product of the extraction of calcium phosphate

$$Ca_3(PO_4)_2 + 6\,HNO_3 + 12\,H_2O \longrightarrow 2\,H_3PO_4 + 3\,Ca(NO_3)_2 + 12\,H_2O$$

What volume of 8.5 M phosphoric acid is generated by the reaction of 4.5 metric tons (4500 kg) of calcium phosphate?

Solution

$$4500\text{ kg } Ca_3(PO_4)_2 \times \left(\frac{1000\text{ g}}{1\text{ kg}}\right) \times \left(\frac{1\text{ mol}}{310\text{ g}}\right) \times \left(\frac{2\,H_3PO_4}{1\,Ca_3(PO_4)_2}\right) \times \left(\frac{1\text{ L}}{8.5\text{ moles}}\right) = 3415.56\text{ L } H_3PO_4$$

Q.19

Write a balanced equation for the acid-base reaction that leads to the production of each of the following salts.

a. $BaSO_4$
b. $MgSO_3$
c. $PbSO_4$
d. $AgCl$

Solution

a. $Ba(OH)_2(aq) + H_2SO_4(aq) \rightleftharpoons BaSO_4(s) + 2\,H_2O(l)$
b. $Mg(OH)_2(s) + H_2SO_3(aq) \rightleftharpoons MgSO_3(s) + 2\,H_2O(l)$
c. $Pb(OH)_2(s) + H_2SO_4(aq) \rightleftharpoons PbSO_4(s) + 2\,H_2O(l)$
d. $AgOH(s) + HCl(aq) \rightleftharpoons AgCl(s) + H_2O(l)$

Q.21

Hydrogen selenide is classified as a binary acid that has similar properties as hydrogen sulfide. Write down the balanced equation of hydrogen selenide reacting with the base potassium hydroxide and name the salt product of the reaction.

Solution

When the acid H_2S reacts with the base KOH, the reaction goes as follows:

$$H_2S + 2\,KOH \longrightarrow K_2S + 2\,H_2O$$

Forming potassium sulfide.

Similarly, since H_2Se has similar properties as H_2S, a similar reaction occurs:

$$H_2Se + 2\,KOH \longrightarrow K_2Se + 2\,H_2O$$

Potassium selenide is the salt product of the reaction.

Q.25

A student working with an unknown solution of hydrochloric acid is assigned the task of finding its concentration. The student places a 200.0 mL sample of the solution in a 350.0 mL Erlenmeyer flask and titrates the solution with a 0.1234 M solution of sodium hydroxide, where a phenolphthalein indicator is used to find the endpoint. The endpoint is found to be 31.416 mL, what is the concentration of the original hydrochloric acid solution sample?

Solution

Remember that in titration of a strong acid and base, when the endpoint is reached the number of moles used is equal, so the number of moles of NaOH at the endpoint are equal to that of HCl. Use this information to find moles of NaOH from the concentration and volume used to titrate.

$$\text{Concentration of X} = \frac{\text{moles of X}}{\text{liters of X}}$$

Use dimensional analysis to convert concentration of NaOH to moles using the known amount of volume titrated, in liters:

$$0.031416 \cancel{\text{ liter}}\ \text{NaOH} = \frac{0.1234\ \text{mol NaOH}}{1.00\ \cancel{\text{liter}}\ \text{NaOH}} = 0.003877\ \text{mol}$$

Now because we know that the moles of NaOH are equal to the moles of HCl we simply plug in our calculated moles and known original sample volume, in liters, to find the concentration of HCl:

$$\text{Concentration of HCl} = \frac{0.003877\ \text{mol HCl}}{0.200\ \text{liters HCl}} = 0.019385\ \text{M HCl}$$

The concentration of the original hydrochloric acid solution sample was, therefore, 0.019385 M.

Q.41

The vapor pressure of salicylic acid $C_7H_6O_3$ at 200°C is 0.1598 atm. A 19.0 g sample of ethanol C_2H_6O is dissolved in 60.0 g of salicylic acid. Calculate the vapor pressure of salicylic acid above the resulting solution.

Solution

First find the molar masses of salicylic acid and ethanol. Then use them to compute the chemical amounts of the two in solution.

$$n_{C_2H_6O} = 19.0\ g\ C_2H_6O \times \frac{1\ mol\ C_2H_6O}{46.068\ g\ C_2H_6O} = 0.4124\ mol\ C_2H_6O$$

$$n_{C_7H_6O_3} = 60.0\ g\ C_7H_6O_3 \times \frac{1\ mol\ C_7H_6O_3}{138.121\ g\ C_7H_6O_3} = 0.4344\ mol\ C_7H_6O_3$$

The mole fraction of ethanol in the solution equals

$$X_{C_2H_6O} = \frac{0.4124}{0.4344 + 0.4124} = 0.4870$$

The change in vapor pressure of the salicylic acid due to the presence of of the ethanol is

$$\Delta P_{C_4H_6O_3} = -X_{C_4H_6O_3} \times P^{\circ}_{C_4H_6O_3} = -0.5130 \times 0.1518\, atm = -0.08198$$

The final vapor pressure of the salicylic acid equals its original vapor pressure P° plus the change. This is 0.1598 atm minus 0.08198 atm, which is 0.07782 atm.

Q.43

When 53 mol of an unknown compound was added to 100 g of water, the normal boiling point of water increased to 101.1°C. What is the boiling point elevation constant of water? The compound does not dissociate in solution.

Solution

The relevant relationship here is the colligative property associated with boiling point elevation

$$\Delta T_b = iK_b m \tag{13.2.E.11}$$

$$\Delta T_b = 101.1^o\, C - 100^o\, C = 1.1^o\, C \tag{13.2.E.12}$$

Since the compound was told to not dissociation, we know that the van't Hoff factors is 1:

$$i = 1 \tag{13.2.E.13}$$

$$m = \frac{\text{mol solute}}{\text{kg solvent}} = \frac{53\, mol}{0.100\, kg} = 0.53 \frac{mol}{g} \tag{13.2.E.14}$$

$$1.1^oC = (1) \times K_b \times (0.53 \frac{mol}{g}) \tag{13.2.E.15}$$

$$K_b = \frac{1.1^oC}{0.53 \frac{mol}{kg}} = 2.075 \frac{^oC\, kg}{mol} \tag{13.2.E.16}$$

This problem does not give the correct constant though 0.513:

https://chem.libretexts.org/Referenc...perties/B5%3A_Ebullioscopic_(Boiling_Point_Elevation)_Constants

Q.45

When 5.82 g of uniformly dissociating unknown salt, YX, is dissolved in 100.0 g of water, the boiling point of the water is raised by 0.20°C. When 7.09 g of uniformly dissociating unknown salt, ZX, is dissolved in 200.0 g of water, the boiling point of the water is raised by 0.30°C. Assuming both have a van't hoff factor of 2, identify the elements that X, Y, and Z represent.

Solution

For both salts, one can utilize the boiling point elevation expression (including the van't hoff factor):

$$\Delta T = i \times K_b \times m$$

and by substituting moles solute over mass solvent into the molality, m, one can derive that:

$$n_{\text{salt}} = \frac{\Delta T \times m_{\text{water}}}{i \times K_b}$$

From this we get the moles of each salt present, and can therefore get their molar mass by dividing their mass by moles present. Next, subtracting the heavier salt by the lighter salt will yield the molar mass of X, $\sim 35.5 \frac{\text{g}}{\text{mol}}$. Subtracting this from the molar masses of each salt will then yield Y and Z respectively.

$\Delta T = i \times m \times K_b = 2 \times m \times 0.512 = 0.2,\ \text{m of YX} = 0.1953 \frac{\text{mol}}{\text{kg}};\ m \times 0.1kg = 0.0195\ \text{mol};\ \frac{5.82}{0.0195} = 298.46\ \frac{\text{g}}{\text{mol}}$

$\Delta T = i \times m \times K_b = 2 \times m \times 0.512 = 0.3,\ m\ of\ \text{ZX} = 0.2930 \frac{\text{mol}}{\text{kg}};\ m \times 0.2kg = 0.0586\ \text{mol};\ \frac{7.09}{0.0586} = 120.99 \frac{\text{g}}{\text{mol}}$

molar mass difference between Y and Z = $298.46 - 120.99 = 177.47 \frac{\text{g}}{\text{mol}}$

Q.47

Camphor is a useful agent for determining solute's molar mass. Camphor's melting point and K_f are given at $451.55\,\mathrm{K}$ and $37.7\frac{\mathrm{K\,kg}}{\mathrm{mol}}$. Find the freezing point of the solution of 0.72 g of glucose is dissolved in the 30.0 g of camphor.

Solution

Since we are evaluating glucose as the solute, $i = 1$.

$$\Delta T = -iK_f m \tag{13.2.E.17}$$

First find number of moles of glucose in the solution using molar mass.

$$\text{Moles}_{\text{glucose}} = \frac{(0.72g)}{(180.1559\frac{g}{mol})} = 0.0040mol \tag{13.2.E.18}$$

Molality then can be determined.

$$m = \frac{(0.0040mol)}{(0.030kg)} = 0.13\frac{mol}{kg} \tag{13.2.E.19}$$

Freezing then can be easily found as such:

$$\Delta T = -iK_f m = -(1)(37.7\frac{^oC\ kg}{mol})(0.13\frac{mol}{kg}) = -4.9^oC \tag{13.2.E.20}$$

The freezing is $451.55K - 4.9K = 446.65K = 173.5^oC$.

Q.48

It is observed that 2 grams of a non-electrolyte solute dissolved in 100 grams of benzene lowered the freezing point of the solution by 0.40°C compared to pure benzene. Given that the freezing point depression constant of benzene is 5.12 K kg/mol, find the molar mass of the solute. If it is given that the molecular formula of the solute is $\mathrm{X_8}$ where X is an element, what is the formula of the solute?

Solution

$$\Delta T = -ik_f m$$

It is given that

$$\Delta T = 0.40^\circ C \tag{13.2.E.21}$$

Since the solution is a non-electrolyte, i=1

Hence,

$$\frac{0.40}{K_f} = m$$

$$m = \frac{\frac{2}{\text{Molecular Mass}}}{100 \times 10^{-3}} = \frac{\frac{2}{\text{Molecular Mass}}}{0.1}$$

Hence, we get

$$\frac{0.40 \times 0.1}{K_f} = \frac{2}{\text{Molecular Mass}}$$

$$\text{Molecular Mass} = \frac{2K_f}{0.40 \times 0.1}$$

Hence, the Molecular Mass of the solute is $256\ \frac{g}{mol}$

Since the Molecular Mass of the solute is $256\ \frac{g}{mol}$, we can say that,

$$\text{Molecular Mass of X} = \frac{256}{8} = 32$$

The solute is S_8.

Q.49

At what temperature does the first ice crystals begin to form in a 27% salt (by mass) aqueous solution of NaCl? As the crystallization of water carries on, the remaining solution becomes more concentrated, so what happens to the freezing point of the solution? Given that the freezing point depression constant (K_f) of water is $1.86 \frac{^oC\,kg}{mol}$.

Solution

$$27\%\ \text{NaCl(aq)} = \frac{27\ g\ \text{NaCl}}{73\ g\ \text{H}_2\text{O}} \tag{13.2.E.22}$$

$$molality = \frac{27\ g\ \text{NaCl}}{73\ g\ \text{H}_2\text{O}} \times \frac{mol\ \text{NaCl}}{58.44\ g} \times \frac{1000\ g}{1\ kg} = 6.33\ m \tag{13.2.E.23}$$

$$\Delta T = -i \times m \times K_p = -2 \times 6.33 \frac{mol}{kg} \times 1.86 \frac{^oC \cdot kg}{mol} = -23.5^oC \tag{13.2.E.24}$$

The first ice crystal begins to appear at -23.5^oC, as the solution becomes more concentrated, its freezing point decreases further because freezing point depression is a colligative property, so the freezing point of a solution is lower than that of the pure solvent and is directly proportional to the molality of the solute.

Q.50

When homemade ice cream is being made, the temperature ranging downward from -3°C are needed. Ice cubes from a freezer have a temperature of about -12°C, which is cold enough; however, when the ice cream mixture is mixed with the ice cubes, the liquid balances out to 0°C, which is too warm. To obtain a liquid that is cold enough, salt NaCl is dissolved in water and ice is added to the saltwater. The salt lowers the freezing point of the water enough so that it can freeze the liquid inside the ice cream maker. The instruction for the ice cream maker say to add one part salt to 11 parts water (by mass). What is the freezing point of this solution in °C? Assume the NaCl dissociates fully into ions, and that the solution is ideal.

Solution

$$\Delta T_f = -ik_f m \tag{13.2.E.25}$$

$$\frac{1.00\ g\,\text{NaCl}}{53.5 \frac{g}{mol}} = 0.01869\ mol\ \text{NaCl} \tag{13.2.E.26}$$

$$m = \frac{0.01869\ mol}{11.00g(\frac{1\ kg}{1000\ g})} = 1.699m \tag{13.2.E.27}$$

$$x - (-12^\circ C) = -(2) \times (1.86 \frac{^\circ C}{m}) \times (1.699m) \tag{13.2.E.28}$$

$$x = -18.32^\circ C \tag{13.2.E.29}$$

Q.53

A sample of a purified unknown compound is dissolved in toluene, diluting the solvent to a volume of 1.05 mL. The resulting solution has an osmotic pressure of 0.025 atm at 275 K. If the solute has a molar mass of 46.06 g/mol, how many grams of the unknown compound were added?

Solution

$$\Pi = \frac{nRT}{V}$$

and we know $T = 275K$, $R = 0.0821 \dfrac{L\ atm}{mol\ K}$ and Π=0.025 atm

Thus V= 1.05 mL

Since we need V in liters because the units of R are $\dfrac{L\ atm}{mol\ K}$, we use unit conversions:

$$1.05\ mL \times \frac{1L}{1000mL} = 0.00105\ L$$

Plug in the values we know to find n

$$0.025 = \frac{n \times 0.0821 \times 275}{0.00105}$$
$$\frac{0.025 \times 0.00105}{0.0821 \times 275} = n$$
$$n = 1.163 \times 10^{-6}$$

Now that we know number of moles we just have to multiply the number of moles by the molar mass to find grams of substance.

$$(1.163 \times 10^{-6}) \times 46.06844 \frac{g}{mol} = 5.356 \times 10^{-5} g$$

Q.57

An amount of hydrogen gas ($\mathrm{H_2}$) with a partial pressure of 4.6 atm is dissolved in water and this solution is sealed. The Henry's Law constant K for this solution at 25^oC is $7.8 \times 10^{-4} \frac{\mathrm{M}}{\mathrm{atm}}$.

a. How many moles of hydrogen gas will dissolve per liter of water? Assume the density of water is $1.0 \frac{\mathrm{grams}}{\mathrm{cm^3}}$ and has not been affected by the temperature.
b. What will the dissolved gas molecules do if the sealed solution is unsealed?

Solution

a) According to Henry's Law,

$$C = k \times P_{\mathrm{gas}}$$

In this equation, C = concentration of gas (M), k = Henry's Law constant ($\frac{M}{atm}$), and P_{gas} = partial pressure of gas.

So, given k and P_{gas}:

$$C = 7.8 \times 10^{-4} \frac{M}{atm} \times 4.6\ atm$$
$$C = 0.003588 \frac{mol\ \mathrm{H_2}}{L_{\mathrm{water}}}$$

b) The partial pressure of $\mathrm{H_2}$ in the Earth's atmosphere is less than 1 atm. When the solution is unsealed, the $\mathrm{H_2}$ molecules will no longer be under enough pressure to dissolve in water, so they will quickly bubble out of the solution and escape as gas into the surroundings.

Q.59

Propene is a colorless organic compound with a weak but unpleasant smell. However, a company can take advantage of its chemical properties to produce propanol:

$$\mathrm{C_3H_6 + H_2O \longrightarrow CH_3(CH_2)_2OH}$$

- The heat of formation of propene is $20.4 \frac{\mathrm{kJ}}{\mathrm{mol}}$.
- The heat of formation of $\mathrm{H_2O}$ is $-241.8 \frac{\mathrm{kJ}}{\mathrm{mol}}$.
- The heat of formation of $\mathrm{CH_3(CH_2)_2OH}$ is $-104.6 \frac{\mathrm{kJ}}{\mathrm{mol}}$.

What suggestions can you give to the company regarding the conditions of pressure and temperature that will have a maximum yield of propanol at equilibrium without calculating the actual data?

Solution

$$\Delta H^o_{f(\text{propene})} = 20.4 \frac{kJ}{mol} \tag{13.2.E.30}$$

$$\Delta H^o_{f(\text{water})} = -241.8 \frac{kJ}{mol} \tag{13.2.E.31}$$

$$\Delta H^o_{f(\text{CH}_3(\text{CH}_2)_2\text{OH})} = -104.6 \frac{kJ}{mol} \tag{13.2.E.32}$$

$$\Delta H^o = \Delta H^o_{f(\text{CH}_3(\text{CH}_2)_2\text{OH})} - \Delta H^o_{f(\text{propene})} - \Delta H^o_{f(\text{water})} \tag{13.2.E.33}$$

$$= -104.6 \frac{kJ}{mol} - (-241.8 \frac{kJ}{mol}) - 20.4 \frac{kJ}{mol} \tag{13.2.E.34}$$

$$= 116.8 \frac{kJ}{mol} > 0$$

It is an endothermic reaction. As a result, a higher temperature is required to maximize the yield of product.

Also, according to the ideal gas law, because the moles of gas are proportional to the volume, and the volume is inverse proportional to the pressure; a higher pressure is required to maximize the yield of product.

Q.61

Suppose heptane and octane form an ideal solution. At 20.0°C, pure heptane has a vapor pressure of $\text{P}_1{}^\circ = 0.0562\ \text{atm}$ while pure octane has a vapor pressure of $\text{P}_2{}^\circ = 0.0145\ \text{atm}$. What is the mole fraction of heptane vapor over a solution of heptane and octane if the solution contained $0.300\ \text{mol}$ heptane and $0.700\ \text{mol}$ octane?

Solution

Since we have been told to assume the solution is ideal, we can use Raoult's law to obtain the partial pressures of heptane and octane, respectively.

$$P_{\text{heptane}} = \left(\frac{0.300\ \text{mol}}{0.300\ \text{mol} + 0.700\ \text{mol}} \right) \times (0.0562\ \text{atm}) = 0.01686\ \text{atm}$$

$$P_{\text{octane}} = \left(\frac{0.700\ \text{mol}}{0.300\ \text{mol} + 0.700\ \text{mol}} \right) \times (0.0145\ \text{atm}) = 0.01015\ \text{atm}$$

Using the relationship between partial pressure and mole fraction, we can obtain the mole fraction of heptane over the solution. Partial pressure and mole fraction can be related through the ideal gas law $P = n\frac{RT}{V}$. Which shows that under constant temperature and pressure, pressure and number of moles are directly related.

$$\chi_{\text{heptane}} = \left(\frac{0.01686\ \text{atm}}{0.01686\ \text{atm} + 0.01015\ \text{atm}} \right) = 0.624$$

Q.63

At 50°C, benzene (C_6H_6) has a vapor pressure of 42.5 kPa and isobutene (C_3H_8) has a vapor pressure of 0.83 torr. When 10.0 g of benzene and 30 g of isobutene are mixed in a solution, they form a nearly ideal solution.

a. Calculate the mole fraction of benzene in the solution.
b. What is the total vapor pressure above the solution in kPa at 50°C ?
c. Calculate the mole fraction of isobutene that exists above the solution in the vapor phase.

Solution

The mole fraction is equal to:

$$\left(\frac{X_A\ mol}{X_A + X_B\ mol}\right)$$

Use dimensional analysis to convert grams to moles:

$$(10.0\ \cancel{g\ C_6H_6})\left(\frac{1\ mol}{78.108\ \cancel{g\ C_6H_6}}\right) = 0.128\ mol$$

$$(30.0\ \cancel{g\ C_3H_8})\left(\frac{1\ mol}{44.094\ \cancel{g\ C_3H_8}}\right) = 0.680\ mol$$

Let:

$X_A =$ the moles of $C_6H_6 = 0.128\ mol$, $X_B =$ the moles of $C_3H_8 = 0.680\ mol$,

$$\chi_B = \frac{0.0929\ kPa}{6.81\ kPa} = 0.0136$$

Plug into the equation and solve:

$$\left(\frac{0.128\ mol}{0.128 + 0.680\ mol}\right) = 0.158$$

b) Since the problem states that the result of mixing the two solutions is nearly ideal, we can assume an ideal solution is formed and use Raoult's Law and we can choose to keep pressure in units of kPa OR torr.

lt's Raoult's Law:

$P_A = \chi_A \times P_A^o$

Here we have chosen to use units of kPa:

$$P_{C_6H_6} = \chi_{C_6H_6} \times P^o_{C_6H_6}$$

$$P_{C_6H_6} = 0.158 \times 42.5\ kPa = 6.72\ kPa$$

To convert torr to kPa:

$$(0.83\ \cancel{torr})\left(\frac{0.133\ kPa}{1\ \cancel{torr}}\right) = 0.1104\ kPa$$

$$P_{C_3H_8} = \chi_{C_3H_8} \times P^o_{C_3H_8}$$

$$P_{C_3H_8} = 0.842 \times 0.1104\ kPa = 0.0929\ kPa$$

Then we add these up to find the total pressure:

$$P_{\text{Total}} = \chi_A P_A^o + \chi_B P_B^o$$

$$P_{\text{Total}} = 6.72\ kPa + 0.0929\ kPa\ = 6.81\ kPa$$

c) To find the mole fraction of isobutene **only** in the vapor phase, we can use partial pressure to represent the amount of gas, becase in mixed gas $n \propto p$:

$$\chi_{\text{isobutene}} = \frac{n_{\text{isobutene}}}{n_{\text{tot}}} = \frac{P_{\text{isobutene}}}{P_{\text{tot}}} = \frac{0.83\ \text{torr}}{6.81\ \text{kPa}} = 0.0162$$

Q.65

A solution is prepared by mixing 2g of $CaCl_2(s)$, 2g of $MgCl_2(s)$, and 3g of $MnO_2(s)$ in enough water to make a total volume of 150 mL. Calculate the concentration of chlorine in the solution in grams per liter.

Solution

$m_{Cl} = 2g\,CaCl_2(\frac{2(35.5g\,Cl)}{110.98g\,CaCl_2}) + 2g\,MgCl_2(\frac{2(35.5g\,Cl)}{95.12g\,MgCl_2})$

$m_{Cl} = 2.77g\,Cl$

mass of chlorine per liter: $\frac{2.77g\,Cl}{150\times10^{-3}L} = 18.5\,\frac{g}{L}$

Q.69

Chromium ion, Cr^{2+}, is a good reducing agent, often being itself turned into Cr^{3+}. Suppose that 10 mL of 0.1 M $Cr(OH)_2$ was needed to reduce completely an 0.05 grams of unknown substance X.

a. If each molecule of X accept just one electron, what is the molecular weight of X?
b. If each molecule of X accept five electrons, what is the molecular weight of X?

Solution

(a) Number of moles of $Cr(OH)_2$ used = $M \times V$

$= 0.1 \times 10\ mL = 1\ mmol = 10^{-3}$ moles

Since only one mole of X was used for every mole of Chromium Hydroxide, the number of moles reacted are equal.

$\frac{Mass}{Molar\ mass}$ = number of moles, hence for X,

$\frac{0.05\ g}{(0.01L\times0.1M)} = 50\,\frac{g}{mol}$

(b) $\frac{0.05\ g}{(0.01L\times0.1M\times5)} = 10\,\frac{g}{mol}$

Q.71

A 0.200 g sample of chloride with unknown purity was dissolved in 200 mL of water was then titrated with $AgNO_3$ solution with a molarity of 0.1 M. After the titration it was determined that 28 mL of $AgNO_3$ was required to fully titrate the sample of chloride. What's the mass percent of chloride in the original dry sample?

Solution

First write the precipitation reaction:

$$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$$

Next we need to determine the amount of moles of Ag used during the titration:

$$\text{mol } Ag^+ = 28\ \cancel{mL}\left(\frac{1\ \cancel{L}}{1000\ \cancel{mL}}\right)\left(\frac{0.1\text{ mol}}{1\ \cancel{L}}\right) = 2.80\times10^{-3}\text{ mol } Ag^+$$

Now that we know the amount of moles of Ag reacted because Ag and Cl combine at a one to one ration we can find the mass of Cl used:

$$\text{mass } Cl^- = 2.80\times10^{-3}\ \cancel{mol}\left(\frac{35.45\text{ g}}{1\ \cancel{mol}}\right) = 9.92\times10^{-2}\text{ g } Cl^-$$

Now that we know the mass of Cl in the unknown we can calculate the mass percent:

$$100\%\left(\frac{0.0992\text{ g}}{0.2\text{g}}\right) = 49.63\%$$

Q.73

At 20°C, the vapor pressure of pure water is 17.5 mmHg. When 110 g of a substance X_y is dissolved in 500 g of water, the vapor pressure of the solution is 15.0 mmHg. Given that this substance has a molecular mass of 12.011 g/mol, what is the molecular formula of this substance X_y. (i.e. what is the number value of subscript y).

Solution

For this question, we can use Raoult's Law

$$P_{\text{solution}} = \chi_{\text{solvent}} \times P^\circ{}_{\text{solvent}}$$

First, we plug in the known values of the pressure of the solution and the pressure of the pure solvent, water, to find the mole fraction.

$$15.0 \text{ mmHg} = \chi_{\text{solvent}} \times 17.5 \text{ mmHg}$$

$$\chi_{\text{solvent}} = 0.8571$$

Next, we can calculate the the number of moles of the solvent from its mass and molecular weight.

$$\text{Moles of solvent} = 500 \text{ g} \times \frac{1}{18.015 \text{ g/mol}} = 27.75 \text{ moles}$$

Next, we can calculate the moles of the solute from the mole fraction of the solvent

$$0.8571 = \frac{27.75 \text{ moles}}{27.75 \text{ moles } + \text{ moles of } X_y}$$

$$\text{moles of } X_y = 4.63 \text{ moles}$$

From here, we can calculate the molecular formula of the substance by dividing the amount of grams per mole used in the solution by the molecular mass of the substance.

$$\frac{110 \text{ g}}{4.63 \text{ moles}} = 23.76 \text{ g/mol}$$

$$(23.76 \text{ g/mol}) \times (\frac{1}{12.011 \text{ g/mol}}) = 1.98$$

$$1.98 \approx 2$$

Thus, the molecular formula of our substance is X_2.

Q.81

The cell membrane of a plant cell is permeable to water. In a salt solution, the plant cells shrivel (lose water) when the concentration is high, and swell (take up water) when the concentration is low. Scientists perform an experiment at 30°C, where an aqueous solution of NaCl with a freezing point of -0.028°C is used to water the plant cells. This causes the plant cells to neither swell nor shrink indicating that the osmotic pressure of the plant cell contents is equal to that of the NaCl solution. Assuming the molarity and molality of the plant cell contents are equal, calculate the osmotic pressure of the solution inside the plant cells. The K_f for the solution is $1.86 \frac{\text{K kg}}{\text{mol}}$.

Solution

Plug in the given values into the equation for freezing point depression to solve for the molality of the solution

$$\Delta T_f = -K_f m$$

$$-0.0218 = -1.86 K \cdot kg \cdot mol^{-1} m$$

$$m = 0.015 \frac{kg}{mol}$$

Because the plant cell neither swells nor shrinks, the molality of the solution is equivalent to the molality of the plant cell contents. According to the question, assume the molarity and molality are equal so concentration

$$c = 0.15 M$$

Use the following equation to calculate for the osmotic pressure, π.

$$\begin{aligned}\pi &= cRT \\ &= (0.15M)(0.08206\frac{L\ atm}{mol\ K})(303.15K) \\ &= 0.374atm\end{aligned}$$

Q.83

Jim loves the smell of grass. He loves it so much that he frequently sniffs the fumes from 1-Hexanol, which is a chemical compound that is known to smell like grass trimmings. Because of his love, he decides to make his garage into a "gas den", and aimed to have 60% of the air in it as 1-Hexanol gas. He achieves this by filling a pool with a mixture of 1-Hexanol and Water. Assume that the air in the "gas den" consists of only the fumes from this mixture. If the pool has 10000L of water in it, how many litres of 1-Hexanol does he need? Use Henry's Law to determine this amount.

Relevant Information:

1-Hexanol:

- Density: $814\frac{kg}{m^3}$
- Molar mass: $107.1748\frac{g}{mol}$
- Henry's Law Constant: $64\frac{molal}{bar}$

Water:

- Density: $1000\frac{kg}{m^3}$

Solution

This problem asks for the amount, in litres, of 1-Hexanol that is required to make Jim's dreams come true. The information given is the density of 1-Hexanol and its molar mass, but since they don't have very much to do with pressure, they can be set aside for now. The question explicitly mentions that Henry's Law should be used, so start be identifying what Henry's Law actually does:

$$C = kP$$

Where C is concentration, k is Henry's Law constant, and P is partial pressure. The question gives out the fact that Jim wants the air in his garage to be 60% 1-Hexanol vapor. Remember the total pressure of air is 1 atm ≈ 1 bar (ignore the error here). Therefore, the partial pressure of 1-hexanol is $1\text{ bar} \times 60\% = 0.6\text{ bar}$. The Henry's Law constant is also provided, and by plugging those two in, the concentration of 1-Hexanol in the desired "solution" (more accurately, giant pool of chemicals) is found. This process is shown below:

$$C = kP = (64\frac{molal}{bar}) \times 0.6\text{ bar} = 38.4$$

This concentration, from the units of k, is in mo*lality*, which is $\frac{mol_{\text{solute}}}{kg_{\text{solvent}}}$. Now all that is left is to convert molality to litres. By utilizing the molar mass of 1-Hexanol:

$$38.4\frac{mol_{\text{solute}}}{kg_{\text{solvent}}} \times 107.1748\frac{g}{mol} \approx 4115.51\frac{g_{\text{solute}}}{kg_{\text{solvent}}}$$

We know that the solvent is water, and that water has a density of $1000\frac{kg}{m^3}$. Also, the conversion rate of m^3 to L is 1:1000. Therefore, the equation can be solved as follows.

$$4115.51\frac{g_{\text{solute}}}{kg_{\text{solvent}}} \times 1000\frac{kg_{H_2O}}{m^3} \times \frac{m^3}{1000\ L_{H_2O}} \approx 4115.51\frac{g_{\text{solute}}}{L_{\text{solvent}}}$$

We now have the value for how many grams of solute (1-Hexanol) there should be per litre of solvent. simply divide this value by the density to obtain litres of 1-Hexanol per litre of water. Multiply this number by the amount of water in the pool to get the desired amount of solute that is needed for the solution! (note that the density was converted to $\frac{g}{L}$,

$$4115.51\frac{g_{\text{solute}}}{L_{\text{solvent}}} \div \left(814000\frac{g_{\text{1-hexanol}}}{L}\right) \times 10000 L_{\text{H}_2\text{O}} = 50.56\,\text{L}$$

~~Therefore, Jim needs 50,560L of 1-Hexanol to put in his pool. That's going to take a big pool!~~

Therefore, Jim needs 50.56L of 1-Hexanol to put in his pool.

Please note that, while various units do appear in the conversions, H_2O can be considered as solute and 1-Hexanol as the solvent, so the units can cancel.

Abstract: Utilize henry's law to find concentration (molality). From that, convert molality to g_{solute} to L_{solute}.

Q.87

A 3.5 gram sample is decomposed into a compound containing nitrogen, hydrogen, and oxygen, together creating 4.00 g of NO_2 and 7.00 g of H_2O. The molar mass of the sample is $78.5\,\frac{\text{g}}{\text{mol}}$. Find the molecular formula of this sample.

Solution

First, the moles of each Nitrogen, Hydrogen, and Oxygen in solution are calculated:

$$mol_N = 4g\,\text{NO}_2 \times \left(\frac{1\ mol\ \text{NO}_2}{46.005\frac{g}{mol}}\right) \times \left(\frac{1\ mol\ N}{1\ mol\ \text{NO}_2}\right) = 0.0869\ mol$$

$$mass_N = \left(14.00\frac{g}{mol}\right)(0.0869 mol) = 1.2172g\,\text{N}$$

$$mol_H = 7g\,\text{H}_2\text{O} \times \left(\frac{1\ mol\ H_2O}{18.02\frac{g}{mol}}\right) \times \left(\frac{2\ mol\ H}{1\ mol\ \text{H}_2\text{O}}\right) = 0.7769\ mol$$

$$mass_H = \left(1.01\frac{g}{mol}\right)(0.7769 mol) = 0.7847g\,\text{H}$$

From these values, moles of O can be calculated to be:

$$3.5\ gram\ sample = grams_N + grams_H + grams_O$$

$$3.5 = 1.2172g + 0.7847g + grams_O$$

$$grams_O = 1.4981g$$

$$mol_O = \frac{1.4981g}{15.9994\frac{g}{mol}} = 0.0936\ mol$$

The mole values for each element create a ratio of $\text{H}_{0.7769}\text{N}_{0.0869}\text{O}_{0.0936}$, creating an empirical formula H_9NO

From here, the molecular formula can be established using the molar mass:

$$\text{Empirical formula mass} = 9\left(1.01\frac{g}{mol\ H}\right) + \left(14.00\frac{g}{mol\ N}\right) + \left(15.9994\frac{g}{mol\ O}\right)$$

$$\text{Empirical formula mass} = 39.0894\frac{g}{mol}$$

$$\text{Sample Mass} = 78.5\frac{g}{mol}$$

$$\frac{78.5\frac{g}{mol}}{39.084\frac{g}{mol}} = 2.00$$

$$2(\text{H}_9\text{NO}) = \text{H}_{18}\text{N}_2\text{O}_2 = \text{Molecular Formula}$$

Q.87

5 grams of a substance containing hydrogen, carbon and oxygen were fully combusted and produced 3.00 grams of H_2O and 7.33 grams of CO_2. When 10.64 grams of the substance was mixed with 0.5 kg of water, the freezing point was found to decrease by 0.0605°C. What is the substance?

Solution

The generic equation for this reaction is

$$C_xH_yO_z + O_2 \longrightarrow H_2O + CO_2$$

The molar masses of carbon, hydrogen, and oxygen are 12.01 g/mol, 1.008 g/mol, and 16.00 g/mol respectively. Therefore the molar masses of water and carbon dioxide are $18.016 \frac{g}{mol}$ and $44.01 \frac{g}{mol}$ These values can be used to determine the mass percent of hydrogen in water

$$\frac{2(1.008)\ \frac{g}{mol}}{18.016\ \frac{g}{mol}} \times 100 = 11.2\%$$

And the mass percent of carbon in carbon dioxide

$$\frac{12.01\ \frac{g}{mol}}{44.01\ \frac{g}{mol}} \times 100 = 27.3\%$$

The mass percents can be used to determine the amount of hydrogen and carbon are present.

$$3.00\ g \times 0.112 = 0.336\ g \text{ of Hydrogen}$$

$$7.33\ g \times 0.273 = 2.001\ g \text{ of Carbon}$$

By subtracting the masses of Carbon and Hydrogen from the original mass of the substance, the mass of oxygen present in the substance can be found

$$5\ g - (0.336\ g + 2.001\ g) = 2.663\ g \text{ of Oxygen}$$

By dividing the masses present by the molar mass, the amount of moles of each element can be determined

$$\frac{0.112\ g}{1.008\ \frac{g}{mol}} = 0.333\ mol \text{ of Hydrogen}$$

$$\frac{2.001\ g}{12.01\ \frac{g}{mol}} = 0.167\ mol \text{ of Carbon}$$

$$\frac{2.663\ g}{16.00\ \frac{g}{mol}} = 0.166\ mol \text{ of Oxygen}$$

By looking at the amount of moles of each element, it can be noticed that there are equal amounts of carbon and oxygen and twice as much hydrogen as carbon or oxygen. Therefore the ratio of $C : H : O$ in the substance is $1 : 2 : 1$. However, the molar mass of the substance remains unknown, but it can be found using the information about the freezing point depression.

From the formula for freezing point depression

$$\Delta T = -i \times k_f \times m$$

$$-0.0605^\circ C = -1 \times 0.512^\circ C\ m^{-1} \times m$$

$$m = \frac{0.0605^\circ C}{0.512 \frac{^\circ C}{m}} = 0.118\ \frac{mol}{kg}$$

By multiply by the mass of solvent (water), we can determine the amount of moles that was dissolved in the water

$$0.118\ \frac{mol}{kg} \times 0.5\ kg = 0.059\ mol$$

The last step in finding the molar mass of the substance is to divide the mass dissolved by the moles dissolved

$$\frac{10.64\ g}{0.059\ mol} = 180.3\ \frac{g}{mol}$$

Now we can find the formula of the substance. The first step is to find the number of moles of the substance combusted

$$\frac{5\ g}{180.3\ \frac{g}{mol}} = 0.0277\ mol$$

We can compare this to the number of carbon moles combusted to determine the number of carbon atoms per molecule of the substance

$$\frac{0.167\ g\ \text{of Carbon}}{0.0277\ mol} = 6\ \text{Carbon atoms}$$

When we apply the number of carbon atoms to the ratio of elements found earlier, the chemical formula comes to be $C_6H_{12}O_6$ which is glucose.

Answer: Glucose

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SECTION OVERVIEW

14.1: Acid–Base Equilibria

An General Chemistry Libretexts Textmap organized around the textbook

Principles of Modern Chemistry

by Oxtoby, Gillis, and Campion

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Acids and bases have been defined differently by three sets of theories. One is the Arrhenius definition, which revolves around the idea that acids are substances that ionize (break off) in an aqueous solution to produce hydrogen (H^+) ions while bases produce hydroxide (OH^-) ions in solution. On the other hand, the Bronsted-Lowry definition defines acids as substances that donate protons (H^+) whereas bases are substances that accept protons. Also, the Lewis theory of acids and bases states that acids are electron pair acceptors while bases are electron pair donors. Acids and bases can be defined by their physical and chemical observations.

14.1.1: Classifications of Acids and Bases

14.1.2: Properties of Acids and Bases in Aqueous Solutions

14.1.3: Acid and Base Strength

14.1.4: Equilibria Involving Weak Acids and Bases

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14.1.E: Acid-Base Equilibria (Exercises)

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14.1.1: Classifications of Acids and Bases

Learning Objectives

- To understand the differences between the three definitions of Acids and Bases
- Identify acids, bases, and conjugate acid-base pairs according to the three definitions of Acids and Bases
- To understand the concept of conjugate acid–base pairs in acid/base reactions
- Write the equation for the proton transfer reaction involving a Brønsted-Lowry acid or base, and show how it can be interpreted as an **electron-pair transfer** reaction, clearly identifying the donor and acceptor.
- Give an example of a **Lewis acid-base reaction** that does not involve protons.

Acids and bases have been known for a long time. When Robert Boyle characterized them in 1680, he noted that acids dissolve many substances, change the color of certain natural dyes (for example, they change litmus from blue to red), and lose these characteristic properties after coming into contact with alkalis (bases). In the eighteenth century, it was recognized that acids have a sour taste, react with limestone to liberate a gaseous substance (now known to be CO_2), and interact with alkalis to form neutral substances. In 1815, Humphry Davy contributed greatly to the development of the modern acid-base concept by demonstrating that hydrogen is the essential constituent of acids. Around that same time, Joseph Louis Gay-Lussac concluded that acids are substances that can neutralize bases and that these two classes of substances can be defined only in terms of each other. The significance of hydrogen was reemphasized in 1884 when Carl Axel Arrhenius defined an acid as a compound that dissolves in water to yield hydrogen cations (now recognized to be hydronium ions) and a base as a compound that dissolves in water to yield hydroxide anions.

Acids and bases are common solutions that exist everywhere. Almost every liquid that we encounter in our daily lives consists of acidic and basic properties, with the exception of water. They have completely different properties and are able to neutralize to form H_2O, which will be discussed later in a subsection. Acids and bases can be defined by their physical and chemical observations (Table 14.1.1.1).

Table 14.1.1.1: General Properties of Acids and Bases

ACIDS	BASES
produce a piercing pain in a wound.	give a slippery feel.
taste sour.	taste bitter.
are colorless when placed in phenolphthalein (an indicator).	are pink when placed in phenolphthalein (an indicator).
are red on blue litmus paper (a pH indicator).	are blue on red litmus paper (a pH indicator).
have a pH<7.	have a pH>7.
produce hydrogen gas when reacted with metals.	
produce carbon dioxide when reacted with carbonates.	
Common examples: Lemons, oranges, vinegar, urine, sulfuric acid, hydrochloric acid	Common Examples: Soap, toothpaste, bleach, cleaning agents, limewater, ammonia water, sodium hydroxide.

Acids and bases in aqueous solutions will conduct electricity because they contain dissolved ions. Therefore, acids and bases are *electrolytes*. Strong acids and bases will be strong **electrolytes**. Weak acids and bases will be weak electrolytes. This affects the amount of conductivity.

In chemistry, acids and bases have been defined differently by **three sets of theories**: One is the Arrhenius definition defined above, which revolves around the idea that acids are substances that ionize (break off) in an aqueous solution to produce hydrogen (H^+) ions while bases produce hydroxide (OH^-) ions in solution. The other two definitions are discussed in detail include the **Brønsted-Lowry definition** the defines acids as substances that donate protons (H^+) whereas bases are substances that accept protons and the **Lewis theory** of acids and bases states that acids are electron pair acceptors while bases are electron pair donors.

Arrhenius Acids and Bases

In 1884, the Swedish chemist Svante Arrhenius proposed two specific classifications of compounds, termed acids and bases. When dissolved in an aqueous solution, certain ions were released into the solution. The Arrhenius definition of acid-base reactions is a development of the "hydrogen theory of acids". It was used to provide a modern definition of acids and bases, and followed from Arrhenius's work with Friedrich Wilhelm Ostwald in establishing the presence of ions in aqueous solution in 1884. This led to Arrhenius receiving the Nobel Prize in Chemistry in 1903.

An **Arrhenius acid** is a compound that increases the concentration of H^+ ions that are present when added to water.

$$HCl(g) \rightarrow H^+(aq) + Cl^-(aq) \tag{14.1.1.1}$$

In this reaction, hydrochloric acid (HCl) gas dissociates into hydrogen (H^+) and chloride (Cl^-) ions when dissolved in water, thereby releasing H^+ ions into solution. These H^+ ions form the hydronium ion (H_3O^+) when they combine with water molecules. Both processes can be represented in a chemical equation by adding H_2O to the reactants side of Equation 14.1.1.1 and switching hydronium ions for free protons.

$$HCl(g) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq) \tag{14.1.1.2}$$

An **Arrhenius base** is a compound that dissociates to yield hydroxide ions (OH^-) in aqueous solution. Common examples of Arrhenus bases include Sodium hydroxide ($NaOH$), Potassium hydroxide (KOH), Magnesium hydroxide $Mg(OH)_2$, and Calcium hydroxide ($Ca(OH)_2$. All of these bases are solids at room temperature and when dissolved in water, will generate a metal cation and the hydroxide ion ((OH^-), for example, Sodium hydroxide

$$NaOH(s) \longrightarrow Na^+(aq) + OH^-(aq) \tag{14.1.1.3}$$

All Arrhenius acids have easily detachable hydrogen that leave to form hydronium ions in solution and all Arrhenius bases have easily detachable OH groups that form hydroxide ions in solution.

Limitation of the Arrhenius Definition of Acids and Bases

The Arrhenius definitions of acidity and alkalinity are restricted to aqueous solutions and refer to the concentration of the solvated ions. Under this definition, pure H_2SO_4 or HCl dissolved in toluene are not acidic, despite the fact that both of these acids will donate a proton to toluene. In addition, under the Arrhenius definition, a solution of sodium amide ($NaNH_2$) in liquid ammonia is not alkaline, despite the fact that the amide ion (NH_2^-) will readily deprotonate ammonia. Thus, the Arrhenius definition can only describe acids and bases in an aqueous environment. The Arrhenius definition can **only** describe acids and bases in protic solvents and environments (e.g., water, alcohols, within proteins etc.).

Brønsted-Lowry Acids and Bases

The Arrhenius definitions identified an acid as a compound that dissolves in water to yield hydronium ions (Equation 14.1.1.2) and a base as a compound that dissolves in water to yield hydroxide ions (Equation 14.1.1.3). As mentioned above, this definition limited. We extended the definition of an acid or a base using the more general definition proposed in 1923 by the Danish chemist Johannes Brønsted and the English chemist Thomas Lowry. Their definition centers on the proton, H^+. A proton is what remains when a normal hydrogen atom, ${}^1_1H$, loses an electron. A compound that donates a proton to another compound is called a **Brønsted-Lowry acid**, and a compound that accepts a proton is called a **Brønsted-Lowry base**. An acid-base reaction is the transfer of a proton from a proton donor (acid) to a proton acceptor (base).

Acids may be compounds such as HCl or H_2SO_4, organic acids like acetic acid (CH_3COOH) or ascorbic acid (vitamin C), or H_2O. Anions (such as HSO_4^-, $H_2PO_4^-$, HS^-, and HCO_3^-) and cations (such as H_3O^+, NH_4^+, and $[Al(H_2O)_6]^{3+}$) may also act as acids.

Bases fall into the same three categories and may be neutral molecules (such as H_2O, NH_3, and CH_3NH_2), anions (such as OH^-, HS^-, HCO_3^-, CO_3^{2-}, F^-, and PO_4^{3-}), or cations (such as $[Al(H_2O)_5OH]^{2+}$). The most familiar bases are ionic compounds such as $NaOH$ and $Ca(OH)_2$, which contain the hydroxide ion, OH^-. The hydroxide ion in these compounds accepts a proton from acids to form water:

$$H^+ + OH^- \rightarrow H_2O \tag{14.1.1.4}$$

We call the product that remains after an acid donates a proton the **conjugate base** of the acid. This species is a base because it can accept a proton (to re-form the acid):

$$\text{acid} \rightleftharpoons \text{proton} + \text{conjugate base}$$

$$\ce{HF} \rightleftharpoons \ce{H^+} + \ce{F^-}$$

$$\ce{H_2SO_4} \rightleftharpoons \ce{H^+} + \ce{HSO_4^-}$$

$$\ce{H_2O} \rightleftharpoons \ce{H^+} + \ce{OH^-}$$

$$\ce{HSO_4^-} \rightleftharpoons \ce{H^+} + \ce{SO_4^{2-}}$$

$$\ce{NH_4^+} \rightleftharpoons \ce{H^+} + \ce{NH_3}$$

We call the product that results when a base accepts a proton the base's **conjugate acid**. This species is an acid because it can give up a proton (and thus re-form the base):

$$\text{base} + \text{proton} \rightleftharpoons \text{conjugate acid}$$

$$\ce{OH^-} + \ce{H^+} \rightleftharpoons \ce{H_2O}$$

$$\ce{H_2O} + \ce{H^+} \rightleftharpoons \ce{H_3O^+}$$

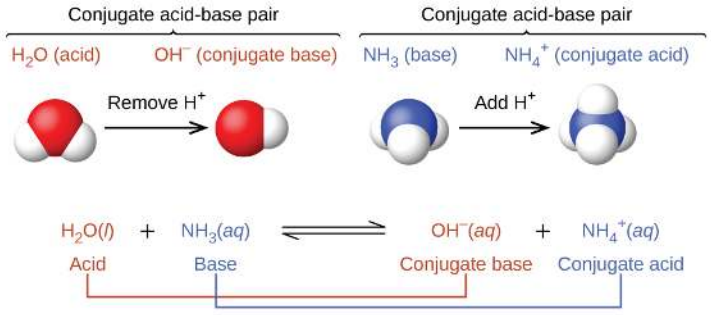
$$\ce{NH_3} + \ce{H^+} \rightleftharpoons \ce{NH_4^+}$$

$$\ce{S^{2-}} + \ce{H^+} \rightleftharpoons \ce{HS^-}$$

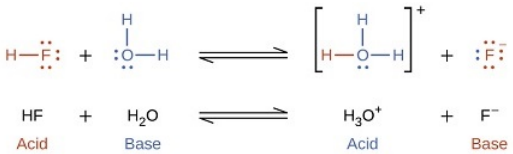
$$\ce{CO_3^{2-}} + \ce{H^+} \rightleftharpoons \ce{HCO_3^-}$$

$$\ce{F^-} + \ce{H^+} \rightleftharpoons \ce{HF}$$

In these two sets of equations, the behaviors of acids as proton donors and bases as proton acceptors are represented in isolation. In reality, all acid-base reactions involve the transfer of protons between acids and bases. For example, consider the acid-base reaction that takes place when ammonia is dissolved in water. A water molecule (functioning as an acid) transfers a proton to an ammonia molecule (functioning as a base), yielding the conjugate base of water, $\ce{OH^-}$, and the conjugate acid of ammonia, $\ce{NH_4^+}$:



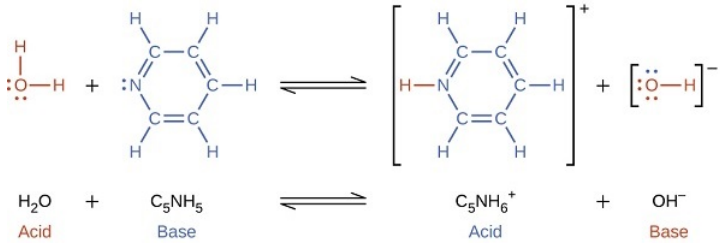
The reaction between a Brønsted-Lowry acid and water is called acid ionization. For example, when hydrogen fluoride dissolves in water and ionizes, protons are transferred from hydrogen fluoride molecules to water molecules, yielding hydronium ions and fluoride ions:



with

$$K = \frac{[\ce{H_3O^+}][\ce{F^-}]}{[\ce{HF}]}$$

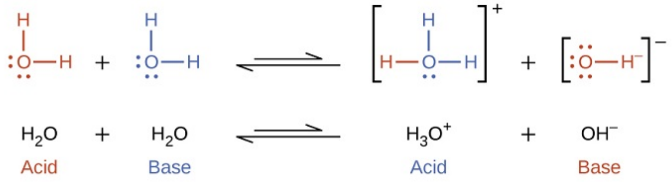
When we add a base to water, a base ionization reaction occurs in which protons are transferred from water molecules to base molecules. For example, adding ammonia to water yields hydroxide ions and ammonium ions:



with

$$K = \frac{[C_5NH_6^+][OH^-]}{[C_5NH_5]}$$

Notice that both these ionization reactions are represented as equilibrium processes. The relative extent to which these acid and base ionization reactions proceed is an important topic treated in a later section of this chapter. In the preceding paragraphs we saw that water can function as either an acid or a base, depending on the nature of the solute dissolved in it. In fact, in pure water or in any aqueous solution, water acts both as an acid and a base. A very small fraction of water molecules donate protons to other water molecules to form hydronium ions and hydroxide ions:



This type of reaction, in which a substance ionizes when one molecule of the substance reacts with another molecule of the same substance, is referred to as **autoionization**. Pure water undergoes autoionization to a very slight extent. Only about two out of every 10^9 molecules in a sample of pure water are ionized at 25 °C. The equilibrium constant for the ionization of water is called the ion-product constant for water (K_w):

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \tag{14.1.1.5}$$

with

$$K_w = [H_3O^+][OH^-] \tag{14.1.1.6}$$

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 approximately 5.1×10^{-13}, roughly 100-times larger than the value at 25 °C.

Example 14.1.1.1: 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, $[H_3O^+] = [OH^-]$. At 25 °C:

$$\begin{aligned} K_w &= [H_3O^+][OH^-] \\ &= [H_3O^+]^2 \\ &= [OH^-]^2 \\ &= 1.0 \times 10^{-14} \end{aligned}$$

So

$$[H_3O^+] = [OH^-] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7}\ M$$

The hydronium ion concentration and the hydroxide ion concentration are the same, and we find that both equal $1.0 \times 10^{-7}\ M$.

? Exercise 14.1.1.1

The ion product of water at 80 °C is 2.4×10^{-13}. What are the concentrations of hydronium and hydroxide ions in pure water at 80 °C?

Answer

$$[H_3O^+] = [OH^-] = 4.9 \times 10^{-7}\ M$$

It is important to realize that the autoionization equilibrium for water is established in all aqueous solutions. Adding an acid or base to water will not change the position of the equilibrium. Example 14.1.1.2 demonstrates the quantitative aspects of this relation between hydronium and hydroxide ion concentrations.

✓ Example 14.1.1.2: The Inverse Proportionality of $[H_3O^+]$ and $[OH^-]$

The Inverse Proportionality of $[H_3O^+]$ and $[OH^-]$ A solution of carbon dioxide in water has a hydronium ion concentration of $2.0 \times 10^{-6}\ M$. What is the concentration of hydroxide ion at 25 °C?

Solution

We know the value of the ion-product constant for water at 25 °C:

$$2\,H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

Thus, we can calculate the missing equilibrium concentration.

Rearrangement of the K_w expression yields that $[OH^-]$ is directly proportional to the inverse of $[H_3O^+]$:

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-6}} = 5.0 \times 10^{-9}$$

The hydroxide ion concentration in water is reduced to $5.0 \times 10^{-9}\ M$ as the hydrogen ion concentration increases to $2.0 \times 10^{-6}\ M$. This is expected from Le Chatelier's principle; the autoionization reaction shifts to the left to reduce the stress of the increased hydronium ion concentration and the $[OH^-]$ is reduced relative to that in pure water.

A check of these concentrations confirms that our arithmetic is correct:

$$K_w = [H_3O^+][OH^-] = (2.0 \times 10^{-6})(5.0 \times 10^{-9}) = 1.0 \times 10^{-14}$$

? Exercise 14.1.1.2

What is the hydronium ion concentration in an aqueous solution with a hydroxide ion concentration of 0.001 M at 25 °C?

Answer

$$[H_3O^+] = 1 \times 10^{-11} M$$

Amphoteric Species

Like water, many molecules and ions may either gain or lose a proton under the appropriate conditions. Such species are said to be amphiprotic. Another term used to describe such species is amphoteric, which is a more general term for a species that may act either as an acid or a base by any definition (not just the Brønsted-Lowry one). Consider for example the bicarbonate ion, which may either donate or accept a proton as shown here:

$$\mathrm{HCO{-}3\,(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)}$$

$$\mathrm{HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)}$$

Example 14.1.1.3: The Acid-Base Behavior of an Amphoteric Substance

Write separate equations representing the reaction of $\mathrm{HSO_3^-}$

a. as an acid with $\mathrm{OH^-}$
b. as a base with HI

Solution

a. $\mathrm{HSO_3^-}(aq) + \mathrm{OH^-}(aq) \rightleftharpoons \mathrm{SO_3^{2-}}(aq) + \mathrm{H_2O}_{(l)}$
b. $\mathrm{HSO_3^-}(aq) + \mathrm{HI}(aq) \rightleftharpoons \mathrm{H_2SO_3}(aq) + \mathrm{I^-}(aq)$

Exercise 14.1.1.3

Write separate equations representing the reaction of $\mathrm{H_2PO_4^-}$

a. as a base with HBr
b. as an acid with $\mathrm{OH^-}$

Answer a

$\mathrm{H_2PO_4^-}(aq) + \mathrm{HBr}(aq) \rightleftharpoons \mathrm{H_3PO_4}(aq) + \mathrm{Br^-}(aq)$

Answer b

$\mathrm{H_2PO_4^-}(aq) + \mathrm{OH^-}(aq) \rightleftharpoons \mathrm{HPO_4^{2-}}(aq) + \mathrm{H_2O}_{(l)}$

Lewis Acids and Bases

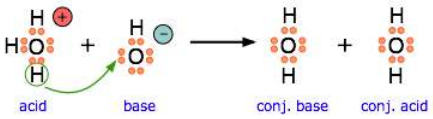
The Brønsted-Lowry proton donor-acceptor concept has been one of the most successful theories of Chemistry. But as with any such theory, it is fair to ask if this is not just a special case of a more general theory that could encompass an even broader range of chemical science. In 1916, G.N. Lewis of the University of California proposed that the *electron pair* is the dominant actor in acid-base chemistry. The Lewis theory did not become very well known until about 1923 (the same year that Brønsted and Lowry published their work), but since then it has been recognized as a very powerful tool for describing chemical reactions of widely different kinds and is widely used in organic and inorganic chemistry. The Brønsted–Lowry concept of acids and bases defines a base as any species that can accept a proton, and an acid as any substance that can donate a proton. Lewis proposed an alternative definition that focuses on *pairs of electrons* instead. According to Lewis:

- An *acid* is a substance that **accepts** a pair of electrons, and in doing so, forms a covalent bond with the entity that supplies the electrons.
- A *base* is a substance that **donates** an unshared pair of electrons to a recipient species with which the electrons can be shared.

> *In modern chemistry, electron donors are often referred to as nucleophiles, while acceptors are electrophiles.*

Lewis Acid-Base Neutralization Involving Electron-Pair Transfer

Just as any Arrhenius acid is also a Brønsted acid, any Brønsted acid is also a Lewis acid, so the various acid-base concepts are all "upward compatible". Although we do not really need to think about electron-pair transfers when we deal with ordinary aqueous-solution acid-base reactions, it is important to understand that it is the opportunity for electron-pair sharing that enables proton transfer to take place.



This equation for a simple acid-base neutralization shows how the Brønsted and Lewis definitions are really just different views of the same process. Take special note of the following points:

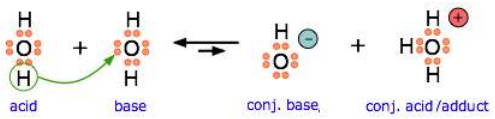
- The arrow shows the movement of a proton from the hydronium ion to the hydroxide ion.
- Note that the electron-pairs themselves do not move; they remain attached to their central atoms. The electron pair on the base is "donated" to the acceptor (the proton) only in the sense that it ends up being *shared* with the acceptor, rather than being the exclusive property of the oxygen atom in the hydroxide ion.
- Although the hydronium ion is the nominal Lewis acid here, it does not itself accept an electron pair, but acts merely as the source of the proton that coordinates with the Lewis base.

Note

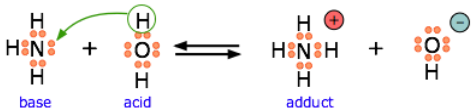
The point about the electron-pair remaining on the donor species is especially important to bear in mind. For one thing, it distinguishes a *Lewis acid-base reaction* from an *oxidation-reduction reaction*, in which a physical transfer of one or more electrons from donor to acceptor does occur.

The product of a Lewis acid-base reaction is known formally as an "**adduct**" or "complex", although we do not ordinarily use these terms for simple proton-transfer reactions such as the one in the above example. Here, the proton combines with the hydroxide ion to form the "adduct" H_2O. The following examples illustrate these points for some other proton-transfer reactions that you should already be familiar with.

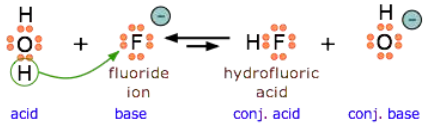
Another example, showing the autoprotolysis of water. Note that the conjugate acid is also the adduct.



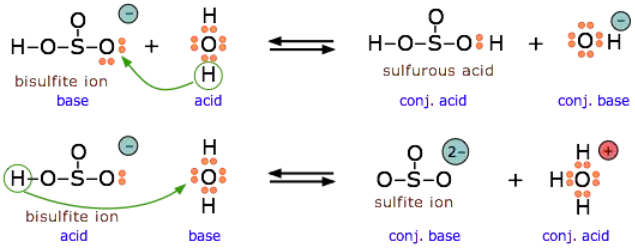
Ammonia is both a Brønsted and a Lewis base, owing to the unshared electron pair on the nitrogen. The reverse of this reaction represents the *hydrolysis* of the ammonium ion.



Because HF is a weak acid, fluoride salts behave as bases in aqueous solution. As a Lewis base, F^- accepts a proton from water, which is transformed into a hydroxide ion.



The bisulfite ion is *amphiprotic* and can act as an electron donor or acceptor.



All Brønsted–Lowry bases (proton acceptors), such as OH^-, H_2O, and NH_3, are also electron-pair donors. Thus the Lewis definition of acids and bases does not contradict the Brønsted–Lowry definition. Rather, it expands the definition of acids to include substances other than the H^+ ion.

Lewis Acid-Base Neutralization without Transferring Protons

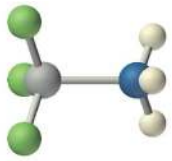
Electron-deficient molecules, such as BCl_3, contain less than an octet of electrons around one atom and have a strong tendency to gain an additional pair of electrons by reacting with substances that possess a lone pair of electrons. Lewis's definition, which is less restrictive than either the Brønsted–Lowry or the Arrhenius definition, grew out of his observation of this tendency. A general Brønsted–Lowry acid–base reaction can be depicted in Lewis electron symbols as follows:

$$\underset{\substack{\text{Lewis acid}\\ \text{Electron-pair}\\ \text{acceptor}}}{H^+} + \underset{\substack{\text{Lewis base}\\ \text{Electron-pair}\\ \text{donor}}}{:B} \longrightarrow H:B^+$$

The proton (H^+), which has no valence electrons, is a Lewis acid because it accepts a lone pair of electrons on the base to form a bond. The proton, however, is just one of many electron-deficient species that are known to react with bases. For example, neutral compounds of boron, aluminum, and the other Group 13 elements, which possess only six valence electrons, have a very strong tendency to gain an additional electron pair. Such compounds are therefore potent Lewis acids that react with an electron-pair donor such as ammonia to form an acid–base adduct, a new covalent bond, as shown here for boron trifluoride (BF_3):

$$\underset{\text{Lewis acid}}{BF_3} + \underset{\text{Lewis base}}{:NH_3} \longrightarrow \underset{\text{Acid-base adduct}}{F_3B:NH_3}$$

The bond formed between a Lewis acid and a Lewis base is a **coordinate covalent bond** because both electrons are provided by only one of the atoms (N, in the case of $F_3B{:}NH_3$). After it is formed, however, a coordinate covalent bond behaves like any other covalent single bond.



Boron trifluoride-ammonia adduct

Species that are very weak Brønsted–Lowry bases can be relatively strong Lewis bases. For example, many of the group 13 trihalides are highly soluble in ethers (R–O–R′) because the oxygen atom in the ether contains two lone pairs of electrons, just as in H_2O. Hence the predominant species in solutions of electron-deficient trihalides in ether solvents is a Lewis acid–base adduct. A reaction of this type is shown in Figure 14.1.1.1for boron trichloride and diethyl ether:

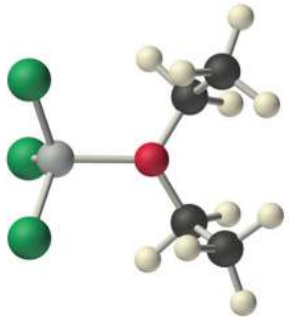
$$\underset{\text{Lewis acid}}{BCl_3} + \underset{\text{Lewis base}}{:\ddot{O}(CH_2CH_3)_2} \longrightarrow \underset{\text{Acid-base adduct}}{Cl_3B:\ddot{O}(CH_2CH_3)_2}$$

Figure 14.1.1.1 Lewis Acid/Base reaction of boron trichloride and diethyl ether reaction

Note

- Electron-deficient molecules (those with less than an octet of electrons) are Lewis acids.
- The acid-base behavior of many compounds can be explained by their Lewis electron structures.

Many molecules with multiple bonds can act as Lewis acids. In these cases, the Lewis base typically donates a pair of electrons to form a bond to the central atom of the molecule, while a pair of electrons displaced from the multiple bond becomes a lone pair on a terminal atom.



Boron trichloride-diethyl ether adduct

Figure 14.1.1.2: The highly electronegative oxygen atoms pull electron density away from carbon, so the carbon atom acts as a Lewis acid. Arrows indicate the direction of electron flow.

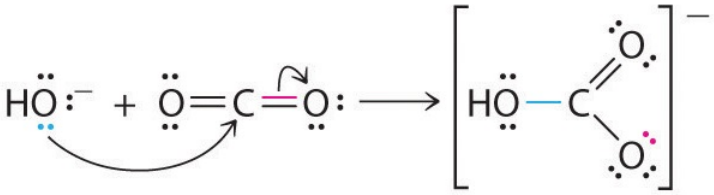


Figure 14.1.1.2 Lewis Acid/Base reaction of the hydroxide ion with carbon dioxide

Example 14.1.1.4

Identify the acid and the base in each Lewis acid–base reaction.

a. $BH_3 + (CH_3)_2S \rightarrow H_3B{:}S(CH_3)_2$
b. $CaO + CO_2 \rightarrow CaCO_3$
c. $BeCl_2 + 2\ Cl^- \rightarrow BeCl_4^{2-}$

Given: reactants and products

Asked for: identity of Lewis acid and Lewis base

Strategy:

In each equation, identify the reactant that is electron deficient and the reactant that is an electron-pair donor. The electron-deficient compound is the Lewis acid, whereas the other is the Lewis base.

Solution:

a. In BH_3, boron has only six valence electrons. It is therefore electron deficient and can accept a lone pair. Like oxygen, the sulfur atom in $(CH_3)_2S$ has two lone pairs. Thus $(CH_3)_2S$ donates an electron pair on sulfur to the boron atom of BH_3. The Lewis base is $(CH_3)_2S$, and the Lewis acid is BH_3.
b. As in the reaction shown in Equation 8.21, CO_2 accepts a pair of electrons from the O^{2-} ion in CaO to form the carbonate ion. The oxygen in CaO is an electron-pair donor, so CaO is the Lewis base. Carbon accepts a pair of electrons, so CO_2 is the Lewis acid.
c. The chloride ion contains four lone pairs. In this reaction, each chloride ion donates one lone pair to $BeCl_2$, which has only four electrons around Be. Thus the chloride ions are Lewis bases, and $BeCl_2$ is the Lewis acid.

Exercise 14.1.1.4A

Identify the acid and the base in each Lewis acid–base reaction.

a. $(CH_3)_2O + BF_3 \rightarrow (CH_3)_2O{:}BF_3$
b. $H_2O + SO_3 \rightarrow H_2SO_4$

Answer a

Lewis base: $(CH_3)_2O$; Lewis acid: BF_3

Answer b

Lewis base: H_2O; Lewis acid: SO_3

? Exercise 14.1.1.4B

Here are several more examples of Lewis acid-base reactions that **cannot** be accommodated within the Brønsted or Arrhenius models. Identify the Lewis acid and Lewis base in each reaction.

a. $Al(OH)_3 + OH^- \rightarrow Al(OH)_4^-$
b. $SnS_2 + S^{2-} \rightarrow SnS_3^{2-}$
c. $Cd(CN)_2 + 2CN^- \rightarrow Cd(CN)_4^{2+}$
d. $AgCl + 2NH_3 \rightarrow Ag(NH_3)_2^+ + Cl^-$
e. $Fe^{2+} + NO \rightarrow Fe(NO)^{2+}$
f. $[Ni^{2+} + 6NH_3 \rightarrow Ni(NH_3)_5^{2+}$



Video 14.1.1.1: Overview of Lewis Acids and Bases

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:

$$2\,H_2O_{(l)} \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

The ion product of water, K_w is the equilibrium constant for the autoionization reaction:

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25\,^\circ C$$

Glossary

acid ionization

reaction involving the transfer of a proton from an acid to water, yielding hydronium ions and the conjugate base of the acid

amphiprotic

species that may either gain or lose a proton in a reaction

amphoteric

species that can act as either an acid or a base

autoionization

reaction between identical species yielding ionic products; for water, this reaction involves transfer of protons to yield hydronium and hydroxide ions

base ionization

reaction involving the transfer of a proton from water to a base, yielding hydroxide ions and the conjugate acid of the base

Brønsted-Lowry acid

proton donor

Brønsted-Lowry base

proton acceptor

conjugate acid

substance formed when a base gains a proton

conjugate base

substance formed when an acid loses a proton

ion-product constant for water (K_w)

equilibrium constant for the autoionization of water

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14.1.2: Properties of Acids and Bases in Aqueous Solutions

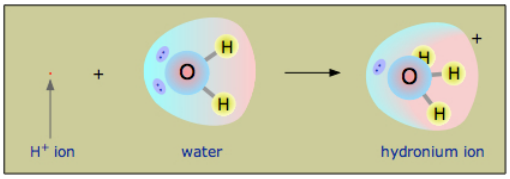
Learning Objectives

- Explain the characterization of aqueous solutions as acidic, basic, or neutral
- To know the relationship between acid or base strength and the magnitude of K_a, K_b, pK_a, and pK_b.
- Express hydronium and hydroxide ion concentrations on the pH and pOH scales
- Perform calculations relating pH and pOH

We now turn our attention to acid–base reactions to see how the concepts of chemical equilibrium and equilibrium constants can deepen our understanding of this kind of chemical behavior. We begin with a qualitative description of acid–base equilibria in terms of the Brønsted–Lowry model and then proceed to a quantitative description the following sections.

Free Hydrogen Ions do not Exist in Water

Owing to the overwhelming excess of H_2O molecules in aqueous solutions, a bare hydrogen ion has no chance of surviving in water. The hydrogen ion in aqueous solution is no more than a proton, a bare nucleus. Although it carries only a single unit of positive charge, this charge is concentrated into a volume of space that is only about a hundred-millionth as large as the volume occupied by the smallest atom. (Think of a pebble sitting in the middle of a sports stadium!) The resulting extraordinarily high *charge density* of the proton strongly attracts it to any part of a nearby atom or molecule in which there is an excess of negative charge. In the case of water, this will be the lone pair (unshared) electrons of the oxygen atom; the tiny proton will be buried within the lone pair and will form a shared-electron (coordinate) bond with it, creating a *hydronium ion*, H_3O^+. In a sense, H_2O is acting as a base here, and the product H_3O^+ is the conjugate acid of water:



Although other kinds of dissolved ions have water molecules bound to them more or less tightly, the interaction between H^+ and H_2O is so strong that writing "$H^+(aq)$" hardly does it justice, although it is formally correct. The formula H_3O^+ more adequately conveys the sense that it is both a molecule in its own right, and is also the conjugate acid of water. However, the equation

$$HA \rightarrow H^+ + A^-$$

is so much easier to write that chemists still use it to represent acid-base reactions in contexts in which the proton donor-acceptor mechanism does not need to be emphasized. Thus it is permissible to talk about "hydrogen ions" and use the formula H^+ in writing chemical equations as long as you remember that they are not to be taken literally in the context of aqueous solutions.

Interestingly, experiments indicate that the proton does not stick to a single H_2O molecule, but changes partners many times per second. This molecular promiscuity, a consequence of the uniquely small size and mass the proton, allows it to move through the solution by rapidly hopping from one H_2O molecule to the next, creating a new H_3O^+ ion as it goes. The overall effect is the same as if the H_3O^+ ion itself were moving. Similarly, a hydroxide ion, which can be considered to be a "proton hole" in the water, serves as a landing point for a proton from another H_2O molecule, so that the OH^- ion hops about in the same way.

The **hydronium** ion is an important factor when dealing with chemical reactions that occur in aqueous solutions. Because hydronium and hydroxide ions can "move without actually moving" and thus without having to plow their way through the solution by shoving aside water molecules as do other ions, solutions which are acidic or alkaline have extraordinarily high *electrical conductivities*. The hydronium ion has a trigonal pyramidal geometry and is composed of three hydrogen atoms and one oxygen atom. There is a lone pair of electrons on the oxygen giving it this shape. The bond angle between the atoms is 113 degrees.

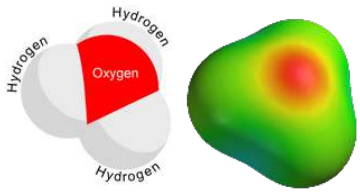


Figure 14.1.2.1. The picture above illustrates the electron density of hydronium. The red area represents oxygen; this is the area where the electrostatic potential is the highest and the electrons are most dense.

As H^+ ions are formed, they bond with H_2O molecules in the solution to form H_3O^+ (the hydronium ion). This is because hydrogen ions do not exist in aqueous solutions, but take the form the hydronium ion, H_3O^+. A reversible reaction is one in which the reaction goes both ways. In other words, the water molecules dissociate while the OH^- ions combine with the H^+ ions to form water. Water has the ability to attract H^+ ions because it is a polar molecule. This means that it has a partial charge, in this case the charge is negative. The partial charge is caused by the fact that oxygen is more electronegative than hydrogen. This means that in the bond between hydrogen and oxygen, oxygen "pulls" harder on the shared electrons thus causing a partial negative charge on the molecule and causing it to be attracted to the positive charge of H^+ to form **hydronium**. Another way to describe why the water molecule is considered polar is through the concept of dipole moment. The electron geometry of water is tetrahedral and the molecular geometry is bent. This bent geometry is asymmetrical, which causes the molecule to be polar and have a dipole moment, resulting in a partial charge.

The pH Scale

As discussed earlier, hydronium and hydroxide ions are present both in pure water and in all aqueous solutions, and their concentrations are inversely proportional as determined by the ion product of water (K_w). The concentrations of these ions in a solution are often critical determinants of the solution's properties and the chemical behaviors of its other solutes, and specific vocabulary has been developed to describe these concentrations in relative terms. A solution is neutral if it contains equal concentrations of hydronium and hydroxide ions; acidic if it contains a greater concentration of hydronium ions than hydroxide ions; and basic if it contains a lesser concentration of hydronium ions than hydroxide ions.

A common means of expressing quantities, the values of which may span many orders of magnitude, is to use a logarithmic scale. One such scale that is very popular for chemical concentrations and equilibrium constants is based on the p-function, defined as shown where "X" is the quantity of interest and "log" is the base-10 logarithm:

$$\mathrm{pX} = -\log \mathrm{X} \tag{14.1.2.1}$$

The pH of a solution is therefore defined as shown here, where $[H_3O^+]$ is the molar concentration of hydronium ion in the solution:

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] \tag{14.1.2.2}$$

Rearranging this equation to isolate the hydronium ion molarity yields the equivalent expression:

$$[\mathrm{H_3O^+}] = 10^{-\mathrm{pH}} \tag{14.1.2.3}$$

Likewise, the hydroxide ion molarity may be expressed as a p-function, or pOH:

$$\mathrm{pOH} = -\log[\mathrm{OH^-}] \tag{14.1.2.4}$$

or

$$[\mathrm{OH^-}] = 10^{-\mathrm{pOH}} \tag{14.1.2.5}$$

Finally, the relation between these two ion concentration expressed as p-functions is easily derived from the K_w expression:

$$\begin{aligned} K_\mathrm{w} &= [\mathrm{H_3O^+}][\mathrm{OH^-}] \\ -\log K_\mathrm{w} &= -\log([H_3O^+][OH^-]) \\ &= -\log[H_3O^+] + -\log[OH^-] \\ pK_w &= pH + pOH \end{aligned}$$

At 25 °C, the value of K_w is 1.0×10^{-14} and so:

$$14.00 = \text{pH} + \text{pOH} \tag{14.1.2.6}$$

The hydronium ion molarity in pure water (or any neutral solution) is $1.0 \times 10^{-7}\ M$ at 25 °C. The pH and pOH of a neutral solution at this temperature are therefore:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(1.0 \times 10^{-7}) = 7.00 \tag{14.1.2.7}$$

$$\text{pOH} = -\log[\text{OH}^-] = -\log(1.0 \times 10^{-7}) = 7.00 \tag{14.1.2.8}$$

And so, at this temperature, acidic solutions are those with hydronium ion molarities greater than $1.0 \times 10^{-7}\ M$ and hydroxide ion molarities less than $1.0 \times 10^{-7}\ M$ (corresponding to pH values less than 7.00 and pOH values greater than 7.00). Basic solutions are those with hydronium ion molarities less than $1.0 \times 10^{-7}\ M$ and hydroxide ion molarities greater than $1.0 \times 10^{-7}\ M$ (corresponding to pH values greater than 7.00 and pOH values less than 7.00).

Since the autoionization constant K_w is temperature dependent, these correlations between pH values and the acidic/neutral/basic adjectives will be different at temperatures other than 25 °C. For example, the hydronium molarity of pure water at 80 °C is 4.9 × 10^{-7} M, which corresponds to pH and pOH values of:

$$\begin{aligned} \text{pH} &= -\log[H_3O^+] \\ &= -\log(4.9 \times 10^{-7}) \\ &= 6.31 \\ \text{pOH} &= -\log[OH^-] \\ &= -\log(4.9 \times 10^{-7}) \\ &= 6.31 \end{aligned}$$

At this temperature, then, neutral solutions exhibit pH = pOH = 6.31, acidic solutions exhibit pH less than 6.31 and pOH greater than 6.31, whereas basic solutions exhibit pH greater than 6.31 and pOH less than 6.31. This distinction can be important when studying certain processes that occur at nonstandard temperatures, such as enzyme reactions in warm-blooded organisms. Unless otherwise noted, references to pH values are presumed to be those at standard temperature (25 °C) (Table 14.1.2.1).

Table 14.1.2.1: Summary of Relations for Acidic, Basic and Neutral Solutions

Classification	Relative Ion Concentrations	pH at 25 °C	pH at 80 °C
acidic	$[H_3O^+] > [OH^-]$	pH < 7	pH < 6.31
neutral	$[H_3O^+] = [OH^-]$	pH = 7	pH = 6.31
basic	$[H_3O^+] < [OH^-]$	pH > 7	pH > 6.31

Figure 14.1.2.2 shows the relationships between $[H_3O^+]$, $[OH^-]$, pH, and pOH, and gives values for these properties at standard temperatures for some common substances.

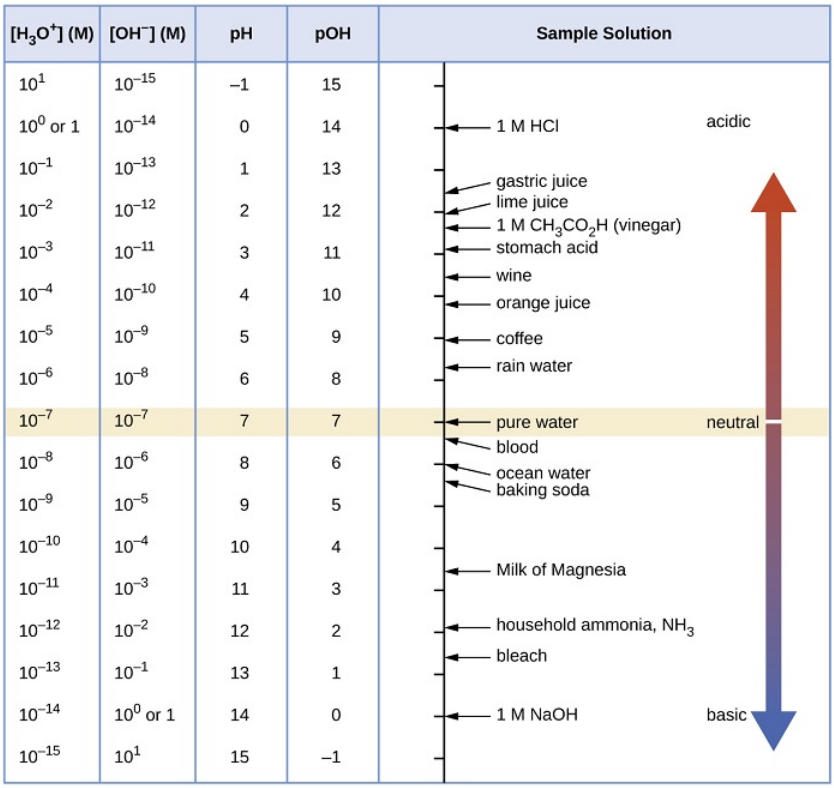


Figure 14.1.2.2: The pH and pOH scales represent concentrations of $[H_3O^+]$ and OH^-, respectively. The pH and pOH values of some common substances at standard temperature (25 °C) are shown in this chart.

✔ Example 14.1.2.1: 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

$$\begin{aligned} \text{pH} &= -\log[H_3O^+] \\ &= -\log(1.2 \times 10^{-3}) \\ &= -(-2.92) = 2.92 \end{aligned}$$

? Exercise 14.1.2.1

Water exposed to air contains carbonic acid, H_2CO_3, due to the reaction between carbon dioxide and water:

$$CO_{2(aq)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)}$$

Air-saturated water has a hydronium ion concentration caused by the dissolved CO_2 of $2.0 \times 10^{-6}\ M$, about 20-times larger than that of pure water. Calculate the pH of the solution at 25 °C.

Answer

5.70

✔ Example 14.1.2.2: Calculation of Hydronium Ion Concentration from pH

Calculate the hydronium ion concentration of blood, the pH of which is 7.3.

Solution

$$\begin{aligned} \mathrm{pH} = -\log[\mathrm{H_3O^+}] &= 7.3 \\ [\mathrm{H_3O^+}] &= 10^{-7.3} \\ [\mathrm{H_3O^+}] &= 5 \times 10^{-8}\ M \end{aligned}$$

(On a calculator take the antilog, or the "inverse" log, of −7.3, or calculate $10^{-7.3}$.)

? Exercise 14.1.2.2A

Calculate the hydronium ion concentration of a solution with a pH of −1.07.

Answer

12 M

This uses the definition of pH that we commonly use:

$$pH = -\log[H_3O^+]$$

So for this solution:

$$\begin{aligned} \mathrm{pH} = -\log[\mathrm{H_3O^+}] &= -1.07 \\ [\mathrm{H_3O^+}] &= 10^{+1.07} \\ &= 12\ (\text{with significant figure}) \end{aligned}$$

However, at this high concentration, the solution will be non-ideal and we have to use the proper definition in terms of hydronium activities

$$pH = -\log a\{H_3O^+\}$$

See this module for more details.

? Exercise 14.1.2.2B

The ionization constant of water Kw at 37 °C is 2.42×10^{-14}. What is the pH for a neutral solution at this human physiological temperature? Is the water acidic, basic or neutral?

Answer

$$\mathrm{Kw} = [\mathrm{H_3O^+}][\mathrm{OH^-}] = 2.42 \times 10^{-14}$$

and

$$\begin{aligned} [\mathrm{H_3O^+}] = [\mathrm{OH^-}] &= \sqrt{2.42 \times 10^{-14}} \\ &= 1.55 \times 10^{-7} \end{aligned}$$

$$pH = -\log[H_3O^+] = -\log 1.55 \times 10^{-7} = 6.81 \qquad (14.1.2.9)$$

If we use the definition of acidic systems like in Figure 14.1.2.2 then we would (incorrectly) argue the solution is acidic. However, since $[\mathrm{OH^-}] = [\mathrm{H_3O^+}]$, the solution is still neutral. This is only a strange idea, if one ignores the temperature dependence of Kw.

Environmental Science

Normal rainwater has a pH between 5 and 6 due to the presence of dissolved CO_2 which forms carbonic acid:

$$\mathrm{H_2O_{(l)} + CO_{2(g)} \longrightarrow H_2CO_{3(aq)}} \qquad (14.1.2.10)$$

$$\mathrm{H_2CO_{3(aq)} \rightleftharpoons H^+_{(aq)} + HCO^-_{3(aq)}} \qquad (14.1.2.11)$$

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:

$$\mathrm{H_2O_{(l)} + SO_{3(g)} \longrightarrow H_2SO_{4(aq)}} \tag{14.1.2.12}$$

$$\mathrm{H_2SO_{4(aq)} \longrightarrow H^+_{(aq)} + HSO^-_{4(aq)}} \tag{14.1.2.13}$$

Carbon dioxide is naturally present in the atmosphere because we and most other organisms produce it as a waste product of metabolism. Carbon dioxide is also formed when fires release carbon stored in vegetation or when we burn wood or fossil fuels. Sulfur trioxide in the atmosphere is naturally produced by volcanic activity, but it also stems from burning fossil fuels, which have traces of sulfur, and from the process of "roasting" ores of metal sulfides in metal-refining processes. Oxides of nitrogen are formed in internal combustion engines where the high temperatures make it possible for the nitrogen and oxygen in air to chemically combine.



Figure 14.1.2.3 (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)

Acid rain is a particular problem in industrial areas where the products of combustion and smelting are released into the air without being stripped of sulfur and nitrogen oxides. In North America and Europe until the 1980s, it was responsible for the destruction of forests and freshwater lakes, when the acidity of the rain actually killed trees, damaged soil, and made lakes uninhabitable for all but the most acid-tolerant species. Acid rain also corrodes statuary and building facades that are made of marble and limestone (Figure 14.1.2.3). 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.

The acidity of a solution is typically assessed experimentally by measurement of its pH. The pOH of a solution is not usually measured, as it is easily calculated from an experimentally determined pH value. The pH of a solution can be directly measured using a pH meter (Figure 14.1.2.4).

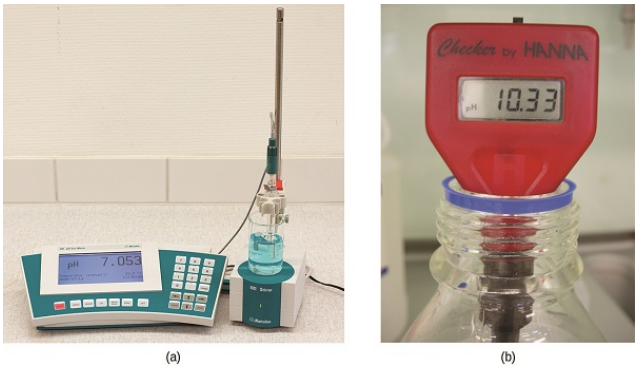


Figure 14.1.2.4 (a) A research-grade pH meter used in a laboratory can have a resolution of 0.001 pH units, an accuracy of ± 0.002 pH units, and may cost in excess of $1000. (b) A portable pH meter has lower resolution (0.01 pH units), lower accuracy (± 0.2 pH units), and a far lower price tag. (credit b: modification of work by Jacopo Werther).

Example 14.1.2.3: Calculation of pOH

What are the pOH and the pH of a 0.0125-M solution of potassium hydroxide, KOH at 25 °C?

Solution

Potassium hydroxide is a highly soluble ionic compound and completely dissociates when dissolved in dilute solution, yielding $[OH^-]$ = 0.0125 M:

$$\text{pOH} = -\log[\text{OH}^-] = -\log 0.0125 \tag{14.1.2.14}$$

$$= -(-1.903) = 1.903 \tag{14.1.2.15}$$

The pH can be found from the pOH:

$$\text{pH} + \text{pOH} = 14.00 \tag{14.1.2.16}$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 1.903 = 12.10 \tag{14.1.2.17}$$

Exercise 14.1.2.3

The hydronium ion concentration of vinegar is approximately $4 \times 10^{-3}\ M$ at 25 °C. What are the corresponding values of pOH and pH?

Answer

pOH = 11.6, pH = 2.4

The pH of a solution may also be visually estimated using colored indicators (Figure 14.1.2.5).



Figure 14.1.2.5 (a) A universal indicator assumes a different color in solutions of different pH values. Thus, it can be added to a solution to determine the pH of the solution. The eight vials each contain a universal indicator and 0.1-M solutions of progressively weaker acids: HCl (pH = l), CH_3CO_2H (pH = 3), and NH_4Cl (pH = 5), deionized water, a neutral substance (pH = 7); and 0.1-M solutions of the progressively stronger bases: KCl (pH = 7), aniline, $C_6H_5NH_2$ (pH = 9), NH_3 (pH = 11), and NaOH (pH = 13). (b) pH paper contains a mixture of indicators that give different colors in solutions of differing pH values. (credit: modification of work by Sahar Atwa).

Summary

The concentration of hydronium ion in a solution of an acid in water is greater than $1.0 \times 10^{-7}\ M$ at 25 °C. The concentration of hydroxide ion in a solution of a base in water is greater than $1.0 \times 10^{-7}\ M$ at 25 °C. The concentration of H_3O^+ in a solution can be expressed as the pH of the solution; $\text{pH} = -\log \text{H}_3\text{O}^+$. The concentration of OH^- can be expressed as the pOH of the solution: $\text{pOH} = -\log[\text{OH}^-]$. In pure water, pH = 7.00 and pOH = 7.00

Key Equations

- $\text{pH} = -\log[\text{H}_3\text{O}^+]$
- $\text{pOH} = -\log[\text{OH}^-]$
- $[H_3O^+] = 10^{-\text{pH}}$
- $[OH^-] = 10^{-\text{pOH}}$
- pH + pOH = pK_w = 14.00 at 25 °C

Glossary

acidic

describes a solution in which $[H_3O^+] > [OH^-]$

basic

describes a solution in which $[H_3O^+] < [OH^-]$

neutral

describes a solution in which $[H_3O^+] = [OH^-]$

pH

logarithmic measure of the concentration of hydronium ions in a solution

pOH

logarithmic measure of the concentration of hydroxide ions in a solution

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14.1.3: Acid and Base Strength

Learning Objectives

- Assess the relative strengths of acids and bases according to their ionization constants
- Rationalize trends in acid–base strength in relation to molecular structure
- Carry out equilibrium calculations for weak acid–base systems

We can rank the strengths of acids by the extent to which they ionize in aqueous solution. The reaction of an acid with water is given by the general expression:

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq) \tag{14.1.3.1}$$

Water is the base that reacts with the acid HA, $\mathrm{A^-}$ is the conjugate base of the acid HA, and the hydronium ion is the conjugate acid of water. A strong acid yields 100% (or very nearly so) of $\mathrm{H_3O^+}$ and $\mathrm{A^-}$ when the acid ionizes in water; Figure 14.1.3.1lists several strong acids. A weak acid gives small amounts of $\mathrm{H_3O^+}$ and $\mathrm{A^-}$.

Figure 14.1.3.1: Some of the common strong acids and bases are listed here.

Six Strong Acids		Six Strong Bases	
$\mathrm{HClO_4}$	perchloric acid	LiOH	lithium hydroxide
HCl	hydrochloric acid	NaOH	sodium hydroxide
HBr	hydrobromic acid	KOH	potassium hydroxide
HI	hydroiodic acid	$\mathrm{Ca(OH)_2}$	calcium hydroxide
$\mathrm{HNO_3}$	nitric acid	$\mathrm{Sr(OH)_2}$	strontium hydroxide
$\mathrm{H_2SO_4}$	sulfuric acid	$\mathrm{Ba(OH)_2}$	barium hydroxide

The relative strengths of acids may be determined by measuring their equilibrium constants in aqueous solutions. In solutions of the same concentration, stronger acids ionize to a greater extent, and so yield higher concentrations of hydronium ions than do weaker acids. The equilibrium constant for an acid is called the acid-ionization constant, K_a. For the reaction of an acid HA:

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq) \tag{14.1.3.2}$$

we write the equation for the ionization constant as:

$$K_\mathrm{a} = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]} \tag{14.1.3.3}$$

where the concentrations are those at equilibrium. Although water is a reactant in the reaction, it is also the solvent. If the solution is assumed to be dilute, the activity of the water is approximated by the activity of pure water, which is defined as having a value of 1. 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. Thus a stronger acid has a larger ionization constant than does a weaker acid. The ionization constants increase as the strengths of the acids increase.

The following data on acid-ionization constants indicate the order of acid strength: $\mathrm{CH_3CO_2H} < \mathrm{HNO_2} < \mathrm{HSO_4^-}$

$$\mathrm{CH_3CO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CH_3CO_2^-}(aq) \qquad K_\mathrm{a} = 1.8 \times 10^{-5}$$

$$\mathrm{HNO_2}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{NO_2^-}(aq) \qquad K_\mathrm{a} = 4.6 \times 10^{-4}$$

$$\mathrm{HSO_4^-}(aq) + \mathrm{H_2O}(aq) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{SO_4^{2-}}(aq) \qquad K_\mathrm{a} = 1.2 \times 10^{-2}$$

Another measure of the strength of an acid is its *percent ionization*. The percent ionization of a weak acid is the ratio of the concentration of the ionized acid to the initial acid concentration, times 100:

$$\% \text{ ionization} = \frac{[H_3O^+]_{eq}}{[HA]_0} \times 100\% \tag{14.1.3.4}$$

Because the ratio includes the initial concentration, the percent ionization for a solution of a given weak acid varies depending on the original concentration of the acid, and actually decreases with increasing acid concentration.

Example 14.1.3.1: 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:

$$\frac{[H_3O^+]_{eq}}{[HNO_2]_0} \times 100$$

The chemical equation for the dissociation of the nitrous acid is:

$$HNO_2(aq) + H_2O(l) \rightleftharpoons NO_2^-(aq) + H_3O^+(aq).$$

Since $10^{-pH} = [H_3O^+]$, we find that $10^{-2.09} = 8.1 \times 10^{-3}\ M$, so that percent ionization (Equation 14.1.3.4) is:

$$\frac{8.1 \times 10^{-3}}{0.125} \times 100 = 6.5\%$$

Remember, the logarithm 2.09 indicates a hydronium ion concentration with only two significant figures.

Exercise 14.1.3.1

Calculate the percent ionization of a 0.10 *M* solution of acetic acid with a pH of 2.89.

Answer

1.3% ionized

We can rank the strengths of bases by their tendency to form hydroxide ions in aqueous solution. The reaction of a Brønsted-Lowry base with water is given by:

$$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq) \tag{14.1.3.5}$$

Water is the acid that reacts with the base, HB^+ is the conjugate acid of the base B, and the hydroxide ion is the conjugate base of water. A strong base yields 100% (or very nearly so) of OH^- and HB^+ when it reacts with water; Figure 14.1.3.1 lists several strong bases. A weak base yields a small proportion of hydroxide ions. Soluble ionic hydroxides such as NaOH are considered strong bases because they dissociate completely when dissolved in water.

As we did with acids, we can measure the relative strengths of bases by measuring their base-ionization constant (K_b) in aqueous solutions. In solutions of the same concentration, stronger bases ionize to a greater extent, and so yield higher hydroxide ion concentrations than do weaker bases. A stronger base has a larger ionization constant than does a weaker base. For the reaction of a base, B:

$$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq), \tag{14.1.3.6}$$

we write the equation for the ionization constant as:

$$K_b = \frac{[HB^+][OH^-]}{[B]} \tag{14.1.3.7}$$

where the concentrations are those at equilibrium. Again, we do not include $[H_2O]$ in the equation because water is the solvent. The chemical reactions and ionization constants of the three bases shown are:

$$\mathrm{NO_2^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{HNO_2}(aq) + \mathrm{OH^-}(aq) \qquad K_\mathrm{b} = 2.17 \times 10^{-11}$$

$$\mathrm{CH_3CO_2^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{CH_3CO_2H}(aq) + \mathrm{OH^-}(aq) \qquad K_\mathrm{b} = 5.6 \times 10^{-10}$$

$$\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{NH_4^+}(aq) + \mathrm{OH^-}(aq) \qquad K_\mathrm{b} = 1.8 \times 10^{-5}$$

A table of ionization constants of weak bases appears in Table E2. As with acids, percent ionization can be measured for basic solutions, but will vary depending on the base ionization constant and the initial concentration of the solution.

Consider the ionization reactions for a conjugate acid-base pair, $\mathrm{HA - A^-}$:

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq) \tag{14.1.3.8}$$

with $K_\mathrm{a} = \dfrac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$.

$$\mathrm{A^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{OH^-}(aq) + \mathrm{HA}(aq) \tag{14.1.3.9}$$

with $K_\mathrm{b} = \dfrac{[\mathrm{HA}][\mathrm{OH}]}{[\mathrm{A^-}]}$.

Adding these two chemical equations yields the equation for the autoionization for water:

$$\cancel{\mathrm{HA}(aq)} + \mathrm{H_2O}(l) + \cancel{\mathrm{A^-}(aq)} + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \cancel{\mathrm{A^-}(aq)} + \mathrm{OH^-}(aq) + \cancel{\mathrm{HA}(aq)}$$

$$2\,\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{OH^-}(aq)$$

As shown in the previous chapter on equilibrium, the K expression for a chemical equation derived from adding two or more other equations is the mathematical product of the other equations' K expressions. Multiplying the mass-action expressions together and cancelling common terms, we see that:

$$K_\mathrm{a} \times K_\mathrm{b} = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]} \times \frac{[\mathrm{HA}][\mathrm{OH^-}]}{[\mathrm{A^-}]} = [\mathrm{H_3O^+}][\mathrm{OH^-}] = K_\mathrm{w} \tag{14.1.3.10}$$

For example, the acid ionization constant of acetic acid ($\mathrm{CH_3COOH}$) is 1.8×10^{-5}, and the base ionization constant of its conjugate base, acetate ion ($\mathrm{CH_3COO^-}$), is 5.6×10^{-10}. The product of these two constants is indeed equal to K_w:

$$K_\mathrm{a} \times K_\mathrm{b} = (1.8 \times 10^{-5}) \times (5.6 \times 10^{-10}) = 1.0 \times 10^{-14} = K_\mathrm{w} \tag{14.1.3.11}$$

The extent to which an acid, HA, donates protons to water molecules depends on the strength of the conjugate base, $\mathrm{A^-}$, of the acid. If $\mathrm{A^-}$ is a strong base, any protons that are donated to water molecules are recaptured by $\mathrm{A^-}$. Thus there is relatively little $\mathrm{A^-}$ and $\mathrm{H_3O^+}$ in solution, and the acid, HA, is weak. If $\mathrm{A^-}$ is a weak base, water binds the protons more strongly, and the solution contains primarily $\mathrm{A^-}$ and $\mathrm{H_3O^+}$—the acid is strong. Strong acids form very weak conjugate bases, and weak acids form stronger conjugate bases (Figure 14.1.3.2).

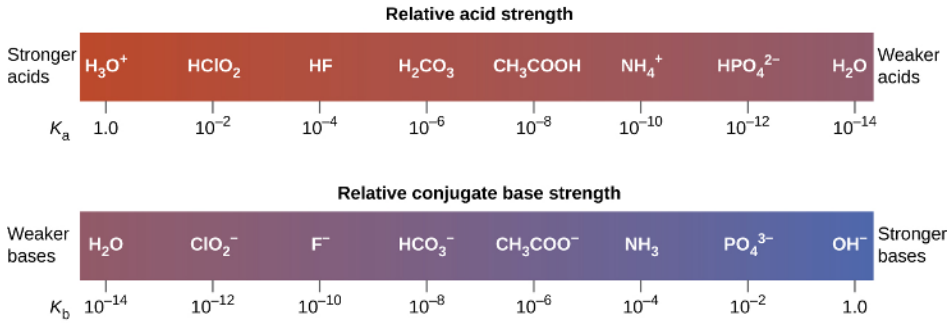


Figure 14.1.3.2: This diagram shows the relative strengths of conjugate acid-base pairs, as indicated by their ionization constants in aqueous solution.

Figure 14.1.3.3 lists a series of acids and bases in order of the decreasing strengths of the acids and the corresponding increasing strengths of the bases. The acid and base in a given row are conjugate to each other.

The first six acids in Figure 14.1.3.3 are the most common strong acids. These acids are completely dissociated in aqueous solution. The conjugate bases of these acids are weaker bases than water. When one of these acids dissolves in water, their protons are completely transferred to water, the stronger base.

Those acids that lie between the hydronium ion and water in Figure 14.1.3.3 form conjugate bases that can compete with water for possession of a proton. Both hydronium ions and nonionized acid molecules are present in equilibrium in a solution of one of these acids. Compounds that are weaker acids than water (those found below water in the column of acids) in Figure 14.1.3.3 exhibit no observable acidic behavior when dissolved in water. Their conjugate bases are stronger than the hydroxide ion, and if any conjugate base were formed, it would react with water to re-form the acid.

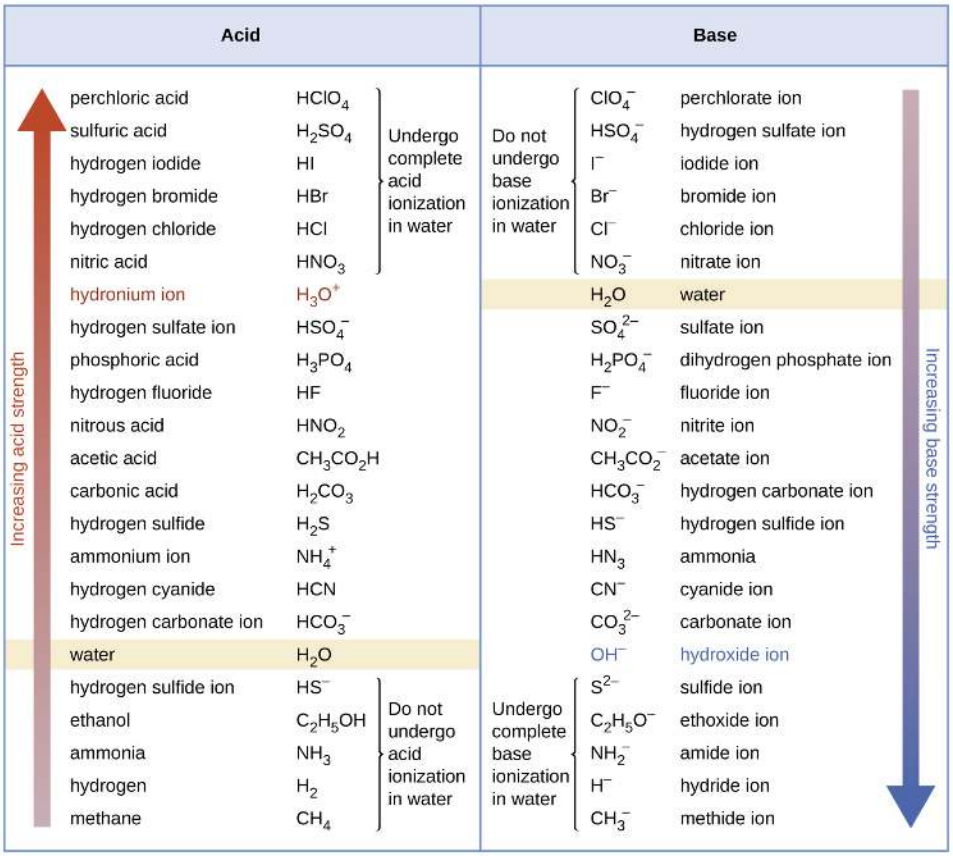


Figure 14.1.3.3: The chart shows the relative strengths of conjugate acid-base pairs.

The extent to which a base forms hydroxide ion in aqueous solution depends on the strength of the base relative to that of the hydroxide ion, as shown in the last column in Figure 14.1.3.3 A strong base, such as one of those lying below hydroxide ion, accepts protons from water to yield 100% of the conjugate acid and hydroxide ion. Those bases lying between water and hydroxide ion accept protons from water, but a mixture of the hydroxide ion and the base results. Bases that are weaker than water (those that lie above water in the column of bases) show no observable basic behavior in aqueous solution.

✔ Example 14.1.3.2: The Product $K_a \times K_b = K_w$

Use the K_b for the nitrite ion, NO_2^-, to calculate the K_a for its conjugate acid.

Solution

K_b for NO_2^- is given in this section as 2.17×10^{-11}. The conjugate acid of NO_2^- is HNO_2; K_a for HNO_2 can be calculated using the relationship:

$$K_a \times K_b = 1.0 \times 10^{-14} = K_w$$

Solving for K_a, we get:

$$K_a = \frac{K_w}{K_b}$$
$$= \frac{1.0 \times 10^{-14}}{2.17 \times 10^{-11}}$$
$$= 4.6 \times 10^{-4}$$

This answer can be verified by finding the K_a for HNO_2 in Table E1

? Exercise 14.1.3.2

We can determine the relative acid strengths of NH_4^+ and HCN by comparing their ionization constants. The ionization constant of HCN is given in Table E1 as 4.9×10^{-10}. The ionization constant of NH_4^+ is not listed, but the ionization constant of its conjugate base, NH_3, is listed as 1.8×10^{-5}. Determine the ionization constant of NH_4^+, and decide which is the stronger acid, HCN or NH_4^+.

Answer

NH_4^+ is the slightly stronger acid (K_a for $NH_4^+ = 5.6 \times 10^{-10}$).

Summary

The strengths of Brønsted-Lowry acids and bases in aqueous solutions can be determined by their acid or base ionization constants. Stronger acids form weaker conjugate bases, and weaker acids form stronger conjugate bases. Thus strong acids are completely ionized in aqueous solution because their conjugate bases are weaker bases than water. Weak acids are only partially ionized because their conjugate bases are strong enough to compete successfully with water for possession of protons. Strong bases react with water to quantitatively form hydroxide ions. Weak bases give only small amounts of hydroxide ion.

Key Equations

- $K_a = \frac{[H_3O^+][A^-]}{[HA]}$
- $K_b = \frac{[HB^+][OH^-]}{[B]}$
- $K_a \times K_b = 1.0 \times 10^{-14} = K_w \text{ (at room temperature)}$

Glossary

acid ionization constant (K_a)
equilibrium constant for the ionization of a weak acid

base ionization constant (K_b)
equilibrium constant for the ionization of a weak base

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

percent ionization
ratio of the concentration of the ionized acid to the initial acid concentration, times 100

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14.1.4: Equilibria Involving Weak Acids and Bases

Learning Objectives

- Rationalize trends in acid–base strength in relation to molecular structure
- Carry out equilibrium calculations for weak acid–base systems

Many acids and bases are weak; that is, they do not ionize fully in aqueous solution. A solution of a weak acid in water is a mixture of the nonionized acid, hydronium ion, and the conjugate base of the acid, with the nonionized acid present in the greatest concentration. Thus, a weak acid increases the hydronium ion concentration in an aqueous solution (but not as much as the same amount of a strong acid).

Acetic acid (CH_3CO_2H) is a weak acid. When we add acetic acid to water, it ionizes to a small extent according to the equation:

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$$

giving an equilibrium mixture with most of the acid present in the nonionized (molecular) form. This equilibrium, like other equilibria, is dynamic; acetic acid molecules donate hydrogen ions to water molecules and form hydronium ions and acetate ions at the same rate that hydronium ions donate hydrogen ions to acetate ions to reform acetic acid molecules and water molecules. We can tell by measuring the pH of an aqueous solution of known concentration that only a fraction of the weak acid is ionized at any moment (Figure 14.1.4.1). The remaining weak acid is present in the nonionized form.

For acetic acid, at equilibrium:

$$K_a = \frac{[H_3O^+][CH_3CO_2^-]}{[CH_3CO_2H]} = 1.8 \times 10^{-5}$$



Figure 14.1.4.1: pH paper indicates that a 0.l-M solution of HCl (beaker on left) has a pH of 1. The acid is fully ionized and $[H_3O^+]$ = 0.1 M. A 0.1-M solution of CH_3CO_2H (beaker on right) has a pH of 3 ($[H_3O^+]$ = 0.001 M) because the weak acid CH_3CO_2H is only partially ionized. In this solution, $[H_3O^+] < [CH_3CO_2H]$. (credit: modification of work by Sahar Atwa)

Table 14.1.4.1: Ionization Constants of Some Weak Acids

Ionization Reaction	K_a at 25 °C
$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$	1.2×10^{-2}
$HF + H_2O \rightleftharpoons H_3O^+ + F^-$	3.5×10^{-4}
$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$	4.6×10^{-4}
$HNCO + H_2O \rightleftharpoons H_3O^+ + NCO^-$	2×10^{-4}
$HCO_2H + H_2O \rightleftharpoons H_3O^+ + HCO_2^-$	1.8×10^{-4}
$CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-$	1.8×10^{-5}
$HClO + H_2O \rightleftharpoons H_3O^+ + ClO^-$	2.9×10^{-8}
$HBrO + H_2O \rightleftharpoons H_3O^+ + BrO^-$	2.8×10^{-9}

Ionization Reaction	K_a at 25 °C
$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$	4.9×10^{-10}

Table 14.1.4.1 gives the ionization constants for several weak acids; additional ionization constants can be found in Table E1.

At equilibrium, a solution of a weak base in water is a mixture of the nonionized base, the conjugate acid of the weak base, and hydroxide ion with the nonionized base present in the greatest concentration. Thus, a weak base increases the hydroxide ion concentration in an aqueous solution (but not as much as the same amount of a strong base).

For example, a solution of the weak base trimethylamine, $(CH_3)_3N$, in water reacts according to the equation:

$$(CH_3)_3N(aq) + H_2O(l) \rightleftharpoons (CH_3)_3NH^+(aq) + OH^-(aq)$$

This gives an equilibrium mixture with most of the base present as the nonionized amine. This equilibrium is analogous to that described for weak acids.

We can confirm by measuring the pH of an aqueous solution of a weak base of known concentration that only a fraction of the base reacts with water (Figure 14.1.4.2). The remaining weak base is present as the unreacted form. The equilibrium constant for the ionization of a weak base, K_b, is called the **ionization constant** of the weak base, and is equal to the reaction quotient when the reaction is at equilibrium. For trimethylamine, at equilibrium:

$$K_b = \frac{[(CH_3)_3NH^+][OH^-]}{[(CH_3)_3N]}$$



Figure 14.1.4.2: pH paper indicates that a 0.1-M solution of NH_3 (left) is weakly basic. The solution has a pOH of 3 ($[OH^-]$ = 0.001 M) because the weak base NH_3 only partially reacts with water. A 0.1-M solution of NaOH (right) has a pOH of 1 because NaOH is a strong base (credit: modification of work by Sahar Atwa).

The ionization constants of several weak bases are given in Table 14.1.4.2 and Table E2.

Table 14.1.4.2: Ionization Constants of Some Weak Bases

Ionization Reaction	**K_b at 25 °C**
$(CH_3)_2NH + H_2O \rightleftharpoons (CH_3)_2NH_2^+ + OH^-$	5.9×10^{-4}
$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$	4.4×10^{-4}
$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$	6.3×10^{-5}
$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	1.8×10^{-5}
$C_6H_5NH_2 + H_2O \rightleftharpoons C_6N_5NH_3^+ + OH^-$	4.3×10^{-10}

Example 14.1.4.3: Determination of K_a from Equilibrium Concentrations

Acetic acid is the principal ingredient in vinegar; that's why it tastes sour. 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?



Vinegar is a solution of acetic acid, a weak acid. (credit: modification of work by “HomeSpot HQ”/Flickr)

Solution

We are asked to calculate an equilibrium constant from equilibrium concentrations. At equilibrium, the value of the equilibrium constant is equal to the reaction quotient for the reaction:

$$\mathrm{CH_3CO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CH_3CO_2^-}(aq)$$

$$\begin{aligned} K_\mathrm{a} &= \frac{[\mathrm{H_3O^+}][\mathrm{CH_3CO_2^-}]}{[\mathrm{CH_3CO_2H}]} \\ &= \frac{(0.00118)(0.00118)}{0.0787} \\ &= 1.77 \times 10^{-5} \end{aligned}$$

? Exercise 14.1.4.3

What is the equilibrium constant for the ionization of the $\mathrm{HSO_4^-}$ ion, the weak acid used in some household cleansers:

$$\mathrm{HSO_4^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{SO_4^{2-}}(aq)$$

In one mixture of $NaHSO_4$ and Na_2SO_4 at equilibrium, $[\mathrm{H_3O^+}] = 0.027\ M$; $[\mathrm{HSO_4^-}] = 0.29\ M$; and $[\mathrm{SO_4^{2-}}] = 0.13\ M$.

Answer

K_a for $\mathrm{HSO_4^-} = 1.2 \times \times 10^{-2}$

✓ Example 14.1.4.4: Determination of K_b from Equilibrium Concentrations

Caffeine, $C_8H_{10}N_4O_2$ is a weak base. What is the value of K_b for caffeine if a solution at equilibrium has $[C_8H_{10}N_4O_2] = 0.050\ M$, $[\mathrm{C_8H_{10}N_4O_2H^+}] = 5.0 \times 10^{-3}\ M$, and $[\mathrm{OH^-}] = 2.5 \times 10^{-3}\ M$?

Solution

At equilibrium, the value of the equilibrium constant is equal to the reaction quotient for the reaction:

$$\mathrm{C_8H_{10}N_4O_2}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{C_8H_{10}N_4O_2H^+}(aq) + \mathrm{OH^-}(aq)$$

so

$$K_\mathrm{b} = \frac{[\mathrm{C_8H_{10}N_4O_2H^+}][\mathrm{OH^-}]}{[\mathrm{C_8H_{10}N_4O_2}]} = \frac{(5.0 \times 10^{-3})(2.5 \times 10^{-3})}{0.050} = 2.5 \times 10^{-4}$$

? Exercise 14.1.4.4

What is the equilibrium constant for the ionization of the $\mathrm{HPO_4^{2-}}$ ion, a weak base:

$$\mathrm{HPO_4^{2-}}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2PO_4^-}(aq) + \mathrm{OH^-}(aq)$$

In a solution containing a mixture of NaH_2PO_4 and Na_2HPO_4 at equilibrium with:

- $[OH^-] = 1.3 \times 10^{-6} M$
- $[H_2PO_4^-]$=0 · 042 M and
- $[HPO_4^{2-}]$=0 · 341 M.

Answer

K_b for $HPO_4^{2-} = 1.6 \times 10^{-7}$

Example 14.1.4.5: Determination of K_a or K_b from pH

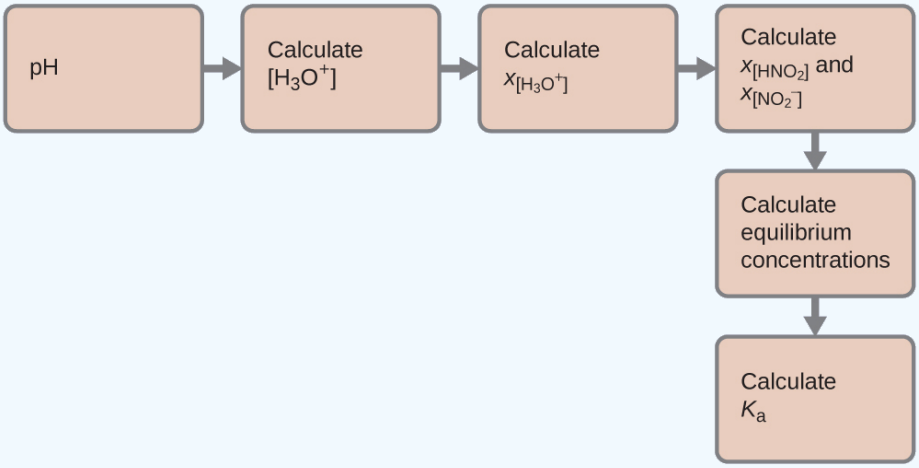
The pH of a 0.0516-*M* solution of nitrous acid, HNO_2, is 2.34. What is its K_a?

$$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$$

Solution

We determine an equilibrium constant starting with the initial concentrations of HNO_2, H_3O^+, and NO_2^- as well as one of the final concentrations, the concentration of hydronium ion at equilibrium. (Remember that pH is simply another way to express the concentration of hydronium ion.)

We can solve this problem with the following steps in which *x* is a change in concentration of a species in the reaction:



We can summarize the various concentrations and changes as shown here (the concentration of water does not appear in the expression for the equilibrium constant, so we do not need to consider its concentration):

	HNO_2 + H_2O ⇌	H_3O^+ +	NO_2^-
Initial concentration (*M*)	0.0516	~0	0
Change (*M*)	−*x*	+ *x*	*x*
Equilibrium concentration (*M*)	$[HNO_2]_i$ + (−*x*) = 0.0516 + (−*x*)	$[H_3O]^+$ + *x* ~0 + *x*	$[NO_2]^-$ + *x* 0.0046

To get the various values in the ICE (Initial, Change, Equilibrium) table, we first calculate $[H_3O^+]$, the equilibrium concentration of H_3O^+, from the pH:

$$[H_3O^+] = 10^{-2.34} = 0.0046\ M$$

The change in concentration of H_3O^+, $x_{[H_3O^+]}$, is the difference between the equilibrium concentration of H_3O^+, which we determined from the pH, and the initial concentration, $[H_3O^+]_i$. The initial concentration of H_3O^+ is its concentration in pure water, which is so much less than the final concentration that we approximate it as zero (~0).

The change in concentration of NO_2^- is equal to the change in concentration of $[H_3O^+]$. For each 1 mol of H_3O^+ that forms, 1 mol of NO_2^- forms. The equilibrium concentration of HNO_2 is equal to its initial concentration plus the change in its concentration.

Now we can fill in the ICE table with the concentrations at equilibrium, as shown here:

	HNO_2 + H_2O ⇌	H_3O^+ +	NO_2^-
Initial concentration (*M*)	0.0516	~0	0
Change (*M*)	−*x*	+ *x* = 0.0046	*x* = 0.0046
Equilibrium concentration (*M*)	0.0470	0.0046	0.0046

Finally, we calculate the value of the equilibrium constant using the data in the table:

$$K_a = \frac{[H_3O^+][NO_2^-]}{[HNO_2]} = \frac{(0.0046)(0.0046)}{(0.0470)} = 4.5 \times 10^{-4}$$

Exercise 14.1.4.5

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 14.1.4.6: Equilibrium Concentrations in a Solution of a Weak Acid

Formic acid, HCO_2H, is the irritant that causes the body's reaction to ant stings.



The pain of an ant's sting is caused by formic acid. (credit: John Tann)

What is the concentration of hydronium ion and the pH in 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

1. Determine x and equilibrium concentrations. The equilibrium expression is:

$$HCO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_2^-(aq)$$

The concentration of water does not appear in the expression for the equilibrium constant, so we do not need to consider its change in concentration when setting up the ICE table.

The table shows initial concentrations (concentrations before the acid ionizes), changes in concentration, and equilibrium concentrations follows (the data given in the problem appear in color):

	HCO_2H +	H_2O ⇌	H_3O^+
Initial concentration (*M*)	0.534	~0	0
Change (*M*)	$-x$	x	x
Equilibrium concentration (*M*)	$0.534 + (-x)$	$0 + x = x$	$0 + x = x$

2. Solve for x and the equilibrium concentrations. At equilibrium:

$$K_a = 1.8 \times 10^{-4} = \frac{[H_3O^+][HCO_2^-]}{[HCO_2H]}$$

$$= \frac{(x)(x)}{0.534 - x} = 1.8 \times 10^{-4}$$

Now solve for x. Because the initial concentration of acid is reasonably large and K_a is very small, we assume that $x << 0.534$, which *permits* us to simplify the denominator term as $(0.534 - x) = 0.534$. This gives:

$$K_a = 1.8 \times 10^{-4} = \frac{x^2}{0.534}$$

Solve for x as follows:

$$x^2 = 0.534 \times (1.8 \times 10^{-4})$$

$$= 9.6 \times 10^{-5}$$

$$x = \sqrt{9.6 \times 10^{-5}}$$

$$= 9.8 \times 10^{-3}$$

To check the assumption that x is small compared to 0.534, we calculate:

$$\frac{x}{0.534} = \frac{9.8 \times 10^{-3}}{0.534}$$

$$= 1.8 \times 10^{-2}\ (1.8\%\ \text{of}\ 0.534)$$

x is less than 5% of the initial concentration; the assumption is valid.

We find the equilibrium concentration of hydronium ion in this formic acid solution from its initial concentration and the change in that concentration as indicated in the last line of the table:

$$[H_3O^+] = 0 + x = 0 + 9.8 \times 10^{-3}\ M.$$

$$= 9.8 \times 10^{-3}\ M$$

The pH of the solution can be found by taking the negative log of the $[H_3O^+]$, so:

$$pH = -\log(9.8 \times 10^{-3}) = 2.01$$

? Exercise 14.1.4.6: acetic acid

Only a small fraction of a weak acid ionizes in aqueous solution. What is the percent ionization of acetic acid in a 0.100-*M* solution of acetic acid, CH_3CO_2H?

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq) \quad K_a = 1.8 \times 10^{-5}$$

Hint

Determine $[CH_3CO_2^-]$ at equilibrium.) Recall that the percent ionization is the fraction of acetic acid that is ionized × 100, or $\frac{[CH_3CO_2^-]}{[CH_3CO_2H]_{\text{initial}}} \times 100$.

Answer

percent ionization = 1.3%

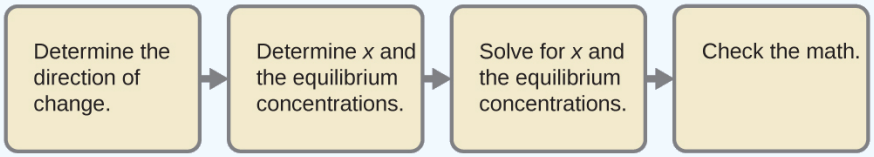
The following example shows that the concentration of products produced by the ionization of a weak base can be determined by the same series of steps used with a weak acid.

Example 14.1.4.7: Equilibrium Concentrations in a Solution of a Weak Base

Find the concentration of hydroxide ion in a 0.25-*M* solution of trimethylamine, a weak base:

$$(CH_3)_3N(aq) + H_2O(l) \rightleftharpoons (CH_3)_3NH^+(aq) + OH^-(aq) \quad K_b = 6.3 \times 10^{-5}$$

Solution This problem requires that we calculate an equilibrium concentration by determining concentration changes as the ionization of a base goes to equilibrium. The solution is approached in the same way as that for the ionization of formic acid in Example 14.1.4.6 The reactants and products will be different and the numbers will be different, but the logic will be the same:



1. Determine x and equilibrium concentrations. The table shows the changes and concentrations:

	$(CH_3)_3N$ + H_2O ⇌	$(CH_3)_3NH^+$	+ OH^-
Initial concentration (*M*)	0.25	0	~0
Change (*M*)	−*x*	*x*	*x*
Equilibrium concentration (*M*)	0.25 + (−*x*)	0 + *x*	~0 + *x*

2. Solve for x and the equilibrium concentrations. At equilibrium:

$$K_b = \frac{[(CH_3)_3NH^+][OH^-]}{[(CH_3)_3N]} = \frac{(x)(x)}{0.25 - x =} 6.3 \times 10^{-5}$$

If we assume that *x* is small relative to 0.25, then we can replace (0.25 − *x*) in the preceding equation with 0.25. Solving the simplified equation gives:

$$x = 4.0 \times 10^{-3}$$

This change is less than 5% of the initial concentration (0.25), so the assumption is justified.

Recall that, for this computation, x is equal to the equilibrium concentration of *hydroxide ion* in the solution (see earlier tabulation):

$$([OH^-] = 0 + x = x = 4.0 \times 10^{-3}\ M$$
$$= 4.0 \times 10^{-3}\ M$$

Then calculate pOH as follows:

$$pOH = -\log(4.3 \times 10^{-3}) = 2.40$$

Using the relation introduced in the previous section of this chapter:

$$pH + pOH = pK_w = 14.00$$

permits the computation of pH:

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 2.37 = 11.60$$

Check the work. A check of our arithmetic shows that $K_b = 6.3 \times 10^{-5}$.

? Exercise 14.1.4.7

a. Show that the calculation in Step 2 of this example gives an *x* of 4.3 × 10^{-3} and the calculation in Step 3 shows K_b = 6.3 × 10^{-5}.

b. Find the concentration of hydroxide ion in a 0.0325-*M* solution of ammonia, a weak base with a K_b of 1.76 × 10^{-5}.

Calculate the percent ionization of ammonia, the fraction ionized × 100, or $\frac{[NH_4^+]}{[NH_3]} \times 100\%$

Answer a

7.56×10^{-4} *M*, 2.33%

Answer b

2.33%

Some weak acids and weak bases ionize to such an extent that the simplifying assumption that *x* is small relative to the initial concentration of the acid or base is inappropriate. As we solve for the equilibrium concentrations in such cases, we will see that we cannot neglect the change in the initial concentration of the acid or base, and we must solve the equilibrium equations by using the quadratic equation.

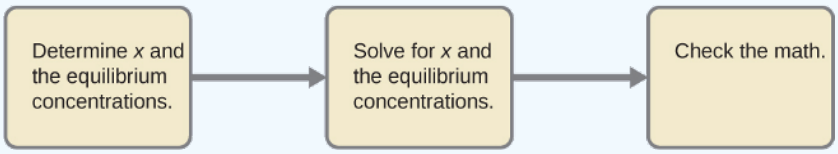
✓ Example 14.1.4.8: Equilibrium Concentrations in a Solution of a Weak Acid

Sodium bisulfate, $NaHSO_4$, is used in some household cleansers because it contains the HSO_4^- ion, a weak acid. What is the pH of a 0.50-*M* solution of HSO_4^-?

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq) \quad K_a = 1.2 \times 10^{-2}$$

Solution

We need to determine the equilibrium concentration of the hydronium ion that results from the ionization of HSO_4^- so that we can use $[H_3O^+]$ to determine the pH. As in the previous examples, we can approach the solution by the following steps:



1. Determine x and equilibrium concentrations. This table shows the changes and concentrations:

	HSO_4^- + H_2O ⇌ H_3O^+ + SO_4^{2-}			
Initial concentration (*M*)	0.50		~0	0
Change (*M*)	−*x*		*x*	*x*
Equilibrium concentration (*M*)	0.50 + (−*x*) = 0.50 − *x*)		0 + *x* = *x*	0 + *x* = *x*

2. Solve for x and the concentrations.

As we begin solving for x, we will find this is more complicated than in previous examples. As we discuss these complications we should not lose track of the fact that it is still the purpose of this step to determine the value of x.

At equilibrium:

$$K_a = 1.2 \times 10^{-2} = \frac{[H_3O^+][SO_4^{2-}]}{[HSO_4^-]} = \frac{(x)(x)}{0.50 - x}$$

If we assume that *x* is small and approximate (0.50 − *x*) as 0.50, we find:

$$x = 7.7 \times 10^{-2}$$

When we check the assumption, we confirm:

$$\frac{x}{[HSO_4^-]_i} \overset{?}{\leq} 0.05$$

which for this system is

$$\frac{x}{0.50} = \frac{7.7 \times 10^{-2}}{0.50} = 0.15(15\%)$$

The value of x is not less than 5% of 0.50, so the assumption is not valid. We need the quadratic formula to find x.

The equation:

$$K_a = 1.2 \times 10^{-2} = \frac{(x)(x)}{0.50 - x}$$

gives

$$6.0 \times 10^{-3} - 1.2 \times 10^{-2} x = x^{2+}$$

or

$$x^{2+} + 1.2 \times 10^{-2} x - 6.0 \times 10^{-3} = 0$$

This equation can be solved using the quadratic formula. For an equation of the form

$$ax^{2+} + bx + c = 0,$$

x is given by the quadratic equation:

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

In this problem, $a = 1$, $b = 1.2 \times 10^{-3}$, and $c = -6.0 \times 10^{-3}$.

Solving for x gives a negative root (which cannot be correct since concentration cannot be negative) and a positive root:

$$x = 7.2 \times 10^{-2}$$

Now determine the hydronium ion concentration and the pH:

$$\begin{aligned}[H_3O^+] &= 0 + x = 0 + 7.2 \times 10^{-2}\ M \\ &= 7.2 \times 10^{-2}\ M\end{aligned}$$

The pH of this solution is:

$$pH = -\log[H_3O^+] = -\log 7.2 \times 10^{-2} = 1.14$$

? Exercise 14.1.4.8

a. Show that the quadratic formula gives $x = 7.2 \times 10^{-2}$.
b. Calculate the pH in a 0.010-*M* solution of caffeine, a weak base:

$$C_8H_{10}N_4O_2(aq) + H_2O(l) \rightleftharpoons C_8H_{10}N_4O_2H^+(aq) + OH^-(aq) \quad K_b = 2.5 \times 10^{-4}$$

Hint

It will be necessary to convert $[OH^-]$ to $[H_3O^+]$ or pOH to pH toward the end of the calculation.

Answer

pH 11.16

The Relative Strengths of Strong Acids and Bases

Strong acids, such as HCl, HBr, and HI, all exhibit the same strength in water. The water molecule is such a strong base compared to the conjugate bases Cl^-, Br^-, and I^- that ionization of these strong acids is essentially complete in aqueous solutions. In solvents less basic than water, we find HCl, HBr, and HI differ markedly in their tendency to give up a proton to the solvent. For example, when dissolved in ethanol (a weaker base than water), the extent of ionization increases in the order $HCl < HBr < HI$, and so HI is demonstrated to be the strongest of these acids. The inability to discern differences in strength among strong acids dissolved in water is known as the leveling effect of water.

Water also exerts a leveling effect on the strengths of strong bases. For example, the oxide ion, O^{2-}, and the amide ion, NH_2^-, are such strong bases that they react completely with water:

$$O^{2-}(aq) + H_2O(l) \longrightarrow OH^-(aq) + OH^-(aq) \tag{14.1.4.1}$$

$$NH_2^-(aq) + H_2O(l) \longrightarrow NH_3(aq) + OH^-(aq) \tag{14.1.4.2}$$

Thus, O^{2-} and NH_2^- appear to have the same base strength in water; they both give a 100% yield of hydroxide ion.

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 $HF < HCl < HBr < HI$. Likewise, for group 16, the order of increasing acid strength is $H_2O < H_2S < H_2Se < H_2Te$. 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 $CH_4 < NH_3 < H_2O < HF$; across the third row, it is $SiH_4 < PH_3 < H_2S < HCl$ (see Figure 14.1.4.3).

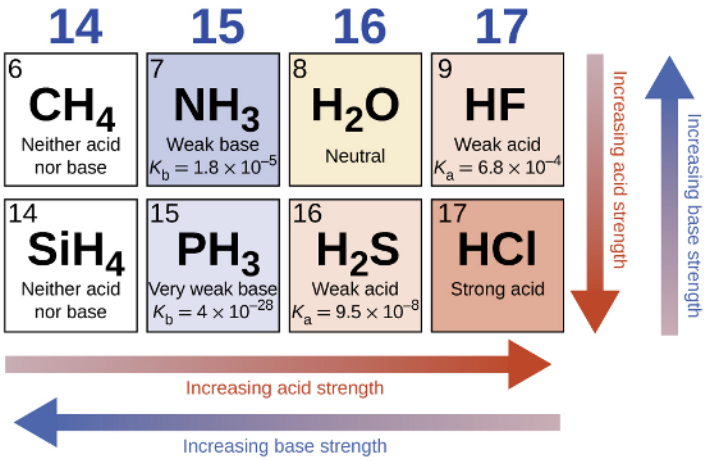
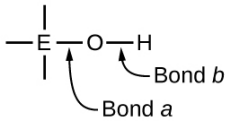


Figure 14.1.4.3: As you move from left to right and down the periodic table, the acid strength increases. As you move from right to left and up, the base strength increases.

Compounds containing oxygen and one or more hydroxyl (OH) groups can be acidic, basic, or amphoteric, depending on the position in the periodic table of the central atom E, the atom bonded to the hydroxyl group. Such compounds have the general formula $O_nE(OH)_m$, and include sulfuric acid, $O_2S(OH)_2$, sulfurous acid, $OS(OH)_2$, nitric acid, O_2NOH, perchloric acid, O_3ClOH, aluminum hydroxide, $Al(OH)_3$, calcium hydroxide, $Ca(OH)_2$, and potassium hydroxide, KOH:



If the central atom, E, has a low electronegativity, its attraction for electrons is low. Little tendency exists for the central atom to form a strong covalent bond with the oxygen atom, and bond *a* between the element and oxygen is more readily broken than bond *b* between oxygen and hydrogen. Hence bond *a* is ionic, hydroxide ions are released to the solution, and the material behaves as a base—this is the case with $Ca(OH)_2$ and KOH. Lower electronegativity is characteristic of the more metallic elements; hence, the metallic elements form ionic hydroxides that are by definition basic compounds.

If, on the other hand, the atom E has a relatively high electronegativity, it strongly attracts the electrons it shares with the oxygen atom, making bond *a* relatively strongly covalent. The oxygen-hydrogen bond, bond *b*, is thereby weakened because electrons are displaced toward E. Bond *b* is polar and readily releases hydrogen ions to the solution, so the material behaves as an acid. High electronegativities are characteristic of the more nonmetallic elements. Thus, nonmetallic elements form covalent compounds containing acidic −OH groups that are called oxyacids.

Increasing the oxidation number of the central atom E also increases the acidity of an oxyacid because this increases the attraction of E for the electrons it shares with oxygen and thereby weakens the O-H bond. Sulfuric acid, H_2SO_4, or $O_2S(OH)_2$ (with a sulfur oxidation number of +6), is more acidic than sulfurous acid, H_2SO_3, or $OS(OH)_2$ (with a sulfur oxidation number of +4). Likewise nitric acid, HNO_3, or O_2NOH (N oxidation number = +5), is more acidic than nitrous acid, HNO_2, or ONOH (N oxidation number = +3). In each of these pairs, the oxidation number of the central atom is larger for the stronger acid (Figure 14.1.4.4).

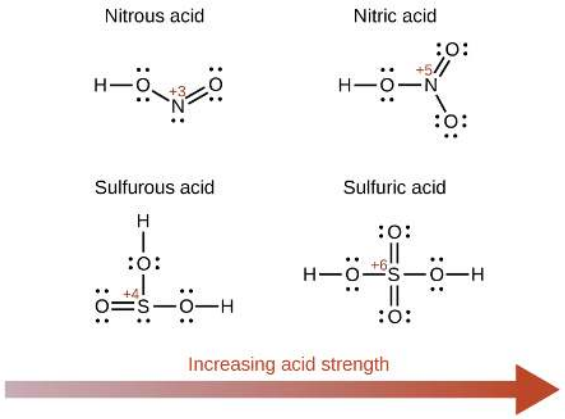


Figure 14.1.4.4: As the oxidation number of the central atom E increases, the acidity also increases.

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 H_2O 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.

Summary

The strengths of Brønsted-Lowry acids and bases in aqueous solutions can be determined by their acid or base ionization constants. Stronger acids form weaker conjugate bases, and weaker acids form stronger conjugate bases. Thus strong acids are completely ionized in aqueous solution because their conjugate bases are weaker bases than water. Weak acids are only partially ionized because their conjugate bases are strong enough to compete successfully with water for possession of protons. Strong bases react with water to quantitatively form hydroxide ions. Weak bases give only small amounts of hydroxide ion. The strengths of the binary acids increase from left to right across a period of the periodic table ($CH_4 < NH_3 < H_2O < HF$), and they increase down a

group (HF < HCl < HBr < HI). The strengths of oxyacids that contain the same central element increase as the oxidation number of the element increases (H_2SO_3 < H_2SO_4). The strengths of oxyacids also increase as the electronegativity of the central element increases [H_2SeO_4 < H_2SO_4].

Key Equations

- $K_\mathrm{a} = \dfrac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$
- $K_\mathrm{b} = \dfrac{[\mathrm{HB^+}][\mathrm{OH^-}]}{[\mathrm{B}]}$
- $K_a \times K_b = 1.0 \times 10^{-14} = K_w \,(\text{at room temperature})$
- $\text{Percent ionization} = \dfrac{[\mathrm{H_3O^+}]_\mathrm{eq}}{[\mathrm{HA}]_0} \times 100$

Glossary

acid ionization constant (K_a)

equilibrium constant for the ionization of a weak acid

base ionization constant (K_b)

equilibrium constant for the ionization of a weak base

leveling effect of water

any acid stronger than $\mathrm{H_3O^+}$, or any base stronger than $\mathrm{OH^-}$ will react with water to form $\mathrm{H_3O^+}$, or $\mathrm{OH^-}$, 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

oxyacid

compound containing a nonmetal and one or more hydroxyl groups

percent ionization

ratio of the concentration of the ionized acid to the initial acid concentration, times 100

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14.1.5: Buffer Solutions

Learning Objectives

- To understand how adding a common ion affects the position of an acid–base equilibrium.
- To know how to use the Henderson-Hasselbalch approximation to calculate the pH of a buffer.

Buffers are solutions that maintain a relatively constant pH when an acid or a base is added. They therefore protect, or "buffer," other molecules in solution from the effects of the added acid or base. Buffers contain either a weak acid (HA) and its conjugate base (A^-) or a weak base (B) and its conjugate acid (BH^+), and they are critically important for the proper functioning of biological systems. In fact, every biological fluid is buffered to maintain its physiological pH.

The Common Ion Effect: Weak Acids Combined with Conjugate Bases

To understand how buffers work, let's look first at how the ionization equilibrium of a weak acid is affected by adding either the conjugate base of the acid or a strong acid (a source of H^+). Le Chatelier's principle can be used to predict the effect on the equilibrium position of the solution. A typical buffer used in biochemistry laboratories contains acetic acid and a salt such as sodium acetate. The dissociation reaction of acetic acid is as follows:

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq) \tag{14.1.5.1}$$

and the equilibrium constant expression is as follows:

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3CO_2H]} \tag{14.1.5.2}$$

Sodium acetate (CH_3CO_2Na) is a strong electrolyte that ionizes completely in aqueous solution to produce Na^+ and $CH_3CO_2^-$ ions. If sodium acetate is added to a solution of acetic acid, Le Chatelier's principle predicts that the equilibrium in Equation 14.1.5.1 will shift to the left, consuming some of the added CH_3COO^- and some of the H^+ ions originally present in solution.

Because Na^+ is a **spectator ion**, it has no effect on the position of the equilibrium and can be ignored. The addition of sodium acetate produces a new equilibrium composition, in which $[H^+]$ is less than the initial value. Because $[H^+]$ has decreased, the pH will be higher. Thus adding a salt of the conjugate base to a solution of a weak acid increases the pH. This makes sense because sodium acetate is a base, and adding any base to a solution of a weak acid should increase the pH.

If we instead add a strong acid such as HCl to the system, $[H^+]$ increases. Once again the equilibrium is temporarily disturbed, but the excess H^+ ions react with the conjugate base ($CH_3CO_2^-$), whether from the parent acid or sodium acetate, to drive the equilibrium to the left. The net result is a new equilibrium composition that has a lower $[CH_3CO_2^-]$ than before. In both cases, only the equilibrium composition has changed; the ionization constant K_a for acetic acid remains the same. Adding a strong electrolyte that contains one ion in common with a reaction system that is at equilibrium, in this case $CH_3CO_2^-$, will therefore shift the equilibrium in the direction that reduces the concentration of the common ion. The shift in equilibrium is via the common ion effect.

> *Adding a common ion to a system at equilibrium affects the equilibrium composition, but not the ionization constant.*

Example 14.1.5.1

A 0.150 M solution of formic acid at 25°C (pKa = 3.75) has a pH of 2.28 and is 3.5% ionized.

a. Is there a change to the pH of the solution if enough solid sodium formate is added to make the final formate concentration 0.100 M (assume that the formic acid concentration does not change)?
b. What percentage of the formic acid is ionized if 0.200 M HCl is added to the system?

Given: solution concentration and pH, pK_a, and percent ionization of acid; final concentration of conjugate base or strong acid added

Asked for: pH and percent ionization of formic acid

Strategy:

A. Write a balanced equilibrium equation for the ionization equilibrium of formic acid. Tabulate the initial concentrations, the changes, and the final concentrations.
B. Substitute the expressions for the final concentrations into the expression for Ka. Calculate $[H^+]$ and the pH of the solution.
C. Construct a table of concentrations for the dissociation of formic acid. To determine the percent ionization, determine the anion concentration, divide it by the initial concentration of formic acid, and multiply the result by 100.

Solution:

A Because sodium formate is a strong electrolyte, it ionizes completely in solution to give formate and sodium ions. The Na^+ ions are spectator ions, so they can be ignored in the equilibrium equation. Because water is both a much weaker acid than formic acid and a much weaker base than formate, the acid–base properties of the solution are determined solely by the formic acid ionization equilibrium:

$$HCO_2H(aq) \rightleftharpoons HCO_2^-(aq) + H^+(aq)$$

The initial concentrations, the changes in concentration that occur as equilibrium is reached, and the final concentrations can be tabulated.

Final Concentration

ICE	$[HCO_2H(aq)]$	$[H^+(aq)]$	$[HCO_2^-(aq)]$
Initial	0.150	1.00×10^{-7}	0.100
Change	−x	+x	+x
Equilibrium	(0.150 − x)	x	(0.100 + x)

B We substitute the expressions for the final concentrations into the equilibrium constant expression and make our usual simplifying assumptions, so

$$\begin{aligned} K_a = \frac{[H^+][HCO_2^-]}{[HCO_2H]} &= \frac{(x)(0.100+x)}{0.150-x} \\ &\approx \frac{x(0.100)}{0.150} \\ &\approx 10^{-3.75} \\ &\approx 1.8 \times 10^{-4} \end{aligned}$$

Rearranging and solving for x,

$$\begin{aligned} x &= (1.8 \times 10^{-4}) \times \frac{0.150\ M}{0.100\ M} \\ &= 2.7 \times 10^{-4} \\ &= [H^+] \end{aligned}$$

The value of x is small compared with 0.150 or 0.100 M, so our assumption about the extent of ionization is justified. Moreover,

$$K_a C_{HA} = (1.8 \times 10^{-4})(0.150) = 2.7 \times 10^{-5}$$

which is greater than 1.0×10^{-6}, so again, our assumption is justified. The final pH is:

$$pH = -\log(2.7 \times 10^{-4}) = 3.57$$

compared with the initial value of 2.29. Thus adding a salt containing the conjugate base of the acid has increased the pH of the solution, as we expect based on Le Chatelier's principle; the stress on the system has been relieved by the consumption of H^+ ions, driving the equilibrium to the left.

C Because HCl is a strong acid, it ionizes completely, and chloride is a spectator ion that can be neglected. Thus the only relevant acid–base equilibrium is again the dissociation of formic acid, and initially the concentration of formate is zero. We can construct a table of initial concentrations, changes in concentration, and final concentrations.

$$HCO_2H(aq) \leftrightharpoons H^+(aq) + HCO_2^-(aq)$$

initial concentrations, changes in concentration, and final concentrations

	$[HCO_2H(aq)]$	$[H^+(aq)]$	$[HCO_2^-(aq)]$
initial	0.150	0.200	0
change	−x	+x	+x
final	(0.150 − x)	(0.200 + x)	x

To calculate the percentage of formic acid that is ionized under these conditions, we have to determine the final $[\mathrm{HCO_2^-}]$. We substitute final concentrations into the equilibrium constant expression and make the usual simplifying assumptions, so

$$K_a = \frac{[H^+][HCO_2^-]}{[HCO_2H]} = \frac{(0.200+x)(x)}{0.150-x} \approx \frac{x(0.200)}{0.150} = 1.80 \times 10^{-4}$$

Rearranging and solving for x,

$$\begin{aligned} x &= (1.80 \times 10^{-4}) \times \frac{0.150\ M}{0.200\ M} \\ &= 1.35 \times 10^{-4} = [HCO_2^-] \end{aligned}$$

Once again, our simplifying assumptions are justified. The percent ionization of formic acid is as follows:

$$\text{percent ionization} = \frac{1.35 \times 10^{-4}\ M}{0.150\ M} \times 100\% = 0.0900\%$$

Adding the strong acid to the solution, as shown in the table, decreased the percent ionization of formic acid by a factor of approximately 38 (3.45%/0.0900%). Again, this is consistent with Le Chatelier's principle: adding $\mathrm{H^+}$ ions drives the dissociation equilibrium to the left.

? Exercise 14.1.5.1

A 0.225 M solution of ethylamine ($\mathrm{CH_3CH_2NH_2}$ with $pK_b = 3.19$) has a pH of 12.08 and a percent ionization of 5.4% at 20°C. Calculate the following:

a. the pH of the solution if enough solid ethylamine hydrochloride ($\mathrm{EtNH_3Cl}$) is added to make the solution 0.100 M in $\mathrm{EtNH_3^+}$
b. the percentage of ethylamine that is ionized if enough solid NaOH is added to the original solution to give a final concentration of 0.050 M NaOH

Answer a

11.16

Answer b

1.3%



A Video Discussing the Common Ion Effect: The Common Ion Effecr(opens in new window) [youtu.be]

The Common Ion Effect: Weak Bases Combined with Conjugate Acids

Now let's suppose we have a buffer solution that contains equimolar concentrations of a weak base (B) and its conjugate acid (BH^+). The general equation for the ionization of a weak base is as follows:

$$B(aq) + H_2O(l) \leftrightharpoons BH^+(aq) + OH^-(aq) \tag{14.1.5.3}$$

If the equilibrium constant for the reaction as written in Equation 14.1.5.3 is small, for example $K_b = 10^{-5}$, then the equilibrium constant for the reverse reaction is very large: $K = \dfrac{1}{K_b} = 10^5$. Adding a strong base such as OH^- to the solution therefore causes the equilibrium in Equation 14.1.5.3 to shift to the left, consuming the added OH^-. As a result, the OH^- ion concentration in solution remains relatively constant, and the pH of the solution changes very little. Le Chatelier's principle predicts the same outcome: when the system is stressed by an increase in the OH^- ion concentration, the reaction will proceed to the left to counteract the stress.

If the pK_b of the base is 5.0, the pK_a of its conjugate acid is

$$pK_a = pK_w - pK_b = 14.0 – 5.0 = 9.0.$$

Thus the equilibrium constant for ionization of the conjugate acid is even smaller than that for ionization of the base. The ionization reaction for the conjugate acid of a weak base is written as follows:

$$BH^+(aq) + H_2O(l) \leftrightharpoons B(aq) + H_3O^+(aq) \tag{14.1.5.4}$$

Again, the equilibrium constant for the reverse of this reaction is very large: K = $1/K_a$ = 10^9. If a strong acid is added, it is neutralized by reaction with the base as the reaction in Equation 14.1.5.4 shifts to the left. As a result, the H^+ ion concentration does not increase very much, and the pH changes only slightly. In effect, a buffer solution behaves somewhat like a sponge that can absorb H^+ and OH^- ions, thereby preventing large changes in pH when appreciable amounts of strong acid or base are added to a solution.

Buffers are characterized by the pH range over which they can maintain a more or less constant pH and by their buffer capacity, the amount of strong acid or base that can be absorbed before the pH changes significantly. Although the useful pH range of a buffer depends strongly on the chemical properties of the weak acid and weak base used to prepare the buffer (i.e., on K), its buffer capacity depends solely on the concentrations of the species in the buffered solution. The more concentrated the buffer solution, the greater its buffer capacity. As illustrated in Figure 14.1.5.1, when $NaOH$ is added to solutions that contain different concentrations of an acetic acid/sodium acetate buffer, the observed change in the pH of the buffer is inversely proportional to the concentration of the buffer. If the buffer capacity is 10 times larger, then the buffer solution can absorb 10 times more strong acid or base before undergoing a significant change in pH.

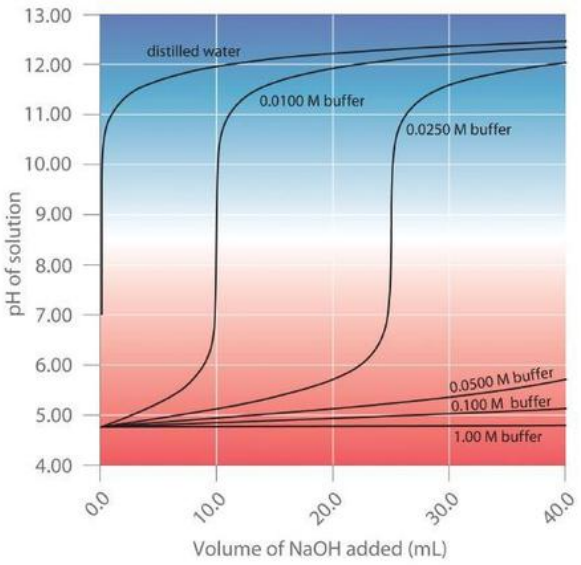


Figure 14.1.5.1: Effect of Buffer Concentration on the Capacity of a Buffer. (CC BY-SA-NC; Anonymous by request)
Graph of pH of solution against volume of NaOH added. Six different buffer concentrations are plotted.

A buffer maintains a relatively constant pH when acid or base is added to a solution. The addition of even tiny volumes of 0.10 M $NaOH$ to 100.0 mL of distilled water results in a very large change in pH. As the concentration of a 50:50 mixture of sodium acetate/acetic acid buffer in the solution is increased from 0.010 M to 1.00 M, the change in the pH produced by the addition of the same volume of $NaOH$ solution decreases steadily. For buffer concentrations of at least 0.500 M, the addition of even 25 mL of the $NaOH$ solution results in only a relatively small change in pH.

Calculating the pH of a Buffer

The pH of a buffer can be calculated from the concentrations of the weak acid and the weak base used to prepare it, the concentration of the conjugate base and conjugate acid, and the pK_a or pK_b of the weak acid or weak base. The procedure is analogous to that used in Example 14.1.5.1 to calculate the pH of a solution containing known concentrations of formic acid and formate.

An alternative method frequently used to calculate the pH of a buffer solution is based on a rearrangement of the equilibrium equation for the dissociation of a weak acid. The simplified ionization reaction is $HA \leftrightharpoons H^+ + A^-$, for which the equilibrium constant expression is as follows:

$$K_a = \frac{[H^+][A^-]}{[HA]} \tag{14.1.5.5}$$

This equation can be rearranged as follows:

$$[H^+] = K_a \frac{[HA]}{[A^-]} \tag{14.1.5.6}$$

Taking the logarithm of both sides and multiplying both sides by −1,

$$-\log[H^+] = -\log K_a - \log\left(\frac{[HA]}{[A^-]}\right) \tag{14.1.5.7}$$

$$= -\log K_a + \log\left(\frac{[A^-]}{[HA]}\right) \tag{14.1.5.8}$$

Replacing the negative logarithms in Equation 14.1.5.8,

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) \tag{14.1.5.9}$$

or, more generally,

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right) \tag{14.1.5.10}$$

Equation 14.1.5.9 and Equation 14.1.5.10 are both forms of the Henderson-Hasselbalch approximation, named after the two early 20th-century chemists who first noticed that this rearranged version of the equilibrium constant expression provides an easy way to calculate the pH of a buffer solution. In general, the validity of the Henderson-Hasselbalch approximation may be limited to solutions whose concentrations are at least 100 times greater than their K_a values.

There are three special cases where the Henderson-Hasselbalch approximation is easily interpreted without the need for calculations:

- $[base] = [acid]$: Under these conditions,

  $$\frac{[base]}{[acid]} = 1$$

  in Equation 14.1.5.10 Because $\log 1 = 0$,

  $$pH = pK_a$$

  regardless of the actual concentrations of the acid and base. Recall that this corresponds to the midpoint in the titration of a weak acid or a weak base.
- $[base]/[acid] = 10$: In Equation 14.1.5.10, because $\log 10 = 1$,

  $$pH = pK_a + 1.$$
- $[base]/[acid] = 100$: In Equation 14.1.5.10, because $\log 100 = 2$,

  $$pH = pK_a + 2.$$

Each time we increase the [base]/[acid] ratio by 10, the pH of the solution increases by 1 pH unit. Conversely, if the [base]/[acid] ratio is 0.1, then pH = pK_a − 1. Each additional factor-of-10 decrease in the [base]/[acid] ratio causes the pH to decrease by 1 pH unit.

> If [base] = [acid] for a buffer, then pH = pK_a. Changing this ratio by a factor of 10 either way changes the pH by ±1 unit.

Example 14.1.5.2

What is the pH of a solution that contains

a. 0.135 M HCO_2H and 0.215 M HCO_2Na? (The pK_a of formic acid is 3.75.)
b. 0.0135 M HCO_2H and 0.0215 M HCO_2Na?
c. 0.119 M pyridine and 0.234 M pyridine hydrochloride? (The pK_b of pyridine is 8.77.)

Given: concentration of acid, conjugate base, and pK_a; concentration of base, conjugate acid, and pK_b

Asked for: pH

Strategy:

Substitute values into either form of the Henderson-Hasselbalch approximation (Equations 14.1.5.9 or 14.1.5.10) to calculate the pH.

Solution:

According to the Henderson-Hasselbalch approximation (Equation 14.1.5.9), the pH of a solution that contains both a weak acid and its conjugate base is

$$pH = pK_a + \log([A-]/[HA]).$$

A

Inserting the given values into the equation,

$$pH = 3.75 + \log\left(\frac{0.215}{0.135}\right)$$
$$= 3.75 + \log 1.593$$
$$= 3.95$$

This result makes sense because the $[A^-]/[HA]$ ratio is between 1 and 10, so the pH of the buffer must be between the pK_a (3.75) and $pK_a + 1$, or 4.75.

B

This is identical to part (a), except for the concentrations of the acid and the conjugate base, which are 10 times lower. Inserting the concentrations into the Henderson-Hasselbalch approximation,

$$pH = 3.75 + \log\left(\frac{0.0215}{0.0135}\right)$$
$$= 3.75 + \log 1.593$$
$$= 3.95$$

This result is identical to the result in part (a), which emphasizes the point that the pH of a buffer depends only on the ratio of the concentrations of the conjugate base and the acid, not on the magnitude of the concentrations. Because the [A⁻]/[HA] ratio is the same as in part (a), the pH of the buffer must also be the same (3.95).

C

In this case, we have a weak base, pyridine (Py), and its conjugate acid, the pyridinium ion (HPy^+). We will therefore use Equation 14.1.5.10, the more general form of the Henderson-Hasselbalch approximation, in which "base" and "acid" refer to the appropriate species of the conjugate acid–base pair. We are given [base] = [Py] = 0.119 M and $[acid] = [HPy^+] = 0.234\ M$. We also are given $pK_b = 8.77$ for pyridine, but we need pK_a for the pyridinium ion. Recall from Equation 16.23 that the pK_b of a weak base and the pK_a of its conjugate acid are related:

$$pK_a + pK_b = pK_w.$$

Thus pK_a for the pyridinium ion is $pK_w - pK_b = 14.00 - 8.77 = 5.23$. Substituting this pK_a value into the Henderson-Hasselbalch approximation,

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right)$$
$$= 5.23 + \log\left(\frac{0.119}{0.234}\right)$$
$$= 5.23\ -0.294$$
$$= 4.94$$

Once again, this result makes sense: the $[B]/[BH^+]$ ratio is about 1/2, which is between 1 and 0.1, so the final pH must be between the pK_a (5.23) and $pK_a - 1$, or 4.23.

? Exercise 14.1.5.2

What is the pH of a solution that contains

a. 0.333 M benzoic acid and 0.252 M sodium benzoate?
b. 0.050 M trimethylamine and 0.066 M trimethylamine hydrochloride?

The pK_a of benzoic acid is 4.20, and the pK_b of trimethylamine is also 4.20.

Answer a

4.08

Answer b

9.68



A Video Discussing Using the Henderson Hasselbalch Equation: Using the Henderson Hasselbalch Equation(opens in new window) [youtu.be] (opens in new window)

The Henderson-Hasselbalch approximation ((Equation 14.1.5.9) can also be used to calculate the pH of a buffer solution after adding a given amount of strong acid or strong base, as demonstrated in Example 14.1.5.3

Example 14.1.5.3

The buffer solution in Example 14.1.5.2contained 0.135 M HCO_2H and 0.215 M HCO_2Na and had a pH of 3.95.

a. What is the final pH if 5.00 mL of 1.00 M HCl are added to 100 mL of this solution?
b. What is the final pH if 5.00 mL of 1.00 M $NaOH$ are added?

Given: composition and pH of buffer; concentration and volume of added acid or base

Asked for: final pH

Strategy:

A. Calculate the amounts of formic acid and formate present in the buffer solution using the procedure from Example 14.1.5.1. Then calculate the amount of acid or base added.
B. Construct a table showing the amounts of all species after the neutralization reaction. Use the final volume of the solution to calculate the concentrations of all species. Finally, substitute the appropriate values into the Henderson-Hasselbalch approximation (Equation 14.1.5.10) to obtain the pH.

Solution:

The added HCl (a strong acid) or NaOH (a strong base) will react completely with formate (a weak base) or formic acid (a weak acid), respectively, to give formic acid or formate and water. We must therefore calculate the amounts of formic acid and formate present after the neutralization reaction.

A We begin by calculating the millimoles of formic acid and formate present in 100 mL of the initial pH 3.95 buffer:

$$100\ \cancel{mL}\left(\frac{0.135\,mmol\ HCO_2H}{\cancel{mL}}\right) = 13.5\,mmol\,HCO_2H$$

$$100\ \cancel{mL}\left(\frac{0.215\,mmol\ HCO_2^-}{\cancel{mL}}\right) = 21.5\,mmol\,HCO_2^-$$

The millimoles of H^+ in 5.00 mL of 1.00 M HCl is as follows:

$$5.00\ \cancel{mL}\left(\frac{1.00\,mmol\ H^+}{\cancel{mL}}\right) = 5\,mmol\,H^+$$

B Next, we construct a table of initial amounts, changes in amounts, and final amounts:

$$\mathrm{HCO}^{2-}(\mathrm{aq}) + \mathrm{H}^{+}(\mathrm{aq}) \rightleftharpoons \mathrm{HCO_2H(aq)}$$

initial amounts, changes in amounts, and final amounts:

	$HCO^{2-}(aq)$	$H^{+}(aq)$	$HCO_2H(aq)$
Initial	21.5 mmol	5.00 mmol	13.5 mmol
Change	−5.00 mmol	−5.00 mmol	+5.00 mmol
Final	16.5 mmol	~0 mmol	18.5 mmol

The final amount of H^+ in solution is given as "~0 mmol." For the purposes of the stoichiometry calculation, this is essentially true, but remember that the point of the problem is to calculate the final $[H^+]$ and thus the pH. We now have all the information we need to calculate the pH. We can use either the lengthy procedure of Example 14.1.5.1 or the Henderson–Hasselbach approximation. Because we have performed many equilibrium calculations in this chapter, we'll take the latter approach. The Henderson-Hasselbalch approximation requires the concentrations of HCO_2^- and HCO_2H, which can be calculated using the number of millimoles (n) of each and the total volume (VT). Substituting these values into the Henderson-Hasselbalch approximation (Equation 14.1.5.10):

$$\begin{aligned} pH &= pK_a + \log\left(\frac{[HCO_2^-]}{[HCO_2H]}\right) \\ &= pK_a + \log\left(\frac{n_{HCO_2^-}/V_f}{n_{HCO_2H}/V_f}\right) \\ &= pK_a + \log\left(\frac{n_{HCO_2^-}}{n_{HCO_2H}}\right) \end{aligned}$$

Because the total volume appears in both the numerator and denominator, it cancels. We therefore need to use only the ratio of the number of millimoles of the conjugate base to the number of millimoles of the weak acid. So

$$\begin{aligned} pH &= pK_a + \log\left(\frac{n_{HCO_2^-}}{n_{HCO_2H}}\right) \\ &= 3.75 + \log\left(\frac{16.5\ mmol}{18.5\ mmol}\right) \\ &= 3.75\ -0.050 = 3.70 \end{aligned}$$

Once again, this result makes sense on two levels. First, the addition of HCl has decreased the pH from 3.95, as expected. Second, the ratio of HCO_2^- to HCO_2H is slightly less than 1, so the pH should be between the pK_a and pK_a − 1.

A The procedure for solving this part of the problem is exactly the same as that used in part (a). We have already calculated the numbers of millimoles of formic acid and formate in 100 mL of the initial pH 3.95 buffer: 13.5 mmol of HCO_2H and 21.5 mmol of HCO_2^-. The number of millimoles of OH^- in 5.00 mL of 1.00 M $NaOH$ is as follows:

B With this information, we can construct a table of initial amounts, changes in amounts, and final amounts.

$$\mathrm{HCO_2H(aq)} + \mathrm{OH}^{-}(\mathrm{aq}) \rightleftharpoons \mathrm{HCO_2^-(aq)} + \mathrm{H_2O(l)}$$

initial amounts, changes in amounts, and final amounts

	$HCO_2H(aq)$	OH^-	$HCO_2^-(aq)$
Initial	13.5 mmol	5.00 mmol	21.5 mmol
Change	−5.00 mmol	−5.00 mmol	+5.00 mmol
Final	8.5 mmol	~0 mmol	26.5 mmol

The final amount of OH^- in solution is not actually zero; this is only approximately true based on the stoichiometric calculation. We can calculate the final pH by inserting the numbers of millimoles of both HCO_2^- and HCO_2H into the simplified Henderson-Hasselbalch expression used in part (a) because the volume cancels:

$$\begin{aligned} pH &= pK_a + \log\left(\frac{n_{HCO_2^-}}{n_{HCO_2H}}\right) \\ &= 3.75 + \log\left(\frac{26.5\ mmol}{8.5\ mmol}\right) \\ &= 3.75 + 0.494 = 4.24 \end{aligned}$$

Once again, this result makes chemical sense: the pH has increased, as would be expected after adding a strong base, and the final pH is between the pK_a and pK_a + 1, as expected for a solution with a HCO_2^-/HCO_2H ratio between 1 and 10.

? Exercise 14.1.5.3

The buffer solution from Example 14.1.5.2 contained 0.119 M pyridine and 0.234 M pyridine hydrochloride and had a pH of 4.94.

a. What is the final pH if 12.0 mL of 1.5 M NaOH are added to 250 mL of this solution?
b. What is the final pH if 12.0 mL of 1.5 M HCl are added?

Answer a

5.30

Answer b

4.42

Only the amounts (in moles or millimoles) of the acidic and basic components of the buffer are needed to use the Henderson-Hasselbalch approximation, not their concentrations.



A Video Discussing the Change in pH with the Addition of a Strong Acid to a Buffer: The Change in pH with the Addition of a Strong Acid to a Buffer(opens in new window) [youtu.be]



The Change in pH with the Addition of a Strong Base to a Buffer:

The Change in pH with the Addition of a Strong Base to a Buffer (opens in new window) [youtu.be]

The results obtained in Example 14.1.5.3 and its corresponding exercise demonstrate how little the pH of a well-chosen buffer solution changes despite the addition of a significant quantity of strong acid or strong base. Suppose we had added the same amount of HCl or $NaOH$ solution to 100 mL of an unbuffered solution at pH 3.95 (corresponding to 1.1×10^{-4} M HCl). In this case, adding 5.00 mL of 1.00 M HCl would lower the final pH to 1.32 instead of 3.70, whereas adding 5.00 mL of 1.00 M $NaOH$ would raise the final pH to 12.68 rather than 4.24. (Try verifying these values by doing the calculations yourself.) Thus the presence of a buffer significantly increases the ability of a solution to maintain an almost constant pH.

> *The most effective buffers contain **equal** concentrations of an acid and its conjugate base.*

A buffer that contains approximately equal amounts of a weak acid and its conjugate base in solution is equally effective at neutralizing either added base or added acid. This is shown in Figure 14.1.5.2 for an acetic acid/sodium acetate buffer. Adding a given amount of strong acid shifts the system along the horizontal axis to the left, whereas adding the same amount of strong base shifts the system the same distance to the right. In either case, the change in the ratio of $CH_3CO_2^-$ to CH_3CO_2H from 1:1 reduces the buffer capacity of the solution.

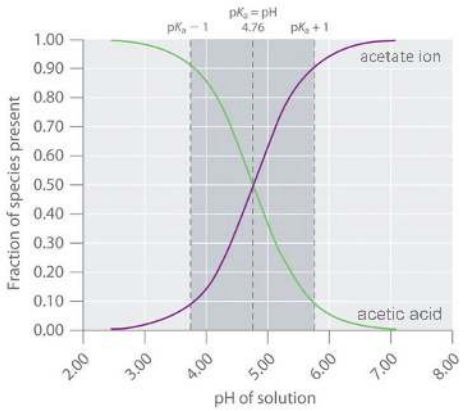


Figure 14.1.5.2: Distribution Curve Showing the Fraction of Acetic Acid Molecules and Acetate Ions as a Function of pH in a Solution of Acetic Acid. The pH range over which the acetic acid/sodium acetate system is an effective buffer (the darker shaded region) corresponds to the region in which appreciable concentrations of both species are present (pH 3.76–5.76, corresponding to $pH = pK_a \pm 1$). (CC BY-SA-NC; Anonymous by request)

Graph of mole fraction against pH of solution. The green line is acetic acid and the purple line is the acetate ion.



A Video Discussing The Buffer Region: The Buffer Region (opens in new window) [youtu.be]

The Relationship between Titrations and Buffers

There is a strong correlation between the effectiveness of a buffer solution and the titration curves discussed in Section 16.5. Consider the schematic titration curve of a weak acid with a strong base shown in Figure 14.1.5.3 As indicated by the labels, the region around pK_a corresponds to the midpoint of the titration, when approximately half the weak acid has been neutralized. This portion of the titration curve corresponds to a buffer: it exhibits the smallest change in pH per increment of added strong base, as shown by the nearly horizontal nature of the curve in this region. The nearly flat portion of the curve extends only from approximately a pH value of 1 unit less than the pK_a to approximately a pH value of 1 unit greater than the pK_a, which is why buffer solutions usually have a pH that is within ±1 pH units of the pK_a of the acid component of the buffer.

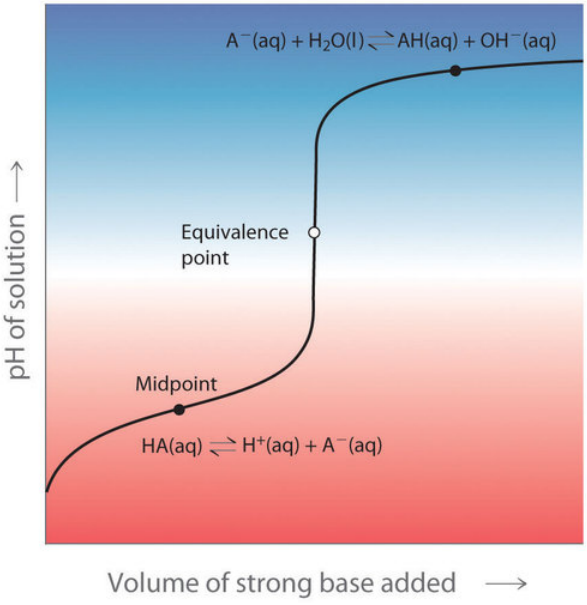


Figure 14.1.5.3: The Relationship between Titration Curves and Buffers. (CC BY-SA-NC; Anonymous by request)

Titration curves graph pH of solution against volume of strong base added. On the curve we look for the midpoints and equivalence points.

This schematic plot of pH for the titration of a weak acid with a strong base shows the nearly flat region of the titration curve around the midpoint, which corresponds to the formation of a buffer. At the lower left, the pH of the solution is determined by the equilibrium for dissociation of the weak acid; at the upper right, the pH is determined by the equilibrium for reaction of the conjugate base with water.

In the region of the titration curve at the lower left, before the midpoint, the acid–base properties of the solution are dominated by the equilibrium for dissociation of the weak acid, corresponding to K_a. In the region of the titration curve at the upper right, after the midpoint, the acid–base properties of the solution are dominated by the equilibrium for reaction of the conjugate base of the

weak acid with water, corresponding to K_b. However, we can calculate either K_a or K_b from the other because they are related by K_w.

Blood: A Most Important Buffer

Metabolic processes produce large amounts of acids and bases, yet organisms are able to maintain an almost constant internal pH because their fluids contain buffers. This is not to say that the pH is uniform throughout all cells and tissues of a mammal. The internal pH of a red blood cell is about 7.2, but the pH of most other kinds of cells is lower, around 7.0. Even within a single cell, different compartments can have very different pH values. For example, one intracellular compartment in white blood cells has a pH of around 5.0.

Because no single buffer system can effectively maintain a constant pH value over the entire physiological range of approximately pH 5.0 to 7.4, biochemical systems use a set of buffers with overlapping ranges. The most important of these is the CO_2/HCO_3^- system, which dominates the buffering action of blood plasma.

The acid–base equilibrium in the CO_2/HCO_3^- buffer system is usually written as follows:

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \tag{14.1.5.11}$$

with $K_a = 4.5 \times 10^{-7}$ and $pK_a = 6.35$ at 25°C. In fact, Equation 14.1.5.11 is a grossly oversimplified version of the CO_2/HCO_3^- system because a solution of CO_2 in water contains only rather small amounts of H_2CO_3. Thus Equation 14.1.5.11does not allow us to understand how blood is actually buffered, particularly at a physiological temperature of 37°C.

As shown in Equation 14.1.5.12, CO_2 is in equilibrium with H_2CO_3, but the equilibrium lies far to the left, with an H_2CO_3/CO_2 ratio less than 0.01 under most conditions:

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \tag{14.1.5.12}$$

with $K' = 4.0 \times 10^{-3}$ at 37°C. The true pK_a of carbonic acid at 37°C is therefore 3.70, not 6.35, corresponding to a K_a of 2.0×10^{-4}, which makes it a much stronger acid than Equation 14.1.5.11suggests. Adding Equation 14.1.5.11and Equation 14.1.5.12and canceling H_2CO_3 from both sides give the following overall equation for the reaction of CO_2 with water to give a proton and the bicarbonate ion:

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \tag{14.1.5.13}$$

with $K' = 4.0 \times 10^{-3} (37^\circ C)$

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \tag{14.1.5.14}$$

with $K_a = 2.0 \times 10^{-4} (37^\circ C)$

$$CO_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \tag{14.1.5.15}$$

with $K = 8.0 \times 10^{-7} (37^\circ C)$

The K value for the reaction in Equation 14.1.5.15is the product of the true ionization constant for carbonic acid (K_a) and the equilibrium constant (K) for the reaction of $CO_2(aq)$ with water to give carbonic acid. The equilibrium equation for the reaction of CO_2 with water to give bicarbonate and a proton is therefore

$$K = \frac{[H^+][HCO_3^-]}{[CO_2]} = 8.0 \times 10^{-7} \tag{14.1.5.16}$$

The presence of a gas in the equilibrium constant expression for a buffer is unusual. According to **Henry's law**,

$$[CO_2] = kP_{CO_2}$$

where k is the Henry's law constant for CO_2, which is $3.0 \times 10^{-5}\ M/mmHg$ at 37°C. Substituting this expression for $[CO_2]$ in Equation 14.1.5.16,

$$K = \frac{[H^+][HCO_3^-]}{(3.0 \times 10^{-5}\ M/mmHg)(P_{CO_2})}$$

where P_{CO_2} is in mmHg. Taking the negative logarithm of both sides and rearranging,

$$pH = 6.10 + \log\left(\frac{[HCO_3^-]}{(3.0 \times 10^{-5} M/mm\ Hg)\ (P_{CO_2})}\right) \tag{14.1.5.17}$$

Thus the pH of the solution depends on both the CO_2 pressure over the solution and $[HCO_3^-]$. Figure 14.1.5.4 plots the relationship between pH and $[HCO_3^-]$ under physiological conditions for several different values of P_{CO_2}, with normal pH and $[HCO_3^-]$ values indicated by the dashed lines.

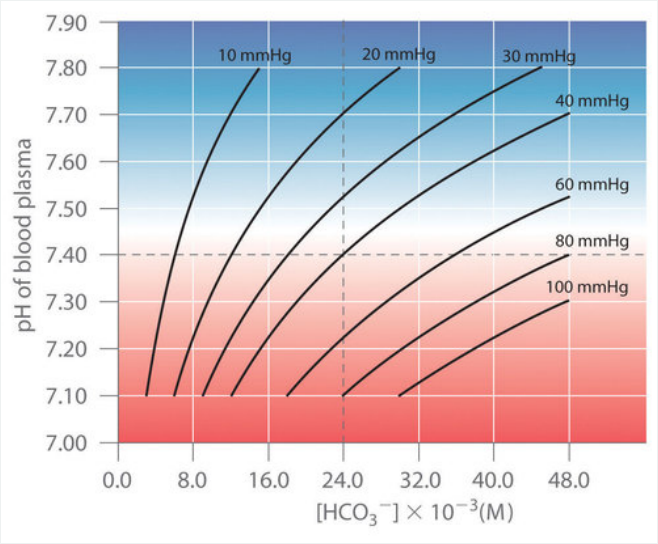


Figure 14.1.5.4: Buffering in Blood: pH versus $[HCO_3^-]$ Curves for Buffers with Different Values of P_{CO_2}. Only those combinations of pH and $[HCO_3^-]$ that lie on a given line are allowed for the particular value of P_{CO_2} indicated. Normal values of blood plasma pH and $[HCO_3^-]$ are indicated by dashed lines. (CC BY-SA-NC; Anonymous by request)

According to Equation 14.1.5.17, adding a strong acid to the CO_2/HCO_3^- system causes $[HCO_3^-]$ to decrease as HCO_3^- is converted to CO_2. Excess CO_2 is released in the lungs and exhaled into the atmosphere, however, so there is essentially no change in P_{CO_2}. Because the change in $[HCO_3^-]/P_{CO_2}$ is small, Equation 14.1.5.17predicts that the change in pH will also be rather small. Conversely, if a strong base is added, the OH^- reacts with CO_2 to form HCO_3^-, but CO_2 is replenished by the body, again limiting the change in both $[HCO_3^-]/P_{CO_2}$ and pH. The CO_2/HCO_3^- buffer system is an example of an open system, in which the total concentration of the components of the buffer change to keep the pH at a nearly constant value.

If a passenger steps out of an airplane in Denver, Colorado, for example, the lower P_{CO_2} at higher elevations (typically 31 mmHg at an elevation of 2000 m versus 40 mmHg at sea level) causes a shift to a new pH and $[HCO_3^-]$. The increase in pH and decrease in $[HCO_3^-]$ in response to the decrease in P_{CO_2} are responsible for the general malaise that many people experience at high altitudes. If their blood pH does not adjust rapidly, the condition can develop into the life-threatening phenomenon known as altitude sickness.



A Video Summary of the pH Curve for a Strong Acid/Strong Base Titration:

Summary of the pH Curve for a Strong Acid/Strong Base Titration(opens in new window) [youtu.be]

Summary

Buffers are solutions that resist a change in pH after adding an acid or a base. Buffers contain a weak acid (HA) and its conjugate weak base (A^-). Adding a strong electrolyte that contains one ion in common with a reaction system that is at equilibrium shifts the equilibrium in such a way as to reduce the concentration of the common ion. The shift in equilibrium is called the common ion effect. Buffers are characterized by their pH range and buffer capacity. The useful pH range of a buffer depends strongly on the chemical properties of the conjugate weak acid–base pair used to prepare the buffer (the K_a or K_b), whereas its buffer capacity depends solely on the concentrations of the species in the solution. The pH of a buffer can be calculated using the Henderson-Hasselbalch approximation, which is valid for solutions whose concentrations are at least 100 times greater than their K_a values. Because no single buffer system can effectively maintain a constant pH value over the physiological range of approximately 5 to 7.4, biochemical systems use a set of buffers with overlapping ranges. The most important of these is the CO_2/HCO_3^- system, which dominates the buffering action of blood plasma.

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14.1.6: Acid-Base Titration Curves

Learning Objectives

- To calculate the pH at any point in an acid–base titration.

In an acid–base titration, a buret is used to deliver measured volumes of an acid or a base solution of known concentration (the titrant) to a flask that contains a solution of a base or an acid, respectively, of unknown concentration (the unknown). If the concentration of the titrant is known, then the concentration of the unknown can be determined. The following discussion focuses on the pH changes that occur during an acid–base titration. Plotting the pH of the solution in the flask against the amount of acid or base added produces a titration curve. The shape of the curve provides important information about what is occurring in solution during the titration.

Titrations of Strong Acids and Bases

Figure *[Math Processing Error]* shows a plot of the pH as 0.20 M *[Math Processing Error]* is gradually added to 50.00 mL of pure water. The pH of the sample in the flask is initially 7.00 (as expected for pure water), but it drops very rapidly as *[Math Processing Error]* is added. Eventually the pH becomes constant at 0.70—a point well beyond its value of 1.00 with the addition of 50.0 mL of *[Math Processing Error]* (0.70 is the pH of 0.20 M HCl). In contrast, when 0.20 M *[Math Processing Error]* is added to 50.00 mL of distilled water, the pH (initially 7.00) climbs very rapidly at first but then more gradually, eventually approaching a limit of 13.30 (the pH of 0.20 M NaOH), again well beyond its value of 13.00 with the addition of 50.0 mL of *[Math Processing Error]* as shown in Figure *[Math Processing Error]*. As you can see from these plots, the titration curve for adding a base is the mirror image of the curve for adding an acid.

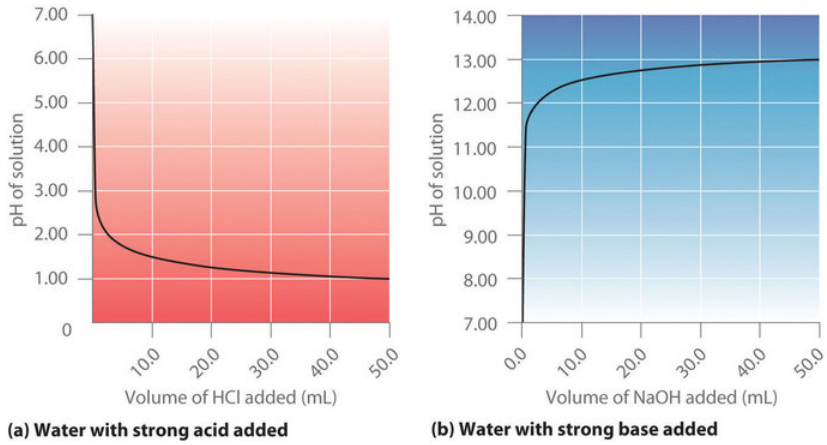


Figure *[Math Processing Error]*: Solution pH as a Function of the Volume of a Strong Acid or a Strong Base Added to Distilled Water. (a) When 0.20 M *[Math Processing Error]* is added to 50.0 mL of distilled water, the pH rapidly decreases until it reaches a minimum at the pH of 0.20 M *[Math Processing Error]*. (b) Conversely, when 0.20 M *[Math Processing Error]* is added to 50.0 mL of distilled water, the pH rapidly increases until it reaches a maximum at the pH of 0.20 M *[Math Processing Error]*. (CC BY-SA-NC; Anonymous by request)

The graphs of water with strong acid added and water with strong base added are inverses of each other.

Suppose that we now add 0.20 M *[Math Processing Error]* to 50.0 mL of a 0.10 M solution of *[Math Processing Error]*. Because *[Math Processing Error]* is a strong acid that is completely ionized in water, the initial *[Math Processing Error]* is 0.10 M, and the initial pH is 1.00. Adding *[Math Processing Error]* decreases the concentration of H+ because of the neutralization reaction (Figure *[Math Processing Error]*):

[Math Processing Error]

Thus the pH of the solution increases gradually. Near the equivalence point, however, the point at which the number of moles of base (or acid) added equals the number of moles of acid (or base) originally present in the solution, the pH increases much more rapidly because most of the *[Math Processing Error]* ions originally present have been consumed. For the titration of a monoprotic strong acid (*[Math Processing Error]*) with a monobasic strong base (*[Math Processing Error]*), we can calculate the volume of base needed to reach the equivalence point from the following relationship:

[Math Processing Error]

If 0.20 M *[Math Processing Error]* is added to 50.0 mL of a 0.10 M solution of *[Math Processing Error]*, we solve for *[Math Processing Error]*:

[Math Processing Error]

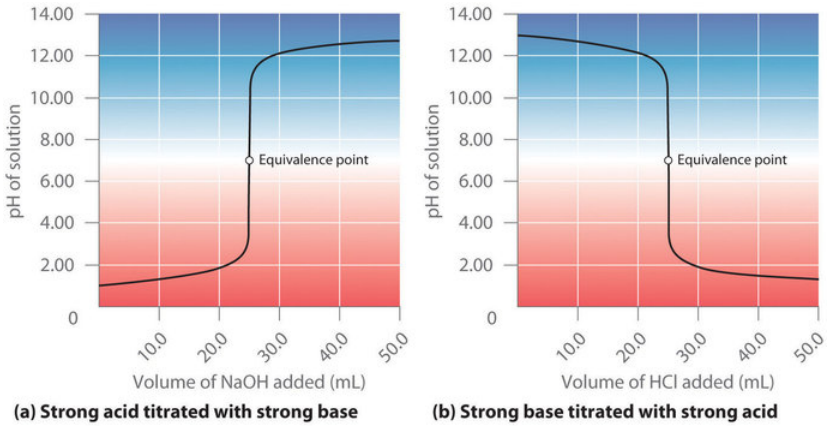


Figure *[Math Processing Error]*: The Titration of (a) a Strong Acid with a Strong Base and (b) a Strong Base with a Strong Acid(a) As 0.20 M *[Math Processing Error]* is slowly added to 50.0 mL of 0.10 M HCl, the pH increases slowly at first, then increases very rapidly as the equivalence point is approached, and finally increases slowly once more. (b) Conversely, as 0.20 M *[Math Processing Error]* is slowly added to 50.0 mL of 0.10 M *[Math Processing Error]*, the pH decreases slowly at first, then decreases very rapidly as the equivalence point is approached, and finally decreases slowly once more. (CC BY-SA-NC; Anonymous by request)

The titration curves of strong acid titrated with strong base and strong base titrated with strong acid are inverses of each other.

At the equivalence point (when 25.0 mL of *[Math Processing Error]* solution has been added), the neutralization is complete: only a salt remains in solution (NaCl), and the pH of the solution is 7.00. Adding more *[Math Processing Error]* produces a rapid increase in pH, but eventually the pH levels off at a value of about 13.30, the pH of 0.20 M *[Math Processing Error]*.

As shown in Figure *[Math Processing Error]*, the titration of 50.0 mL of a 0.10 M solution of *[Math Processing Error]* with 0.20 M *[Math Processing Error]* produces a titration curve that is nearly the mirror image of the titration curve in Figure *[Math Processing Error]*. The pH is initially 13.00, and it slowly decreases as *[Math Processing Error]* is added. As the equivalence point is approached, the pH drops rapidly before leveling off at a value of about 0.70, the pH of 0.20 M *[Math Processing Error]*.

The titration of either a strong acid with a strong base or a strong base with a strong acid produces an S-shaped curve. The curve is somewhat asymmetrical because the steady increase in the volume of the solution during the titration causes the solution to become more dilute. Due to the leveling effect, the shape of the curve for a titration involving a strong acid and a strong base depends on only the concentrations of the acid and base, not their identities.

> The shape of the titration curve involving a strong acid and a strong base depends only on their concentrations, not their identities.

✔ Example *[Math Processing Error]*: Hydrochloric Acid

Calculate the pH of the solution after 24.90 mL of 0.200 M *[Math Processing Error]* has been added to 50.00 mL of 0.100 M *[Math Processing Error]*.

Given: volumes and concentrations of strong base and acid

Asked for: pH

Strategy:

A. Calculate the number of millimoles of *[Math Processing Error]* and *[Math Processing Error]* to determine which, if either, is in excess after the neutralization reaction has occurred. If one species is in excess, calculate the amount that remains after the neutralization reaction.
B. Determine the final volume of the solution. Calculate the concentration of the species in excess and convert this value to pH.

Solution

A Because 0.100 mol/L is equivalent to 0.100 mmol/mL, the number of millimoles of *[Math Processing Error]* in 50.00 mL of 0.100 M *[Math Processing Error]* can be calculated as follows:

[Math Processing Error]

The number of millimoles of *[Math Processing Error]* added is as follows:

[Math Processing Error]

Thus *[Math Processing Error]* is in excess. To completely neutralize the acid requires the addition of 5.00 mmol of *[Math Processing Error]* to the *[Math Processing Error]* solution. Because only 4.98 mmol of *[Math Processing Error]* has been added, the amount of excess *[Math Processing Error]* is 5.00 mmol − 4.98 mmol = 0.02 mmol of *[Math Processing Error]*.

B The final volume of the solution is 50.00 mL + 24.90 mL = 74.90 mL, so the final concentration of *[Math Processing Error]* is as follows:

[Math Processing Error]

Hence,

[Math Processing Error]

This is significantly less than the pH of 7.00 for a neutral solution.

? Exercise *[Math Processing Error]*

Calculate the pH of a solution prepared by adding *[Math Processing Error]* of *[Math Processing Error]* *[Math Processing Error]* to *[Math Processing Error]* of a *[Math Processing Error]* solution of *[Math Processing Error]*.

Answer

11.6



pH after the addition of 10 ml of Strong Base to a Strong Acid:

https://youtu.be/_cM1_-kdJ20 (opens in new window)



pH at the Equivalence Point in a Strong Acid/Strong Base Titration:

https://youtu.be/7POGDA5Ql2M

Titrations of Weak Acids and Bases

In contrast to strong acids and bases, the shape of the titration curve for a weak acid or a weak base depends dramatically on the identity of the acid or the base and the corresponding *[Math Processing Error]* or *[Math Processing Error]*. As we shall see, the pH also changes much more gradually around the equivalence point in the titration of a weak acid or a weak base. As you learned previously, *[Math Processing Error]* of a solution of a weak acid (HA) is not equal to the concentration of the acid but depends on both its *[Math Processing Error]* and its concentration. Because only a fraction of a weak acid dissociates, *[Math Processing Error]* is less than *[Math Processing Error]*. Thus the pH of a solution of a weak acid is greater than the pH of a solution of a strong acid of the same concentration.

Figure *[Math Processing Error]* shows the titration curve for 50.0 mL of a 0.100 M solution of acetic acid with 0.200 M *[Math Processing Error]* superimposed on the curve for the titration of 0.100 M *[Math Processing Error]* shown in part (a) in Figure *[Math Processing Error]*. Below the equivalence point, the two curves are very different. Before any base is added, the pH of the acetic acid solution is greater than the pH of the *[Math Processing Error]* solution, and the pH changes more rapidly during the first part of the titration. Note also that the pH of the acetic acid solution at the equivalence point is greater than 7.00. That is, at the equivalence point, the solution is basic. In addition, the change in pH around the equivalence point is only about half as large as for the *[Math Processing Error]* titration; the magnitude of the pH change at the equivalence point depends on the *[Math Processing Error]* of the acid being titrated. Above the equivalence point, however, the two curves are identical. Once the acid has been neutralized, the pH of the solution is controlled only by the amount of excess *[Math Processing Error]* present, regardless of whether the acid is weak or strong.

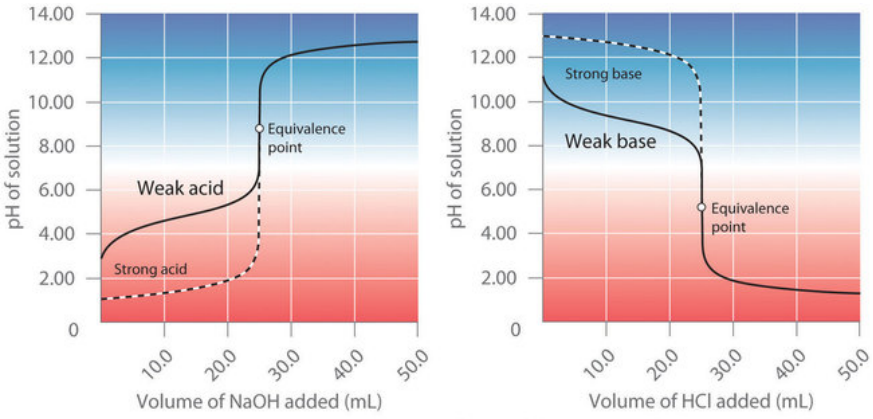


Figure *[Math Processing Error]*: The Titration of (a) a Weak Acid with a Strong Base and (b) a Weak Base with a Strong Acid. (a) As 0.200 M *[Math Processing Error]* is slowly added to 50.0 mL of 0.100 M acetic acid, the pH increases slowly at first, then increases rapidly as the equivalence point is approached, and then again increases more slowly. The corresponding curve for the titration of 50.0 mL of 0.100 M *[Math Processing Error]* with 0.200 M *[Math Processing Error]* is shown as a dashed line. (b) As 0.200 M *[Math Processing Error]* is slowly added to 50.0 mL of 0.100 M NH3, the pH decreases slowly at first, then decreases rapidly as the equivalence point is approached, and then again decreases more slowly. The corresponding curve for the titration of 50.0 mL of 0.100 M *[Math Processing Error]* with 0.200 M *[Math Processing Error]* is shown as a dashed line. (CC BY-SA-NC; Anonymous by request)

The titration curves of weak acid titrated with strong base and weak base titrated with strong acid are inverse of each other. These curves are shorter than the titration curves with strong acid and strong base.

> The shape of the titration curve of a weak acid or weak base depends heavily on their identities and the *[Math Processing Error]* or *[Math Processing Error]*.

The titration curve in Figure *[Math Processing Error]* was created by calculating the starting pH of the acetic acid solution before any *[Math Processing Error]* is added and then calculating the pH of the solution after adding increasing volumes of *[Math Processing Error]*. The procedure is illustrated in the following subsection and Example *[Math Processing Error]* for three points on the titration curve, using the *[Math Processing Error]* of acetic acid (4.76 at 25°C; *[Math Processing Error]*.

Calculating the pH of a Solution of a Weak Acid or a Weak Base

As explained discussed, if we know *[Math Processing Error]* or *[Math Processing Error]* and the initial concentration of a weak acid or a weak base, we can calculate the pH of a solution of a weak acid or a weak base by setting up a ICE table (i.e, initial concentrations, changes in concentrations, and final concentrations). In this situation, the initial concentration of acetic acid is 0.100 M. If we define *[Math Processing Error]* as *[Math Processing Error]* due to the dissociation of the acid, then the table of concentrations for the ionization of 0.100 M acetic acid is as follows:

[Math Processing Error]

table of concentrations for the ionization of 0.100 M acetic acid

ICE	*[Math Processing Error]*	*[Math Processing Error]*	*[Math Processing Error]*
initial	0.100	*[Math Processing Error]*	0
change	−x	+x	+x
final	0.100 − x	x	x

In this and all subsequent examples, we will ignore *[Math Processing Error]* and *[Math Processing Error]* due to the autoionization of water when calculating the final concentration. However, you should use Equation 16.45 and Equation 16.46 to check that this assumption is justified.

Inserting the expressions for the final concentrations into the equilibrium equation (and using approximations),

[Math Processing Error]

Solving this equation gives *[Math Processing Error]*. Thus the pH of a 0.100 M solution of acetic acid is as follows:

[Math Processing Error]



pH at the Start of a Weak Acid/Strong Base Titration: https://youtu.be/AtdBKfrfJNg

Calculating the pH during the Titration of a Weak Acid or a Weak Base

Now consider what happens when we add 5.00 mL of 0.200 M *[Math Processing Error]* to 50.00 mL of 0.100 M *[Math Processing Error]* (part (a) in Figure *[Math Processing Error]*). Because the neutralization reaction proceeds to completion, all of the *[Math Processing Error]* ions added will react with the acetic acid to generate acetate ion and water:

[Math Processing Error]

All problems of this type must be solved in two steps: a stoichiometric calculation followed by an equilibrium calculation. In the first step, we use the stoichiometry of the neutralization reaction to calculate the amounts of acid and conjugate base present in solution after the neutralization reaction has occurred. In the second step, we use the equilibrium equation to determine *[Math Processing Error]* of the resulting solution.

Step 1

To determine the amount of acid and conjugate base in solution after the neutralization reaction, we calculate the amount of *[Math Processing Error]* in the original solution and the amount of *[Math Processing Error]* in the *[Math Processing Error]* solution that was added. The acetic acid solution contained

[Math Processing Error]

The *[Math Processing Error]* solution contained

5.00 mL=1.00 mmol *[Math Processing Error]*

Comparing the amounts shows that *[Math Processing Error]* is in excess. Because *[Math Processing Error]* reacts with *[Math Processing Error]* in a 1:1 stoichiometry, the amount of excess *[Math Processing Error]* is as follows:

5.00 mmol *[Math Processing Error]* − 1.00 mmol *[Math Processing Error]* = 4.00 mmol *[Math Processing Error]*

Each 1 mmol of *[Math Processing Error]* reacts to produce 1 mmol of acetate ion, so the final amount of *[Math Processing Error]* is 1.00 mmol.

The stoichiometry of the reaction is summarized in the following ICE table, which shows the numbers of moles of the various species, not their concentrations.

[Math Processing Error]

ICE table

ICE	*[Math Processing Error]*	*[Math Processing Error]*	*[Math Processing Error]*
initial	5.00 mmol	1.00 mmol	0 mmol
change	−1.00 mmol	−1.00 mmol	+1.00 mmol

ICE	*[Math Processing Error]*	*[Math Processing Error]*	*[Math Processing Error]*
final	4.00 mmol	0 mmol	1.00 mmol

This ICE table gives the initial amount of acetate and the final amount of *[Math Processing Error]* ions as 0. Because an aqueous solution of acetic acid always contains at least a small amount of acetate ion in equilibrium with acetic acid, however, the initial acetate concentration is not actually 0. The value can be ignored in this calculation because the amount of *[Math Processing Error]* in equilibrium is insignificant compared to the amount of *[Math Processing Error]* added. Moreover, due to the autoionization of water, no aqueous solution can contain 0 mmol of *[Math Processing Error]*, but the amount of *[Math Processing Error]* due to the autoionization of water is insignificant compared to the amount of *[Math Processing Error]* added. We use the initial amounts of the reactants to determine the stoichiometry of the reaction and defer a consideration of the equilibrium until the second half of the problem.

Step 2

To calculate *[Math Processing Error]* at equilibrium following the addition of *[Math Processing Error]*, we must first calculate [*[Math Processing Error]*] and *[Math Processing Error]* using the number of millimoles of each and the total volume of the solution at this point in the titration:

[Math Processing Error] [Math Processing Error] [Math Processing Error]

Knowing the concentrations of acetic acid and acetate ion at equilibrium and *[Math Processing Error]* for acetic acid (*[Math Processing Error]*), we can calculate *[Math Processing Error]* at equilibrium:

[Math Processing Error]

[Math Processing Error]

Calculating *[Math Processing Error]* gives

[Math Processing Error]

Comparing the titration curves for *[Math Processing Error]* and acetic acid in Figure *[Math Processing Error]*, we see that adding the same amount (5.00 mL) of 0.200 M *[Math Processing Error]* to 50 mL of a 0.100 M solution of both acids causes a much smaller pH change for *[Math Processing Error]* (from 1.00 to 1.14) than for acetic acid (2.88 to 4.16). This is consistent with the qualitative description of the shapes of the titration curves at the beginning of this section. In Example *[Math Processing Error]*, we calculate another point for constructing the titration curve of acetic acid.



pH Before the Equivalence Point of a Weak Acid/Strong Base Titration:

https://youtu.be/znpwGCsefXc

Example *[Math Processing Error]*

What is the pH of the solution after 25.00 mL of 0.200 M *[Math Processing Error]* is added to 50.00 mL of 0.100 M acetic acid?

Given: volume and molarity of base and acid

Asked for: pH

Strategy:

A. Write the balanced chemical equation for the reaction. Then calculate the initial numbers of millimoles of *[Math Processing Error]* and *[Math Processing Error]*. Determine which species, if either, is present in excess.
B. Tabulate the results showing initial numbers, changes, and final numbers of millimoles.
C. If excess acetate is present after the reaction with *[Math Processing Error]*, write the equation for the reaction of acetate with water. Use a tabular format to obtain the concentrations of all the species present.
D. Calculate *[Math Processing Error]* using the relationship *[Math Processing Error]*. Calculate [OH−] and use this to calculate the pH of the solution.

Solution

A Ignoring the spectator ion (*[Math Processing Error]*), the equation for this reaction is as follows:

[Math Processing Error]

The initial numbers of millimoles of *[Math Processing Error]* and *[Math Processing Error]* are as follows:

25.00 mL(0.200 mmol OH−mL=5.00 mmol *[Math Processing Error]*

[Math Processing Error]

The number of millimoles of *[Math Processing Error]* equals the number of millimoles of *[Math Processing Error]*, so neither species is present in excess.

B Because the number of millimoles of *[Math Processing Error]* added corresponds to the number of millimoles of acetic acid in solution, this is the equivalence point. The results of the neutralization reaction can be summarized in tabular form.

[Math Processing Error]

results of the neutralization reaction

ICE	*[Math Processing Error]*	*[Math Processing Error]*	*[Math Processing Error]*
initial	5.00 mmol	5.00 mmol	0 mmol
change	−5.00 mmol	−5.00 mmol	+5.00 mmol
final	0 mmol	0 mmol	5.00 mmol

C Because the product of the neutralization reaction is a weak base, we must consider the reaction of the weak base with water to calculate [H+] at equilibrium and thus the final pH of the solution. The initial concentration of acetate is obtained from the neutralization reaction:

[Math Processing Error]

The equilibrium reaction of acetate with water is as follows:

[Math Processing Error]

The equilibrium constant for this reaction is

[Math Processing Error]

where *[Math Processing Error]* is the acid ionization constant of acetic acid. We therefore define x as *[Math Processing Error]* produced by the reaction of acetate with water. Here is the completed table of concentrations:

[Math Processing Error]

completed table of concentrations

	[Math Processing Error]	[Math Processing Error]	[Math Processing Error]
initial	0.0667	0	1.00 × 10−7
change	−x	+x	+x
final	(0.0667 − x)	x	x

D We can obtain *[Math Processing Error]* by substituting the known values into Equation *[Math Processing Error]*:

[Math Processing Error]

Substituting the expressions for the final values from the ICE table into Equation *[Math Processing Error]* and solving for *[Math Processing Error]*:

[Math Processing Error]

Thus *[Math Processing Error]* and the pH of the final solution is 8.794 (Figure *[Math Processing Error]*). As expected for the titration of a weak acid, the pH at the equivalence point is greater than 7.00 because the product of the titration is a base, the acetate ion, which then reacts with water to produce *[Math Processing Error]*.

? Exercise *[Math Processing Error]*

Calculate the pH of a solution prepared by adding 45.0 mL of a 0.213 M *[Math Processing Error]* solution to 125.0 mL of a 0.150 M solution of ammonia. The *[Math Processing Error]* of ammonia is 4.75 at 25°C.

Answer

9.23

As shown in part (b) in Figure *[Math Processing Error]*, the titration curve for NH3, a weak base, is the reverse of the titration curve for acetic acid. In particular, the pH at the equivalence point in the titration of a weak base is less than 7.00 because the titration produces an acid.

The identity of the weak acid or weak base being titrated strongly affects the shape of the titration curve. Figure *[Math Processing Error]* illustrates the shape of titration curves as a function of the *[Math Processing Error]* or the *[Math Processing Error]*. As the acid or the base being titrated becomes weaker (its *[Math Processing Error]* or *[Math Processing Error]* becomes larger), the pH change around the equivalence point decreases significantly. With very dilute solutions, the curve becomes so shallow that it can no longer be used to determine the equivalence point.

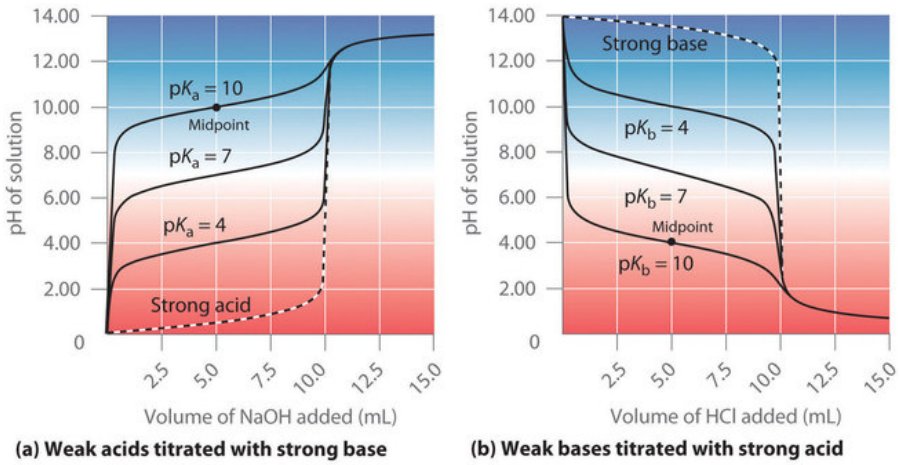


Figure *[Math Processing Error]*: Effect of Acid or Base Strength on the Shape of Titration Curves. Unlike strong acids or bases, the shape of the titration curve for a weak acid or base depends on the *[Math Processing Error]* or *[Math Processing Error]* of the weak acid or base being titrated. (a) Solution pH as a function of the volume of 1.00 M *[Math Processing Error]* added to 10.00 mL of 1.00 M solutions of weak acids with the indicated *[Math Processing Error]* values. (b) Solution pH as a function of the volume of 1.00 M *[Math Processing Error]* added to 10.00 mL of 1.00 M solutions of weak bases with the indicated *[Math Processing Error]* values. The shapes of the two sets of curves are essentially identical, but one is flipped vertically in relation to the other. Midpoints are indicated for the titration curves corresponding to *[Math Processing Error]* = 10 and *[Math Processing Error]* = 10. (CC BY-SA-NC; Anonymous by request)

The titration curves of weak acids with strong base and weak bases titrated with strong acid are inverses of each other. Three weak acids and three weak bases with pKa and pKb of 4, 7, and 10 are used.

One point in the titration of a weak acid or a weak base is particularly important: the midpoint of a titration is defined as the point at which exactly enough acid (or base) has been added to neutralize one-half of the acid (or the base) originally present and occurs halfway to the equivalence point. The midpoint is indicated in Figures *[Math Processing Error]* and *[Math Processing Error]* for the two shallowest curves. By definition, at the midpoint of the titration of an acid, [HA] = [A−]. Recall that the ionization constant for a weak acid is as follows:

[Math Processing Error]

If *[Math Processing Error]*, this reduces to *[Math Processing Error]*. Taking the negative logarithm of both sides,

[Math Processing Error]

From the definitions of *[Math Processing Error]* and pH, we see that this is identical to

[Math Processing Error]

Thus the pH at the midpoint of the titration of a weak acid is equal to the *[Math Processing Error]* of the weak acid, as indicated in part (a) in Figure *[Math Processing Error]* for the weakest acid where we see that the midpoint for *[Math Processing Error]* = 10 occurs at pH = 10. Titration methods can therefore be used to determine both the concentration and the *[Math Processing Error]* (or the *[Math Processing Error]*) of a weak acid (or a weak base).

> The pH at the midpoint of the titration of a weak acid is equal to the *[Math Processing Error]* of the weak acid.

Titrations of Polyprotic Acids or Bases

When a strong base is added to a solution of a polyprotic acid, the neutralization reaction occurs in stages. The most acidic group is titrated first, followed by the next most acidic, and so forth. If the *[Math Processing Error]* values are separated by at least three *[Math Processing Error]* units, then the overall titration curve shows well-resolved “steps” corresponding to the titration of each proton. A titration of the triprotic acid *[Math Processing Error]* with *[Math Processing Error]* is illustrated in Figure *[Math Processing Error]* and shows two well-defined steps: the first midpoint corresponds to *[Math Processing Error]*1, and the second midpoint corresponds to *[Math Processing Error]*$_2$. Because HPO_4^{2-} is such a weak acid, *[Math Processing Error]*$_3$ has such a high value that the third step cannot be resolved using 0.100 M *[Math Processing Error]* as the titrant.

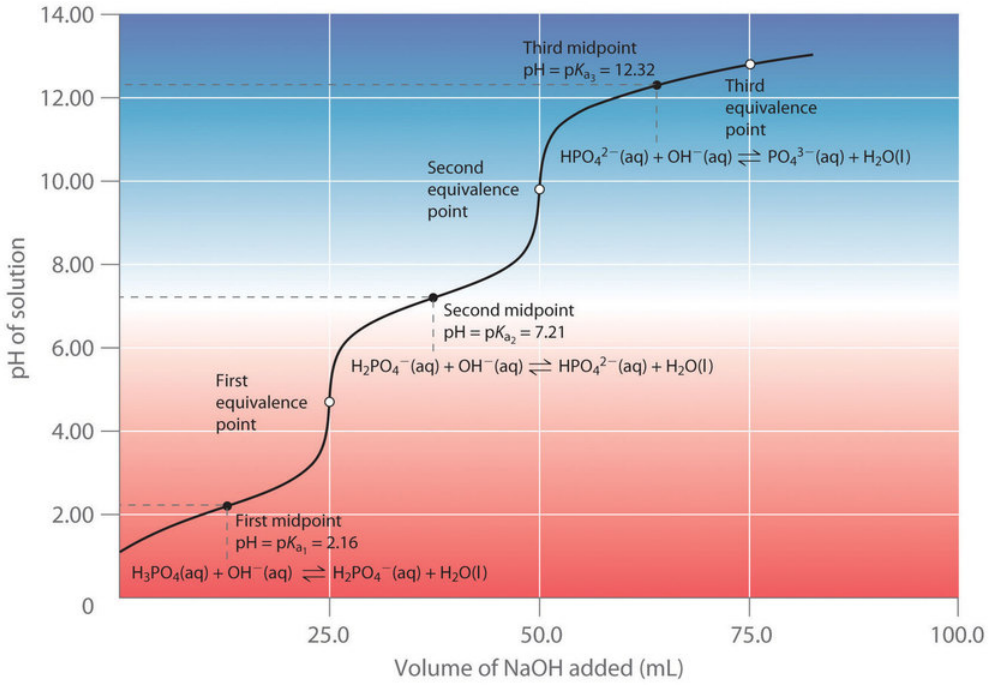
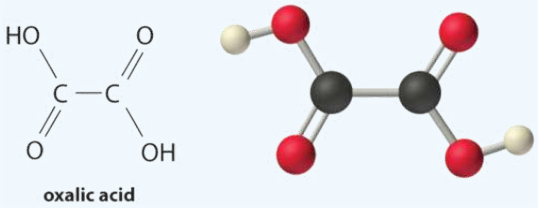


Figure *[Math Processing Error]*: Titration Curve for Phosphoric Acid (*[Math Processing Error]*, a Typical Polyprotic Acid. The curve for the titration of 25.0 mL of a 0.100 M *[Math Processing Error]* solution with 0.100 M *[Math Processing Error]* along with the species in solution at each Ka is shown. Note the two distinct equivalence points corresponding to deprotonation of *[Math Processing Error]* at pH ≈ 4.6 and *[Math Processing Error]* at pH ≈ 9.8. Because *[Math Processing Error]* is a very weak acid, the third equivalence point, at pH ≈ 13, is not well defined. (CC BY-SA-NC; Anonymous by request)

The titration curve for the reaction of a polyprotic base with a strong acid is the mirror image of the curve shown in Figure *[Math Processing Error]*. The initial pH is high, but as acid is added, the pH decreases in steps if the successive *[Math Processing Error]* values are well separated. Table E1 lists the ionization constants and *[Math Processing Error]* values for some common polyprotic acids and bases.

✔ Example *[Math Processing Error]*

Calculate the pH of a solution prepared by adding 55.0 mL of a 0.120 M *[Math Processing Error]* solution to 100.0 mL of a 0.0510 M solution of oxalic acid (*[Math Processing Error]*), a diprotic acid (abbreviated as *[Math Processing Error]*). Oxalic acid, the simplest dicarboxylic acid, is found in rhubarb and many other plants. Rhubarb leaves are toxic because they contain the calcium salt of the fully deprotonated form of oxalic acid, the oxalate ion (*[Math Processing Error]*, abbreviated *[Math Processing Error]*).Oxalate salts are toxic for two reasons. First, oxalate salts of divalent cations such as *[Math Processing Error]* are insoluble at neutral pH but soluble at low pH. As a result, calcium oxalate dissolves in the dilute acid of the stomach, allowing oxalate to be absorbed and transported into cells, where it can react with calcium to form tiny calcium oxalate crystals that damage tissues. Second, oxalate forms stable complexes with metal ions, which can alter the distribution of metal ions in biological fluids.



oxalic acid

Given: volume and concentration of acid and base

Asked for: pH

Strategy:

A. Calculate the initial millimoles of the acid and the base. Use a tabular format to determine the amounts of all the species in solution.
B. Calculate the concentrations of all the species in the final solution. Determine *[Math Processing Error]* and convert this value to pH.

Solution:

A Table E5 gives the *[Math Processing Error]* values of oxalic acid as 1.25 and 3.81. Again we proceed by determining the millimoles of acid and base initially present:

[Math Processing Error]

[Math Processing Error]

The strongest acid (*[Math Processing Error]*) reacts with the base first. This leaves (6.60 − 5.10) = 1.50 mmol of *[Math Processing Error]* to react with Hox−, forming ox^{2-} and H_2O. The reactions can be written as follows:

[Math Processing Error]

[Math Processing Error]

In tabular form,

Solutions to Example 17.3.3

	[Math Processing Error]	*[Math Processing Error]*	*[Math Processing Error]*	*[Math Processing Error]*
initial	5.10 mmol	6.60 mmol	0 mmol	0 mmol
change (step 1)	−5.10 mmol	−5.10 mmol	+5.10 mmol	0 mmol
final (step 1)	0 mmol	1.50 mmol	5.10 mmol	0 mmol
change (step 2)	—	−1.50 mmol	−1.50 mmol	+1.50 mmol
final	0 mmol	0 mmol	3.60 mmol	1.50 mmol

B The equilibrium between the weak acid (*[Math Processing Error]*) and its conjugate base (*[Math Processing Error]*) in the final solution is determined by the magnitude of the second ionization constant, *[Math Processing Error]*. To calculate the pH of the solution, we need to know *[Math Processing Error]*, which is determined using exactly the same method as in the acetic acid titration in Example *[Math Processing Error]*:

[Math Processing Error]

Thus the concentrations of *[Math Processing Error]* and *[Math Processing Error]* are as follows:

[Math Processing Error]

[Math Processing Error]

We can now calculate [H+] at equilibrium using the following equation:

[Math Processing Error]

Rearranging this equation and substituting the values for the concentrations of *[Math Processing Error]* and *[Math Processing Error]*,

[Math Processing Error]

So

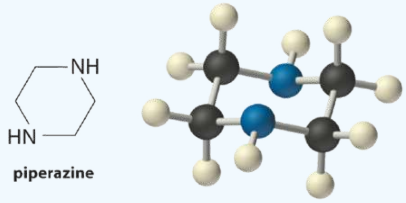
[Math Processing Error]

This answer makes chemical sense because the pH is between the first and second *[Math Processing Error]* values of oxalic acid, as it must be. We added enough hydroxide ion to completely titrate the first, more acidic proton (which should give us a pH greater than *[Math Processing Error]*), but we added only enough to titrate less than half of the second, less acidic proton, with *[Math Processing Error]*. If we had added exactly enough hydroxide to completely titrate the first proton plus half of the

second, we would be at the midpoint of the second step in the titration, and the pH would be 3.81, equal to *[Math Processing Error]*.

? Exercise *[Math Processing Error]*: Piperazine

Piperazine is a diprotic base used to control intestinal parasites (“worms”) in pets and humans. A dog is given 500 mg (5.80 mmol) of piperazine (*[Math Processing Error]* = 4.27, *[Math Processing Error]* = 8.67). If the dog’s stomach initially contains 100 mL of 0.10 M *[Math Processing Error]* (pH = 1.00), calculate the pH of the stomach contents after ingestion of the piperazine.



Answer

pH=4.9

Indicators

In practice, most acid–base titrations are not monitored by recording the pH as a function of the amount of the strong acid or base solution used as the titrant. Instead, an acid–base indicator is often used that, if carefully selected, undergoes a dramatic color change at the pH corresponding to the equivalence point of the titration. Indicators are weak acids or bases that exhibit intense colors that vary with pH. The conjugate acid and conjugate base of a good indicator have very different colors so that they can be distinguished easily. Some indicators are colorless in the conjugate acid form but intensely colored when deprotonated (phenolphthalein, for example), which makes them particularly useful.

We can describe the chemistry of indicators by the following general equation:

[Math Processing Error]

where the protonated form is designated by *[Math Processing Error]* and the conjugate base by *[Math Processing Error]*. The ionization constant for the deprotonation of indicator *[Math Processing Error]* is as follows:

[Math Processing Error]

The *[Math Processing Error]* (its *[Math Processing Error]*) determines the pH at which the indicator changes color.

Many different substances can be used as indicators, depending on the particular reaction to be monitored. For example, red cabbage juice contains a mixture of colored substances that change from deep red at low pH to light blue at intermediate pH to yellow at high pH. Similarly, *Hydrangea macrophylla* flowers can be blue, red, pink, light purple, or dark purple depending on the soil pH (Figure *[Math Processing Error]*). Acidic soils will produce blue flowers, whereas alkaline soils will produce pinkish flowers.

Irrespective of the origins, a good indicator must have the following properties:

- The color change must be easily detected.
- The color change must be rapid.
- The indicator molecule must not react with the substance being titrated.
- To minimize errors, the indicator should have a *[Math Processing Error]* that is within one pH unit of the expected pH at the equivalence point of the titration.



Figure *[Math Processing Error]*: Naturally occurring pH indicators can be found in red cabbage and Hydrangea macrophylla flowers. Red Cabbage image (CC BY-SA 3.0; KENPEI via Wikipedia) and Hydrangea macrophylla flowers (pixabay).

Synthetic indicators have been developed that meet these criteria and cover virtually the entire pH range. Figure *[Math Processing Error]* shows the approximate pH range over which some common indicators change color and their change in color. In addition, some indicators (such as thymol blue) are polyprotic acids or bases, which change color twice at widely separated pH values.

Indicator	pK_{in}	Color change
Alizarin yellow R	11.0	yellow to red
Thymolphthalein	9.9	colorless to blue
Phenolphthalein	9.5	colorless to pink
Thymol blue	9.2	yellow to blue
Phenol red	7.4	yellow to red
Bromothymol blue	7.3	yellow to blue
Bromocresol purple	6.4	yellow to purple
Ethyl red	5.4	colorless to red
Resorcin blue	5.3	red to blue
Resazurin	5.1	orange to violet
Methyl red	5.0	red to yellow
Bromophenol blue	4.1	yellow to blue
Thymol blue	1.7	red to yellow
Malachite green	1.3	yellow to turquoise
Methyl violet	0.8	yellow to blue

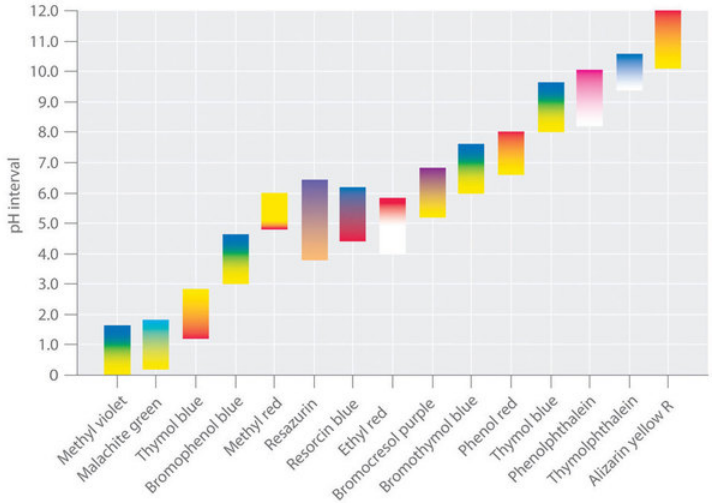


Figure *[Math Processing Error]*: Some Common Acid–Base Indicators. Approximate colors are shown, along with *[Math Processing Error]* values and the pH range over which the color changes. (CC BY-SA-NC; Anonymous by request)

It is important to be aware that an indicator does not change color abruptly at a particular pH value; instead, it actually undergoes a pH titration just like any other acid or base. As the concentration of HIn decreases and the concentration of In− increases, the color of the solution slowly changes from the characteristic color of HIn to that of In−. As we will see later, the [In−]/[HIn] ratio changes from 0.1 at a pH one unit below pKin to 10 at a pH one unit above pKin. Thus most indicators change color over a pH range of about two pH units.

We have stated that a good indicator should have a pKin value that is close to the expected pH at the equivalence point. For a strong acid–strong base titration, the choice of the indicator is not especially critical due to the very large change in pH that occurs around the equivalence point. In contrast, using the wrong indicator for a titration of a weak acid or a weak base can result in relatively large errors, as illustrated in Figure *[Math Processing Error]*. This figure shows plots of pH versus volume of base added for the titration of 50.0 mL of a 0.100 M solution of a strong acid (HCl) and a weak acid (acetic acid) with 0.100 M *[Math Processing Error]*. The pH ranges over which two common indicators (methyl red, *[Math Processing Error]*, and phenolphthalein, *[Math Processing Error]*) change color are also shown. The horizontal bars indicate the pH ranges over which both indicators change color cross the *[Math Processing Error]* titration curve, where it is almost vertical. Hence both indicators change color when essentially the same volume of *[Math Processing Error]* has been added (about 50 mL), which corresponds to the equivalence point. In contrast, the titration of acetic acid will give very different results depending on whether methyl red or phenolphthalein is used as the indicator. Although the pH range over which phenolphthalein changes color is slightly greater than the pH at the equivalence point of the strong acid titration, the error will be negligible due to the slope of this portion of the titration curve. Just as with the *[Math Processing Error]* titration, the phenolphthalein indicator will turn pink when about 50 mL of *[Math Processing Error]* has been added to the acetic acid solution. In contrast, methyl red begins to change from red to yellow around

pH 5, which is near the midpoint of the acetic acid titration, not the equivalence point. Adding only about 25–30 mL of *[Math Processing Error]* will therefore cause the methyl red indicator to change color, resulting in a huge error.

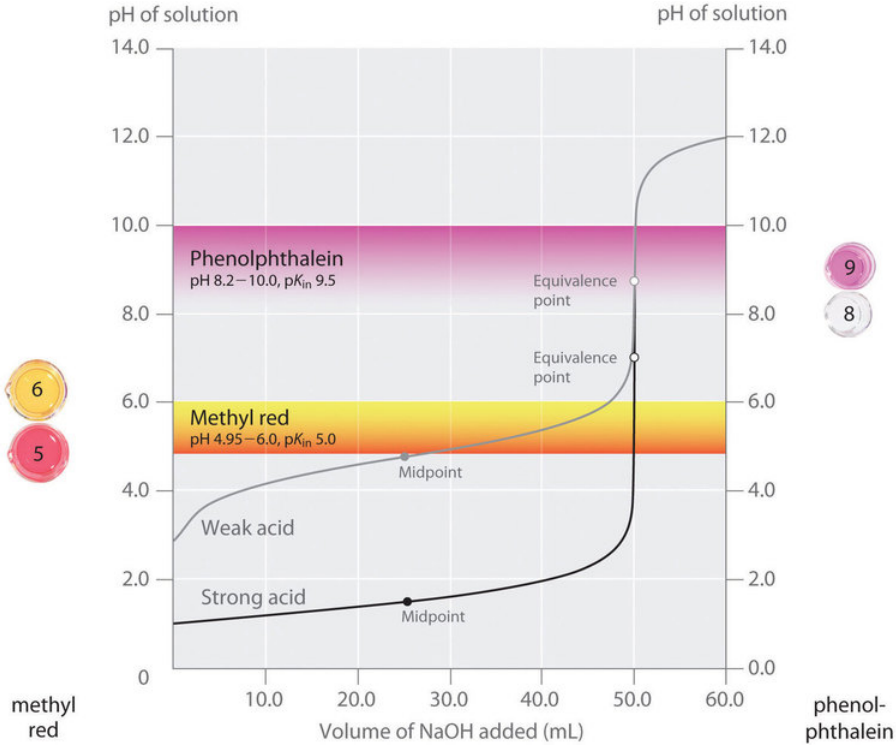


Figure *[Math Processing Error]*: Choosing the Correct Indicator for an Acid–Base Titration. (CC BY-SA-NC; Anonymous by request)

If the pH of the solution is between 4.95 and 6 then methyl red should be used. If the pH is between 8,2 and 10 then phenolphthalein should be used.

The graph shows the results obtained using two indicators (methyl red and phenolphthalein) for the titration of 0.100 M solutions of a strong acid (HCl) and a weak acid (acetic acid) with 0.100 M *[Math Processing Error]*. Due to the steepness of the titration curve of a strong acid around the equivalence point, either indicator will rapidly change color at the equivalence point for the titration of the strong acid. In contrast, the pKin for methyl red (5.0) is very close to the *[Math Processing Error]* of acetic acid (4.76); the midpoint of the color change for methyl red occurs near the midpoint of the titration, rather than at the equivalence point.

In general, for titrations of strong acids with strong bases (and vice versa), any indicator with a pKin between about 4.0 and 10.0 will do. For the titration of a weak acid, however, the pH at the equivalence point is greater than 7.0, so an indicator such as phenolphthalein or thymol blue, with pKin > 7.0, should be used. Conversely, for the titration of a weak base, where the pH at the equivalence point is less than 7.0, an indicator such as methyl red or bromocresol blue, with pKin < 7.0, should be used.

The existence of many different indicators with different colors and pKin values also provides a convenient way to estimate the pH of a solution without using an expensive electronic pH meter and a fragile pH electrode. Paper or plastic strips impregnated with combinations of indicators are used as “pH paper,” which allows you to estimate the pH of a solution by simply dipping a piece of pH paper into it and comparing the resulting color with the standards printed on the container (Figure *[Math Processing Error]*).

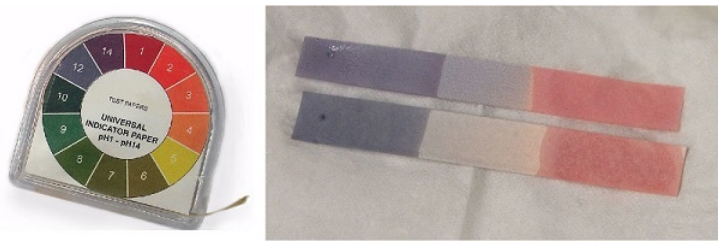


Figure *[Math Processing Error]*: pH Paper. pH paper contains a set of indicators that change color at different pH values. The approximate pH of a solution can be determined by simply dipping a paper strip into the solution and comparing the color to the standards provided. (CC BY-SA-NC; Anonymous by request)



pH Indicators: pH Indicators(opens in new window) [youtu.be]

Summary and Takeaway

Plots of acid–base titrations generate titration curves that can be used to calculate the pH, the pOH, the *[Math Processing Error]*, and the *[Math Processing Error]* of the system. The shape of a titration curve, a plot of pH versus the amount of acid or base added, provides important information about what is occurring in solution during a titration. The shapes of titration curves for weak acids and bases depend dramatically on the identity of the compound. The equivalence point of an acid–base titration is the point at which exactly enough acid or base has been added to react completely with the other component. The equivalence point in the titration of a strong acid or a strong base occurs at pH 7.0. In titrations of weak acids or weak bases, however, the pH at the equivalence point is greater or less than 7.0, respectively. The pH tends to change more slowly before the equivalence point is reached in titrations of weak acids and weak bases than in titrations of strong acids and strong bases. The pH at the midpoint, the point halfway on the titration curve to the equivalence point, is equal to the *[Math Processing Error]* of the weak acid or the *[Math Processing Error]* of the weak base. Thus titration methods can be used to determine both the concentration and the *[Math Processing Error]* (or the *[Math Processing Error]*) of a weak acid (or a weak base). Acid–base indicators are compounds that change color at a particular pH. They are typically weak acids or bases whose changes in color correspond to deprotonation or protonation of the indicator itself.

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14.1.7: Polyprotic Acids

Learning Objectives

- Extend previously introduced equilibrium concepts to acids and bases that may donate or accept more than one proton

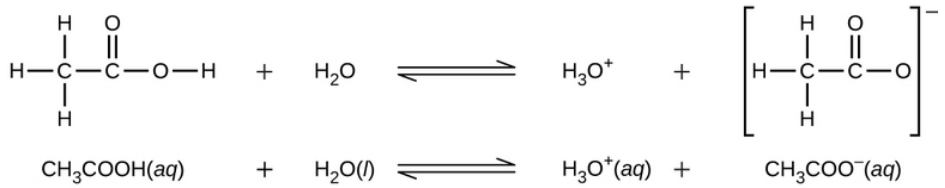
We can classify acids by the number of protons per molecule that they can give up in a reaction. Acids such as HCl, $\mathrm{HNO_3}$, and HCN that contain one ionizable hydrogen atom in each molecule are called monoprotic acids. Their reactions with water are:

$$\mathrm{HCl}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{H_3O^+}(aq) + \mathrm{Cl^-}(aq)$$

$$\mathrm{HNO_3}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{H_3O^+}(aq) + \mathrm{NO_3^-}(aq)$$

$$\mathrm{HCN}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{H_3O^+}(aq) + \mathrm{CN^-}(aq)$$

Even though it contains four hydrogen atoms, acetic acid, $\mathrm{CH_3CO_2H}$, is also monoprotic because only the hydrogen atom from the carboxyl group ($-\mathrm{COOH}$) reacts with bases:



This image contains two equilibrium reactions. The first shows a C atom bonded to three H atoms and another C atom. The second C atom is double bonded to an O atom and also forms a single bond to another O atom. The second O atom is bonded to an H atom. There is a plus sign and then the molecular formula H subscript 2 O. An equilibrium arrow follows the H subscript 2 O. To the right of the arrow is H subscript 3 O superscript positive sign. There is a plus sign. The final structure shows a C atom bonded the three H atoms and another C atom. This second C atom is double bonded to an O atom and single bonded to another O atom. The entire structure is in brackets and a superscript negative sign appears outside the brackets. The second reaction shows C H subscript 3 C O O H (a q) plus H subscript 2 O (l) equilibrium arrow H subscript 3 O (a q) plus C H subscript 3 C O O superscript negative sign (a q).

Similarly, monoprotic bases are bases that will accept a single proton.

Diprotic Acids

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:

- **The first ionization is**

$$\mathrm{H_2SO_4}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HSO_4^-}(aq)$$

with $K_{\mathrm{a1}} > 10^2$; $complete\ dissociation$.

- **The second ionization is**

$$\mathrm{HSO_4^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{SO_4^{2-}}(aq)$$

with $K_{\mathrm{a2}} = 1.2 \times 10^{-2}$.

This stepwise ionization process occurs for all polyprotic acids. When we make a solution of a weak diprotic acid, we get a solution that contains a mixture of acids. Carbonic acid, $\mathrm{H_2CO_3}$, is an example of a weak diprotic acid. The first ionization of carbonic acid yields hydronium ions and bicarbonate ions in small amounts.

- **First Ionization**

$$\mathrm{H_2CO_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HCO_3^-}(aq)$$

with

$$K_{\mathrm{H_2CO_3}} = \frac{[\mathrm{H_3O^+}][\mathrm{HCO_3^-}]}{[\mathrm{H_2CO_3}]} = 4.3 \times 10^{-7}$$

The bicarbonate ion can also act as an acid. It ionizes and forms hydronium ions and carbonate ions in even smaller quantities.

- **Second Ionization**

$$\mathrm{HCO_3^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CO_3^{2-}}(aq)$$

with

$$K_{\mathrm{HCO_3^-}} = \frac{[\mathrm{H_3O^+}][\mathrm{CO_3^{2-}}]}{[\mathrm{HCO_3^-}]} = 4.7 \times 10^{-11}$$

$K_{\mathrm{H_2CO_3}}$ is larger than $K_{\mathrm{HCO_3^-}}$ by a factor of 10^4, so H_2CO_3 is the dominant producer of hydronium ion in the solution. This means that little of the $\mathrm{HCO_3^-}$ formed by the ionization of H_2CO_3 ionizes to give hydronium ions (and carbonate ions), and the concentrations of H_3O^+ and $\mathrm{HCO_3^-}$ 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 can simplify our work considerably because we can determine the concentration of H_3O^+ and the conjugate base from the first ionization, then determine the concentration of the conjugate base of the second ionization in a solution with concentrations determined by the first ionization.

Example 14.1.7.1: Ionization of a Diprotic Acid

When we buy soda water (carbonated water), we are buying a solution of carbon dioxide in water. The solution is acidic because CO_2 reacts with water to form carbonic acid, H_2CO_3. What are $[\mathrm{H_3O^+}]$, $[\mathrm{HCO_3^-}]$, and $[\mathrm{CO_3^{2-}}]$ in a saturated solution of CO_2 with an initial $[H_2CO_3]$ = 0.033 *M*?

$$\mathrm{H_2CO_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HCO_3^-}(aq) \quad K_{\mathrm{a1}} = 4.3 \times 10^{-7} \qquad \text{(equilibrium step 1)}$$

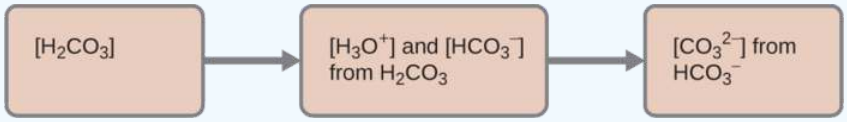
$$\mathrm{HCO_3^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CO_3^{2-}}(aq) \quad K_{\mathrm{a2}} = 4.7 \times 10^{-11} \qquad \text{(equilibrium step 2)}$$

Solution

As indicated by the ionization constants, H_2CO_3 is a much stronger acid than $\mathrm{HCO_3^-}$, so $\mathrm{H_2CO_3}$ is the dominant producer of hydronium ion in solution. Thus there are two parts in the solution of this problem:

1. Using the customary four steps, we determine the concentration of H_3O^+ and $\mathrm{HCO_3^-}$ produced by ionization of H_2CO_3.
2. Then we determine the concentration of $\mathrm{CO_3^{2-}}$ in a solution with the concentration of H_3O^+ and $\mathrm{HCO_3^-}$ determined in (1).

To summarize:



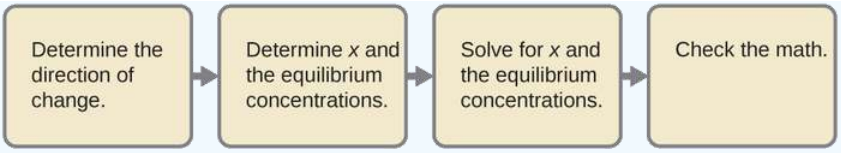
Four tan rectangles are shown that are connected with right pointing arrows. The first is labeled “left bracket H subscript 2 C O subscript 3 right bracket.” The second is labeled “left bracket H subscript 3 O superscript plus right bracket and left bracket H C O subscript 3 superscript negative right bracket from H subscript 2 C O subscript 3.” The third is labeled “left bracket C O subscript 3 superscript 2 negative right bracket from H C O subscript 3 superscript negative.”

1. First Ionization: Determine the concentrations of $\mathrm{H_3O^+}$ *and* $\mathrm{HCO_3^-}$.

Since equilibrium step 1 is has a much bigger $K_{a1} = 4.3 \times 10^{-7}$ than $K_{a2} = 4.7 \times 10^{-11}$ for equilibrium step 2, we can safely ignore the second ionization step and focus only on the first step (but address it in next part of problem).

$$\mathrm{H_2CO_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HCO_3^-}(aq) \quad K_{\mathrm{a1}} = 4.3 \times 10^{-7}$$

As for the ionization of any other weak acid:



Four tan rectangles are shown that are connected with right pointing arrows. The first is labeled “Determine the direction of change.” The second is labeled “Determine x and the equilibrium concentrations.” The third is labeled “Solve for x and the equilibrium concentrations.” The fourth is labeled “Check the math.”

An abbreviated table of changes and concentrations shows:

Abbreviated table of changes and concentrations

ICE Table	$H_2CO_3(aq)$	$H_2O(l)$	$H_3O^+(aq)$	$HCO_3^-(aq)$
Initial (M)	$0.033\ M$	-	0	0
Change (M)	$-x$	-	$+x$	$+x$
Equilibrium (M)	$0.033\ M - x$	-	x	x

Substituting the equilibrium concentrations into the equilibrium constant gives us:

$$K_{H_2CO_3} = \frac{[H_3O^+][HCO_3^-]}{[H_2CO_3]} = \frac{(x)(x)}{0.033 - x} = 4.3 \times 10^{-7}$$

Solving the preceding equation making our standard assumptions gives:

$$x = 1.2 \times 10^{-4}$$

Thus:

$$[H_2CO_3] = 0.033\ M$$

$$[H_3O^+] = [HCO_3^-] = 1.2 \times 10^{-4}\ M$$

2. Second Ionization: Determine the concentration of CO_3^{2-} in a solution at equilibrium.

Since the equilibrium step 1 is has a much bigger K_a than equilibrium step 2, we can the equilibrium conditions calculated from first part of example as the initial conditions for an ICER Table for the equilibrium step 2:

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$$

ICER Table for the equilibrium step 2:

ICE Table	$HCO_3^-(aq)$	$H_2O(l)$	$H_3O^+(aq)$	$CO_3^{2-}(aq)$
Initial (M)	$1.2 \times 10^{-4}\ M$	-	$1.2 \times 10^{-4}\ M$	0
Change (M)	$-y$	-	$+y$	$+y$
Equilibrium (M)	$1.2 \times 10^{-4}\ M - y$	-	$1.2 \times 10^{-4}\ M + y$	y

$$K_{HCO_3^-} = \frac{[H_3O^+][CO_3^{2-}]}{[HCO_3^-]}$$

$$= \frac{(1.2 \times 10^{-4}\ M + y)(y)}{(1.2 \times 10^{-4}\ M - y)}$$

To avoid solving a quadratic equation, we can assume $y \ll 1.2 \times 10^{-4}\ M$ so

$$K_{HCO_3^-} = 4.7 \times 10^{-11} \approx \frac{(1.2 \times 10^{-4}\ M)(y)}{(1.2 \times 10^{-4}\ M)}$$

Rearranging to solve for y

$$y \approx \frac{(4.7 \times 10^{-11})(1.2 \times 10^{-4}\ M)}{1.2 \times 10^{-4}\ M}$$

$$[\mathrm{CO_3^{2-}}] = y \approx 4.7 \times 10^{-11}$$

To summarize:

In part 1 of this example, we found that the $\mathrm{H_2CO_3}$ in a 0.033-*M* solution ionizes slightly and at equilibrium $[\mathrm{H_2CO_3}] = 0.033\ M$, $[\mathrm{H_3O^+}] = 1.2 \times 10^{-4}$, and $[\mathrm{HCO_3^-}] = 1.2 \times 10^{-4}\ M$. In part 2, we determined that $[\mathrm{CO_3^{2-}}] = 5.6 \times 10^{-11}\ M$.

? Exercise 14.1.7.2: Hydrogen Sulfide

The concentration of H_2S in a saturated aqueous solution at room temperature is approximately 0.1 *M*. Calculate $[\mathrm{H_3O^+}]$, $[\mathrm{HS^-}]$, and $[\mathrm{S^{2-}}]$ in the solution:

$$\mathrm{H_2S}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HS^-}(aq) \quad K_{\mathrm{a1}} = 8.9 \times 10^{-8}$$

$$\mathrm{HS^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{S^{2-}}(aq) \quad K_{\mathrm{a2}} = 1.0 \times 10^{-19}$$

Answer

$[\mathrm{H_2S}] = 0.1M$, $[\mathrm{H_3O^+}] = [HS^-] = 0.0001\ M$, $[S^{2-}] = 1 \times 10^{-19}\ M$

We note that the concentration of the sulfide ion is the same as K_{a2}. This is due to the fact that each subsequent dissociation occurs to a lesser degree (as acid gets weaker).

Triprotic Acids

A triprotic acid is an acid that has three dissociable protons that undergo stepwise ionization: Phosphoric acid is a typical example:

- **The first ionization is**

$$\mathrm{H_3PO_4}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{H_2PO_4^-}(aq)$$

with $K_{\mathrm{a1}} = 7.5 \times 10^{-3}$.

- **The second ionization is**

$$\mathrm{H_2PO_4^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HPO_4^{2-}}(aq)$$

with $K_{\mathrm{a2}} = 6.2 \times 10^{-8}$.

- **The third ionization is**

$$\mathrm{HPO_4^{2-}}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{PO_4^{3-}}(aq)$$

with $K_{\mathrm{a3}} = 4.2 \times 10^{-13}$.

As with the diprotic acids, the differences in the ionization constants of these reactions tell us that in each successive step the degree of ionization is significantly weaker. 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, the calculations can be broken down into a series of parts similar to those for diprotic acids.

Polyprotic bases can accept more than one hydrogen ion in solution. The carbonate ion is an example of a diprotic base, since it can accept up to two protons. Solutions of alkali metal carbonates are quite alkaline, due to the reactions:

$$\mathrm{H_2O}(l) + \mathrm{CO_3^{2-}}(aq) \rightleftharpoons \mathrm{HCO_3^-}(aq) + \mathrm{OH^-}(aq)$$

and

$$\mathrm{H_2O}(l) + \mathrm{HCO_3^-}(aq) \rightleftharpoons \mathrm{H_2CO_3}(aq) + \mathrm{OH^-}(aq)$$

Summary

An acid that contains more than one ionizable proton is a polyprotic acid. The protons of these acids ionize in steps. The differences in the acid ionization constants for the successive ionizations of the protons in a polyprotic acid usually vary by roughly five orders of magnitude. As long as the difference between the successive values of K_a of the acid is greater than about a factor of 20, it is appropriate to break down the calculations of the concentrations of the ions in solution into a series of steps.

Glossary

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

monoprotic acid
: acid containing one ionizable hydrogen atom per molecule

stepwise ionization
: process in which an acid is ionized by losing protons sequentially

triprotic acid
: acid that contains three ionizable hydrogen atoms per molecule; ionization of triprotic acids occurs in three steps

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14.1.8: Organic Acids and Bases - Structure and Reactivity

Learning Objectives

- To understand how molecular structure affects the strength of an acid or base.

We have seen that the strengths of acids and bases vary over many orders of magnitude. In this section, we explore some of the structural and electronic factors that control the acidity or basicity of a molecule.

Bond Strengths

In general, the stronger the A– H or B– H^+ bond, the less likely the bond is to break to form H^+ ions and thus the less acidic the substance. This effect can be illustrated using the hydrogen halides:

Relative Acid Strength	HF	HCl	HBr	HI
H–X Bond Energy (kJ/mol)	570	432	366	298
pKa	3.20	−6.1	−8.9	−9.3

The trend in bond energies is due to a steady decrease in overlap between the 1s orbital of hydrogen and the valence orbital of the halogen atom as the size of the halogen increases. The larger the atom to which H is bonded, the weaker the bond. Thus the bond between H and a large atom in a given family, such as I or Te, is weaker than the bond between H and a smaller atom in the same family, such as F or O. As a result, acid strengths of binary hydrides increase as we go down a column of the periodic table. For example, the order of acidity for the binary hydrides of Group 16 elements is as follows, with pK_a values in parentheses:

$$H_2O(14.00 = pK_w) < H_2S(7.05) < H_2Se(3.89) < H_2Te(2.6) \tag{14.1.8.1}$$

Stability of the Conjugate Base

Whether we write an acid–base reaction as $AH \rightleftharpoons A^- + H^+$ or as $BH^+ \rightleftharpoons B + H^+$, the conjugate base ($A^-$ or B) contains one more lone pair of electrons than the parent acid (AH or BH^+). Any factor that stabilizes the lone pair on the conjugate base favors dissociation of H^+ and makes the parent acid a stronger acid. Let's see how this explains the relative acidity of the binary hydrides of the elements in the second row of the periodic table. The observed order of increasing acidity is the following, with pKa values in parentheses:

$$CH_4(\ 50) \ll NH_3(\ 36) < H_2O(14.00) < HF(3.20) \tag{14.1.8.2}$$

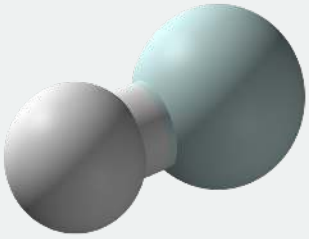
Consider, for example, the compounds at both ends of this series: methane and hydrogen fluoride. The conjugate base of CH_4 is CH_3^-, and the conjugate base of HF is F^-. Because fluorine is much more electronegative than carbon, fluorine can better stabilize the negative charge in the F^- ion than carbon can stabilize the negative charge in the CH3− ion. Consequently, HF has a greater tendency to dissociate to form H^+ and F^- than does methane to form H^+ and CH_3^-, making HF a much stronger acid than CH_4.

The same trend is predicted by analyzing the properties of the conjugate acids. For a series of compounds of the general formula HE, as the electronegativity of E increases, the E–H bond becomes more polar, favoring dissociation to form E^- and H^+. Due to both the increasing stability of the conjugate base and the increasing polarization of the E–H bond in the conjugate acid, acid strengths of binary hydrides increase as we go from left to right across a row of the periodic table.

Acid strengths of binary hydrides increase as we go down a column or from left to right across a row of the periodic table.

the strongest acid Known: The hydrohelium Cation

The storngest acid, the weaker the covalent bond to a hydrogen atom. So the strongest acid possible is the molecule with the weakest bond. That is the hydrohelium (1+) cation, HeH^+, which is a positively charged ion formed by the reaction of a proton with a helium atom in the gas phase. It was first produced in the laboratory in 1925 and is isoelectronic with molecular hydrogen (\ce{H2}). It is the strongest known acid, with a proton affinity of 177.8 kJ/mol.



Ball and stick model of the hydrohelium ion. (CC BY-SA 3.0; CCoil).

HeH^+ cannot be prepared in a condensed phase, as it would protonate any anion, molecule or atom with which it were associated. However it is possible to estimate a *hypothetical* aqueous acidity using Hess's law:

$HHe^+(g)$	→	$H^+(g)$	+ He(g)	+178 kJ/mol
$HHe^+(aq)$	→	$HHe^+(g)$		+973 kJ/mol
$H^+(g)$	→	$H^+(aq)$		−1530 kJ/mol
He(g)	→	He(aq)		+19 kJ/mol
$HHe^+(aq)$	→	$H^+(aq)$	+ He(aq)	−360 kJ/mol

A free energy change of dissociation of −360 kJ/mol is equivalent to a pK_a of −63.

It has been suggested that HeH^+ should occur naturally in the interstellar medium, but it has not yet been detected.

Inductive Effects

Atoms or groups of atoms in a molecule other than those to which H is bonded can induce a change in the distribution of electrons within the molecule. This is called an inductive effect, and, much like the coordination of water to a metal ion, it can have a major effect on the acidity or basicity of the molecule. For example, the hypohalous acids (general formula HOX, with X representing a halogen) all have a hydrogen atom bonded to an oxygen atom. In aqueous solution, they all produce the following equilibrium:

$$HOX_{(aq)} \rightleftharpoons H^+_{(aq)} + OX^-(aq) \tag{14.1.8.3}$$

The acidities of these acids vary by about three orders of magnitude, however, due to the difference in electronegativity of the halogen atoms:

HOX	Electronegativity of X	pKa
HOCl	3.0	7.40
HOBr	2.8	8.55
HOI	2.5	10.5

As the electronegativity of X increases, the distribution of electron density within the molecule changes: the electrons are drawn more strongly toward the halogen atom and, in turn, away from the H in the O–H bond, thus weakening the O–H bond and allowing dissociation of hydrogen as H^+.

The acidity of oxoacids, with the general formula $HOXO_n$ (with n = 0−3), depends strongly on the number of terminal oxygen atoms attached to the central atom X. As shown in Figure 14.1.8.1, the K_a values of the oxoacids of chlorine increase by a factor of about 10^4 to 10^6 with each oxygen as successive oxygen atoms are added. The increase in acid strength with increasing number of terminal oxygen atoms is due to both an inductive effect and increased stabilization of the conjugate base.

> *Any inductive effect that withdraws electron density from an O–H bond increases the acidity of the compound.*

Because oxygen is the second most electronegative element, adding terminal oxygen atoms causes electrons to be drawn away from the O–H bond, making it weaker and thereby increasing the strength of the acid. The colors in Figure 14.1.8.1 show how the electrostatic potential, a measure of the strength of the interaction of a point charge at any place on the surface of the molecule, changes as the number of terminal oxygen atoms increases. In Figure 14.1.8.1 and Figure 14.1.8.2, blue corresponds to low electron densities, while red corresponds to high electron densities. The oxygen atom in the O–H unit becomes steadily less red from $HClO$ to $HClO_4$ (also written as $HOClO_3$, while the H atom becomes steadily bluer, indicating that the electron density on the O–H unit decreases as the number of terminal oxygen atoms increases. The decrease in electron density in the O–H bond weakens it, making it easier to lose hydrogen as H^+ ions, thereby increasing the strength of the acid.

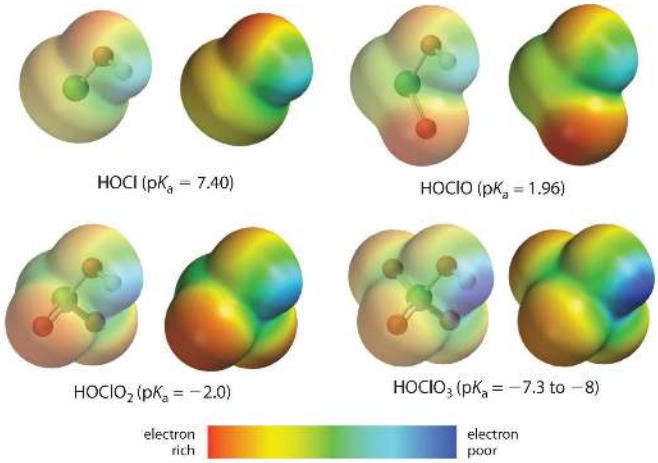
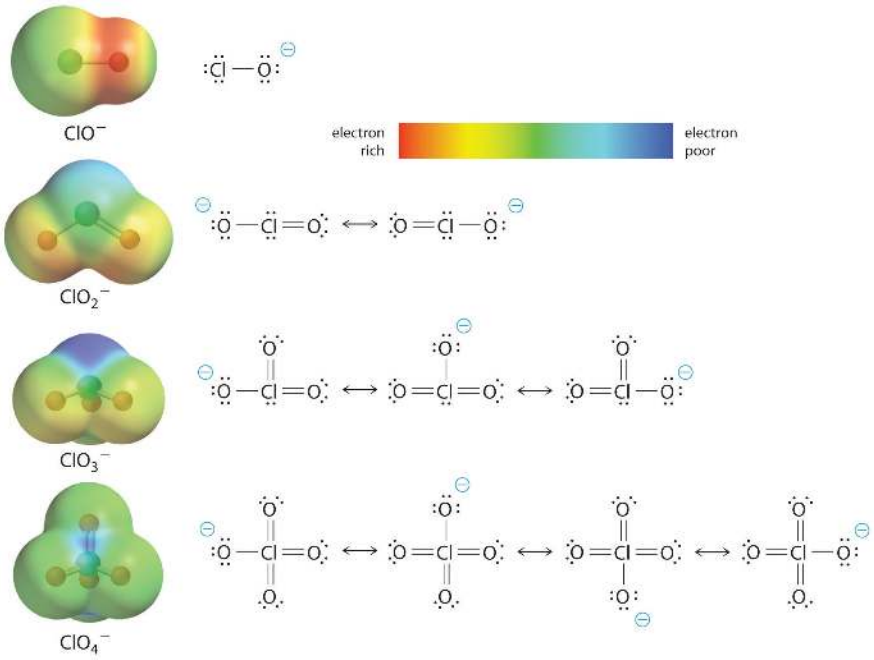


Figure 14.1.8.1: The Relationship between the Acid Strengths of the Oxoacids of Chlorine and the Electron Density on the O–H Unit. These electrostatic potential maps show how the electron density on the O–H unit decreases as the number of terminal oxygen atoms increases. Blue corresponds to low electron densities, whereas red corresponds to high electron densities. Source: Chlorine oxoacids pKa values from J. R. Bowser, Inorganic Chemistry (Pacific Grove, CA: Brooks-Cole,1993).

At least as important, however, is the effect of delocalization of the negative charge in the conjugate base. As shown in Figure 14.1.8.2, the number of resonance structures that can be written for the oxoanions of chlorine increases as the number of terminal oxygen atoms increases, allowing the single negative charge to be delocalized over successively more oxygen atoms.

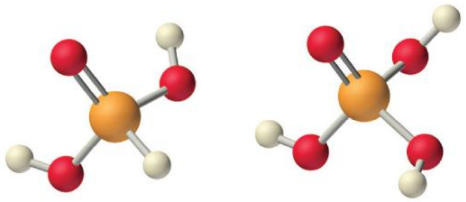
Electron delocalization in the conjugate base increases acid strength.

The electrostatic potential plots in Figure 14.1.8.2 demonstrate that the electron density on the terminal oxygen atoms decreases steadily as their number increases. The oxygen atom in ClO^- is red, indicating that it is electron rich, and the color of oxygen progressively changes to green in ClO_4^+, indicating that the oxygen atoms are becoming steadily less electron rich through the series. For example, in the perchlorate ion (ClO_4^-), the single negative charge is delocalized over all four oxygen atoms, whereas in the hypochlorite ion (OCl^-), the negative charge is largely localized on a single oxygen atom (Figure 14.1.8.2). As a result, the perchlorate ion has no localized negative charge to which a proton can bind. Consequently, the perchlorate anion has a much lower affinity for a proton than does the hypochlorite ion, and perchloric acid is one of the strongest acids known.



As the number of terminal oxygen atoms increases, the number of resonance structures that can be written for the oxoanions of chlorine also increases, and the single negative charge is delocalized over more oxygen atoms. As these electrostatic potential plots demonstrate, the electron density on the terminal oxygen atoms decreases steadily as their number increases. As the electron density on the oxygen atoms decreases, so does their affinity for a proton, making the anion less basic. As a result, the parent oxoacid is more acidic.

Similar inductive effects are also responsible for the trend in the acidities of oxoacids that have the same number of oxygen atoms as we go across a row of the periodic table from left to right. For example, H_3PO_4 is a weak acid, H_2SO_4 is a strong acid, and $HClO_4$ is one of the strongest acids known. The number of terminal oxygen atoms increases steadily across the row, consistent with the observed increase in acidity. In addition, the electronegativity of the central atom increases steadily from P to S to Cl, which causes electrons to be drawn from oxygen to the central atom, weakening the O–H bond and increasing the strength of the oxoacid.



Careful inspection of the data in Table 14.1.8.1 shows two apparent anomalies: carbonic acid and phosphorous acid. If carbonic acid (H_2CO_3) were a discrete molecule with the structure $(HO)_2C{=}O$, it would have a single terminal oxygen atom and should be comparable in acid strength to phosphoric acid (H_3PO_4), for which pKa1 = 2.16. Instead, the tabulated value of pK_{a1} for carbonic acid is 6.35, making it about 10,000 times weaker than expected. As we shall see, however, H_2CO_3 is only a minor component of the aqueous solutions of CO_2 that are referred to as carbonic acid. Similarly, if phosphorous acid (H_3PO_3) actually had the structure $(HO)_3P$, it would have no terminal oxygen atoms attached to phosphorous. It would therefore be expected to be about as strong an acid as $HOCl$ (pKa = 7.40). In fact, the pK_{a1} for phosphorous acid is 1.30, and the structure of phosphorous acid is $(HO)_2P(=O)H$ with one H atom directly bonded to P and one P=O bond. Thus the pKa1 for phosphorous acid is similar to that of other oxoacids with one terminal oxygen atom, such as H_3PO_4. Fortunately, phosphorous acid is the only common oxoacid in which a hydrogen atom is bonded to the central atom rather than oxygen.

Table 14.1.8.1: Values of pKa for Selected Polyprotic Acids and Bases

Polyprotic Acids	Formula	pK_{a1}	pK_{a2}	pK_{a3}
carbonic acid*	"H_2CO_3"	6.35	10.33	
citric acid	$HO_2CCH-2C(OH)(CO_2H)CH_2CO_2H$	3.13	4.76	6.40
malonic acid	$HO-2CCH_2CO_2H$	2.85	5.70	
oxalic acid	HO_2CCO_2H	1.25	3.81	
phosphoric acid	H_3PO_4	2.16	7.21	12.32
phosphorous acid	H_3PO_3	1.3	6.70	
succinic acid	$HO_2CCH_2CH_2CO_2H$	4.21	5.64	
sulfuric acid	H_2SO_4	−2.0	1.99	
sulfurous acid*	"H_2SO_3"	1.85	7.21	
Polyprotic Bases	**Formula**	pK_{b1}	pK_{b2}	
ethylenediamine	$H_2N(CH_2)_2NH_2$	4.08	7.14	
piperazine	$HN(CH_2CH_2)_2NH$	4.27	8.67	
propylenediamine	$H_2N(CH_2)_3NH_2$	3.45	5.12	

*H_2CO_3 and H_2SO_3 are at best minor components of aqueous solutions of $CO_{2(g)}$ and $SO_{2(g)}$, respectively, but such solutions are commonly referred to as containing carbonic acid and sulfurous acid, respectively.

Inductive effects are also observed in organic molecules that contain electronegative substituents. The magnitude of the electron-withdrawing effect depends on both the nature and the number of halogen substituents, as shown by the pKa values for several acetic acid derivatives:

$$pK_aCH_3CO_2H4.76 < CH_2ClCO_2H2.87 < CHCl_2CO_2H1.35 < CCl_3CO_2H0.66 < CF_3CO_2H0.52$$

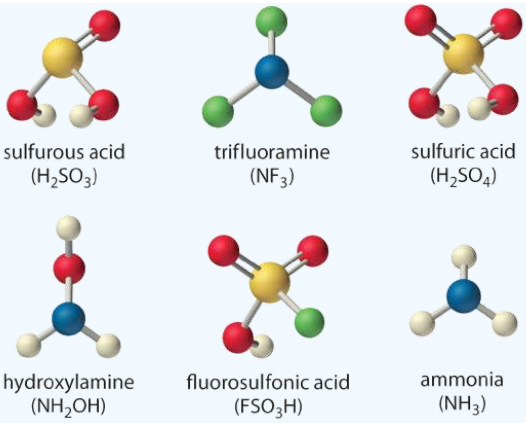
As you might expect, fluorine, which is more electronegative than chlorine, causes a larger effect than chlorine, and the effect of three halogens is greater than the effect of two or one. Notice from these data that inductive effects can be quite large. For instance, replacing the $-CH_3$ group of acetic acid by a $-CF_3$ group results in about a 10,000-fold increase in acidity!

Example 14.1.8.1

Arrange the compounds of each series in order of increasing acid or base strength.

a. sulfuric acid [H_2SO_4, or $(HO)_2SO_2$], fluorosulfonic acid (FSO_3H, or FSO_2OH), and sulfurous acid [H_2SO_3, or $(HO)_2SO$]
b. ammonia (NH_3), trifluoramine (NF_3), and hydroxylamine (NH_2OH)

The structures are shown here.



Given: series of compounds

Asked for: relative acid or base strengths

Strategy:

Use relative bond strengths, the stability of the conjugate base, and inductive effects to arrange the compounds in order of increasing tendency to ionize in aqueous solution.

Solution:

Although both sulfuric acid and sulfurous acid have two –OH groups, the sulfur atom in sulfuric acid is bonded to two terminal oxygen atoms versus one in sulfurous acid. Because oxygen is highly electronegative, sulfuric acid is the stronger acid because the negative charge on the anion is stabilized by the additional oxygen atom. In comparing sulfuric acid and fluorosulfonic acid, we note that fluorine is more electronegative than oxygen. Thus replacing an –OH by –F will remove more electron density from the central S atom, which will, in turn, remove electron density from the S–OH bond and the O–H bond. Because its O–H bond is weaker, FSO_3H is a stronger acid than sulfuric acid. The predicted order of acid strengths given here is confirmed by the measured pKa values for these acids:

$$pKaH_2SO_31.85 < H_2SO_4^{-2} < FSO_3H - 10$$

The structures of both trifluoramine and hydroxylamine are similar to that of ammonia. In trifluoramine, all of the hydrogen atoms in NH3 are replaced by fluorine atoms, whereas in hydroxylamine, one hydrogen atom is replaced by OH. Replacing the three hydrogen atoms by fluorine will withdraw electron density from N, making the lone electron pair on N less available to bond to an H^+ ion. Thus NF_3 is predicted to be a much weaker base than NH_3. Similarly, because oxygen is more electronegative than hydrogen, replacing one hydrogen atom in NH_3 by OH will make the amine less basic. Because oxygen is less electronegative than fluorine and only one hydrogen atom is replaced, however, the effect will be smaller. The predicted order of increasing base strength shown here is confirmed by the measured pK_b values:

$$pK_bNF_3 — << NH_2OH8.06 < NH_34.75$$

Trifluoramine is such a weak base that it does not react with aqueous solutions of strong acids. Hence its base ionization constant has never been measured.

? Exercise 14.1.8.1

Arrange the compounds of each series in order of

a. decreasing acid strength: H_3PO_4, $CH_3PO_3H_2$, and $HClO_3$.
b. increasing base strength: CH_3S^-, OH^-, and CF_3S^-.

Answer a

$HClO-3 > CH_3PO_3H_2 > H_3PO_4$

Answer a

$CF_3S^- < CH_3S^- < OH^-$

Summary

Inductive effects and charge delocalization significantly influence the acidity or basicity of a compound. The acid–base strength of a molecule depends strongly on its structure. The weaker the A–H or B–H+ bond, the more likely it is to dissociate to form an H^+ ion. In addition, any factor that stabilizes the lone pair on the conjugate base favors the dissociation of H^+, making the conjugate acid a stronger acid. Atoms or groups of atoms elsewhere in a molecule can also be important in determining acid or base strength through an inductive effect, which can weaken an O– H bond and allow hydrogen to be more easily lost as H^+ ions.

Contributors and Attributions

- Anonymous

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14.1.9: A Deeper Look - Exact Treatment of Acid-Base Equilibria

Learning Objectives

- Calculate the pH when two weak acids are present in a solution.
- Calculate the pH when the concentration of the acid is very dilute.
- Calculate the pH by including the autoionization of water.

A common paradigm in solving for pHs in weak acids and bases is that the equilibria of solutions containing one weak acid or one weak base. In most cases, the amount of $\mathrm{H^+}$ from the autoionization of water is negligible. For very dilute solutions, the amount of $\mathrm{H^+}$ ions from the autoionization of water must also be taken into account. Thus, a strategy is given here to deal with these systems.

When two or more acids are present in a solution, the concentration of $\mathrm{H^+}$ (or pH) of the solution depends on the concentrations of the acids and their acidic constants K_a. The hydrogen ion is produced by the ionization of all acids, but the ionizations of the acids are governed by their equilibrium constants, K_a's. Similarly, the concentration of $\mathrm{OH^-}$ ions in a solution containing two or more weak bases depends on the concentrations and K_b values of the bases. For simplicity, we consider two acids in this module, but the strategies used to discuss equilibria of two acids apply equally well to that of two bases.

Dissociation of Acids and Bases in Water Couple Two Equilibria with a Common Ion $\mathrm{H^+}$

If the pH is between 6 and 8, the contribution due to autoionization of water to $[\mathrm{H^+}]$ should also be considered. When autoionization of water is considered, the method is called the **exact pH calculation** or the **exact treatment**. This method is illustrated below. When the contribution of pH due to self-ionization of water cannot be neglected, there are two coupled equilibria to consider:

$$\mathrm{HA} \rightleftharpoons \mathrm{H^+} + \mathrm{A^-} \tag{14.1.9.1}$$

ICE Table	HA	$\mathrm{H^+}$	$\mathrm{A^-}$
Initial	C	0	0
Change	$-x$	x	x
Equilibrium	$C-x$	x	x

and

$$\mathrm{H_2O} \rightleftharpoons \mathrm{H^+} + \mathrm{OH^-} \tag{14.1.9.2}$$

ICE Table	$\mathrm{H_2O}$	$\mathrm{H^+}$	$\mathrm{OH^-}$
Equilibrium	-	y	y

Thus,

$$[\mathrm{H^+}] = (x+y) \tag{14.1.9.3}$$
$$[\mathrm{A^-}] = x \tag{14.1.9.4}$$
$$[\mathrm{OH^-}] = y \tag{14.1.9.5}$$

and the two equilibrium constants are

$$K_\mathrm{a} = \frac{(x+y)\,x}{C-x} \tag{14.1.9.6}$$

and

$$K_\mathrm{w} = (x+y)\,y \tag{14.1.9.7}$$

Although you may use the method of successive approximation, the formula to calculate the pH can be derived directly from Equations 14.1.9.6 and 14.1.9.7. Solving for x from Equation 14.1.9.7 gives

$$x = \frac{K_w}{y} - y \tag{14.1.9.8}$$

and substituting this expression into 14.1.9.6results in

$$K_a = \frac{(x+y)\left(\frac{K_w}{y} - y\right)}{C - \frac{K_w}{y} + y} \tag{14.1.9.9}$$

Rearrange this equation to give:

$$[H^+] = (x+y) \tag{14.1.9.10}$$

$$= \frac{C - \frac{K_w}{y} + y}{\frac{K_w}{y} - y} K_a \tag{14.1.9.11}$$

Note that

$$\frac{K_w}{y} = [H^+] \tag{14.1.9.12}$$

so

$$y = \frac{K_w}{[H^+]}. \tag{14.1.9.13}$$

Thus, we get:

$$[H^+] = \frac{C - [H^+] + \frac{K_w}{[H^+]}}{[H^+] - \frac{K_w}{[H^+]}} K_a \tag{14.1.9.14}$$

As written, Equation 14.1.9.14is complicated, but can be put into a polynomial form

$$[H^+]^3 + K_a[H^+]^2 - (K_w + CK_a)[H^+] - K_w K_a = 0 \tag{14.1.9.15}$$

Solving for the exact hydronium concentration requires solving a third-order polynomial. While this is analytically feasible, it is an awkward equation to handle. Instead, we often consider two approximations to Equation 14.1.9.15that can made under limiting conditions.

Case 1: High Concentration Approximation

If $[H^+] > 1 \times 10^{-6}$, then

$$\frac{K_w}{[H^+]} < 1 \times 10^{-8}. \tag{14.1.9.16}$$

This is small indeed compared to $[H^+]$ and C in Equation 14.1.9.14 Thus,

$$[H^+] \approx \frac{C - [H^+]}{[H^+]} K_a \tag{14.1.9.17}$$

$$[H^+]^2 + K_a[H^+] - CK_a \approx 0 \tag{14.1.9.18}$$

Equation 14.1.9.18is a quadratic equation with two solutions. However, only one will be positive and real:

$$[H^+] \approx \frac{-K_a + \sqrt{K_a^2 + 4CK_a}}{2} \tag{14.1.9.19}$$

Case 2: Low Concentration Approximation

If $[H^+] \ll C$, then

$$C - [H^+] \approx C \tag{14.1.9.20}$$

Equation 14.1.9.14can be simplified

$$[H^+] \approx \frac{C}{[H^+]}\ K_\text{a} \tag{14.1.9.21}$$

$$[H^+] \approx \sqrt{CK_\text{a}} \tag{14.1.9.22}$$

The treatment presented in deriving Equation 14.1.9.14is more general, and may be applied to problems involving two or more weak acids in one solution.

Example 14.1.9.1

Calculate the $[\text{H}^+]$, $[\text{Ac}^-]$, and $[\text{Cc}^-]$ when the solution contains 0.200 M HAc ($K_a = 1.8 \times 10^{-5}$), and 0.100 M HCc (the acidity constant $K_c = 1.4 \times 10^{-3}$). (HAc is acetic acid whereas HCc is chloroacetic acid).

Solution

Assume x and y to be the concentrations of Ac^- and Cc^-, respectively, and write the concentrations below the equations:

$$\begin{array}{ccccc} \text{HAc} & \rightleftharpoons & \text{H}^+ & + & \text{Ac}^- \\ 0.200 - x & & x & & x \end{array}$$

$$\begin{array}{ccccc} \text{HCc} & \rightleftharpoons & \text{H}^+ & + & \text{Cc}^- \\ 0.100 - y & & y & & y \end{array}$$

$$[\text{H}^+] = (x + y)$$

Thus, you have

$$\frac{(x+y)\,x}{0.200 - x} = 1.8 \times 10^{-5} \tag{14.1.9.23}$$

$$\frac{(x+y)\,y}{0.100 - y} = 1.4 \times 10^{-3} \tag{14.1.9.24}$$

Solving for x and y from Equations 14.1.9.23and 14.1.9.24may seem difficult, but you can often make some assumptions to simplify the solution procedure. Since HAc is a weaker acid than is HCc, you expect x << y. Further, y << 0.100. Therefore, $x + y \approx y$ and 0.100 - y => 0.100. Equation 14.1.9.24becomes:

$$\frac{(y)\,y}{0.100} = 1.4 \times 10^{-3} \tag{14.1.9.25}$$

which leads to

$$\begin{aligned} y &= (1.4 \times 10^{-3} \times 0.100)^{1/2} \\ &= 0.012 \end{aligned}$$

Substituting y in Equation 14.1.9.23results in

$$\frac{(x+0.012)\,x}{0.200 - x} = 1.8 \times 10^{-5} \tag{14.1.9.26}$$

This equation is easily solved, but you may further assume that $0.200 - x \approx 0.200$, since $x << 0.200$. Thus,

$$\begin{aligned} x &= \frac{-0.012 + (1.44 \times 10^{-4} + 1.44 \times 10^{-5})^{1/2}}{2} \\ &= 2.9 \times 10^{-4} \quad \longleftarrow \text{Small indeed compared to } 0.200 \end{aligned}$$

You had a value of 0.012 for y by neglecting the value of x in Equation 14.1.9.24 You can now recalculate the value for y by substituting values for x and y in Equation 14.1.9.24

$$\frac{(2.9\times10^{-4}+y)\,y}{0.100-0.012}=1.4\times10^{-3} \tag{14.1.9.27}$$

Solving for y in the above equation gives

$$y=0.011$$

You have improved the y value from 0.012 to 0.011. Substituting the new value for y in a successive approximation to recalculate the value for x improves its value from 2.9×10^{-4} to a new value of 3.2×10^{-4}. Use your calculator to obtain these values. Further refinement does not lead to any significant changes for x or y.

Discussion

You should write down these calculations on your note pad, since reading alone does not lead to thorough understanding.

Example 14.1.9.2

A weak acid HA has a K_a value of 4.0×10^{-11}. What are the pH and the equilibrium concentration of A^- in a solution of 0.0010 M HA?

Solution

For the solution of this problem, two methods are given here. If you like the x and y representation, you may use method (a).

Method (a)

The two equilibrium equations are:

$$\begin{array}{ccccc} HA & \rightleftharpoons & H^+ & + & A^-; \\ 0.0010-x & & x & & x \end{array} \tag{14.1.9.28}$$

$$\begin{array}{ccccc} H_2O & \rightleftharpoons & H^+ & + & OH^- \\ & & y & & y \end{array}$$

$$[H^+]=(x+y) \tag{14.1.9.29}$$

$$\frac{(x+y)\,x}{0.0010-x}=4.0\times10^{-}11 \tag{14.1.9.30}$$

(14.1.9.31)

$$(x+y)\,y=1\times10^{-}14 \tag{14.1.9.32}$$

Assume y << x, and x << 0.0010, then you have

$$\frac{(x)\,x}{0.0010}=4.0\times10^{-11} \tag{14.1.9.33}$$

$$x=(0.0010\times4.0e^{-11})^{1/2} \tag{14.1.9.34}$$

$$=2.0\times10^{-7} \tag{14.1.9.35}$$

Substituting $2.0\times^{-7}$ for x in 4 and solving the quadratic equation for y gives,

$$(2.0\times10^{-}7+y)\,y=1\times10^{-14}$$

$$y=4.1\times10^{-8}$$

Substituting 4.1×10^{-8} in Equation 14.1.9.30, but still approximating 0.0010-x by 0.0010:

$$\frac{(x+4.1\times10^{-8})\,x}{0.0010}=4.0\times10^{-11} \tag{14.1.9.36}$$

Solving this quadratic equation for a positive root results in

$$x = 1.8 \times 10^{-7}\ \text{M} \longleftarrow \text{Recall } x = [\text{A}^-]$$

$$\begin{aligned}[\text{H}^+] &= x + y \\ &= (1.8 + 0.41)\, 1 \times 10^{-7} \\ &= 2.2 \times 10^{-7} \\ \text{pH} &= 6.65\end{aligned}$$

The next method uses the formula derived earlier.

Method (b)

Using the formula from the exact treatment, and using 2×10^{-7} for all the $[\text{H}^+]$ values on the right hand side, you obtain a new value of $[\text{H}^+]$ on the left hand side,

$$\begin{aligned}[\text{H}^+] &= \frac{C - [\text{H}^+] + \dfrac{K_\text{w}}{[\text{H}^+]}}{[\text{H}^+] - \dfrac{K_\text{w}}{[\text{H}^+]}} K_\text{a} \\ &= 2.24 \times 10^{-7} \\ \text{pH} &= 6.65\end{aligned}$$

The new $[\text{H}^+]$ enables you to recalculate $[\text{A}^-]$ from the formula:

$$\begin{aligned}(2.24 \times 10^{-7})[\text{A}^-] &= CK_\text{a} \\ [\text{A}^-] &= \frac{(0.0010)(4.0 \times 10^{-11})}{2.24 \times 10^{-7}} \\ &= 1.8 \times 10^{-7}\end{aligned}$$

DISCUSSION

You may have attempted to use the approximation method:

$$\begin{aligned}x &= (CK_\text{a})^{1/2} \\ &= 2.0 \times 10^{-7}\ \text{M A}^-,\ \text{or H}^+;\ \text{pH} = 6.70\end{aligned}$$

and obtained a pH of 6.70, which is greater than 6.65 by less than 1%. However, when an approximation is made, you have no confidence in the calculated pH of 6.70.

Summary

Water is both an acid and a base due to the autoionization,

$$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$$

However, the amount of H^+ ions from water may be very small compared to the amount from an acid if the concentration of the acid is high. When calculating $[\text{H}^+]$ in an acidic solution, approximation method or using the quadratic formula has been discussed in the modules on weak acids.

Contributors and Attributions

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14.1.E: Acid-Base Equilibria (Exercises)

These are homework exercises to accompany the Textmap created for "Principles of Modern Chemistry" by Oxtoby et al. Complementary General Chemistry question banks can be found for other Textmaps and can be accessed here.

Q3

Vinegar contains acetic acid $\mathrm{CH_3COOH}$. What species serves as a base when vinegar is mixed with baking soda, sodium bicarbonate, during the preparation of bread?

Solution

$$NaHCO_3 + CH_3COOH \rightarrow NaCH_3COO + CO_2 + H_2O$$

$\mathrm{NaHCO_3}$ serves as the base.

Q7

a. Thinking of acid-base reaction in terms of oxide donors and oxide acceptors, is the base oxide donors or oxide acceptors?
b. Identify the acid and base in the reaction:

$$\mathrm{CaO + CO_2 \rightleftharpoons CaCO_3}$$

Solution

a. The base is the oxide donor. We can distinctly see this in the autoionization of H_2O, where OH^- counts as the basic part
b. CaO is the base, and CO_2 is the acid.

Q5

Baking soda known as $\mathrm{NaHCO_3}$ is formed by adding water and carbon dioxide to sodium carbonate.

a. Write a balanced equation for this chemical reaction
b. Is this a Brønsted-Lowry acid-base reaction? What is a Brønsted-Lowry acid? What is a Brønsted-Lowry base?

Solution

a. $\mathrm{Na_2CO_3 + H_2O + CO_2 \rightarrow 2NaHCO_3}$
b. This is not a Brønsted-Lowry acid-base reaction because it does not involve a transfer of an H^+ ion. A Brønsted-Lowry acid is a proton donor, and a Brønsted-Lowry base is a proton acceptor.

Q9

Identify each of the following oxides as an acid or base anhydride:

a. CaO
b. $\mathrm{P_2O_5}$

Solution

a. CaO is the base anhydride of calcium hydroxide $\mathrm{Ca(OH)_2}$.
b. $\mathrm{P_2O_5}$ is the acid anhydride of phosphoric acid $\mathrm{H_3PO_4}$.

Q11

Al(III) oxide is amphorteric. What is the balanced chemical equation of Al(III) oxide react with aqueous $\mathrm{H_2SO_4}$? What is the balanced equation of it reacts with KOH?

Solution

$$\mathrm{Al_2O_3(s) + 3\,H_2SO_4(aq) \rightleftharpoons Al_2(SO_4)_3(aq) + 3\,H_2O(l)}$$

\ce{Al2O3 + 2KOH + 3H2O \rightleftharpoons 2KAl(OH)4 \nonumber

Q13

The $[H_3O^+]$ concentration in a glass of orange juice is 3.96 x 10^{-5} M. What is the juice's pH?

Solution

$$pH = -\log[H_3O+]$$

Since the concentration of hydronium ions is given, the pH calculation is as follows:

$$pH = -\log[3.96 \times 10^{-5}] = 4.4023$$

pH is a measure of hydrogen ions in a solution. This concentration defines the acidity or alkalinity of a solution.

Q17

The pK_w of an unknown salty water at 25 °C is 13.665. This differs from the usual K_w of 14.00 at this temperature because dissolved salts make this unknown salty water a non- ideal solution. If the pH in the salty water is 7.8, what are the concentrations of H_3O^+ and OH^- in the salty water at 25 °C?

Solution

$\mathrm{pH} = -\log[\mathrm{H_3O^+}]$, hence,

$[\mathrm{H_3O^+}] = 10^{-7.8} = 1.5849 \times 10^{-}8\ \mathrm{M}$

Since $\mathrm{pK_w} = [\mathrm{OH^-}][\mathrm{H_3O^+}]$,

$[\mathrm{OH^-}] = \frac{10^{-13.665}}{1.5849 \times 10^{-8}\ \mathrm{M}} = 1.3645 \times 10^{-6}\mathrm{M}$

Q19

When rubidium (Rb) solid is added to water, there is an instantaneous and vigorous reaction (i.e., an explosion) as this video demonstrates. Based on this information, which of these two equations is a more accurate representation the reaction?

$$2\,\mathrm{Rb(s)} + 2\,\mathrm{H_2O(l)} \rightarrow 2\,\mathrm{RbOH(aq)} + \mathrm{H_2(aq)}$$

$$2\,\mathrm{Rb(s)} + 2\,\mathrm{H_3O^+(aq)} \rightarrow 2\,\mathrm{Rb^+(aq)} + \mathrm{H_2(aq)} + 2\,\mathrm{H_2O(l)}$$

Solution

The equation:

$$2\,\mathrm{Rb(s)} + 2\,\mathrm{H_2O(l)} \rightarrow 2\,\mathrm{RbOH(aq)} + \mathrm{H_2(aq)}$$

Is a better representation of Rb being placed into water. It represents the direct interaction between the alkali metal and water. We know from the problem that the reaction is fast, vigorous, and forceful. The second equation represents a reaction in equilibrium, one that we would expect to be slow as there are only 1x10^{-7}mol/L of H_3O^+ in a 1L of water. Even if the reaction were vigorous at the low concentration of hydronium ions, there would not be enough of them to keep up with the speed of the reaction (they would become a limiting reactant), hence slowing or stopping the reaction from proceeding.

Q23

In the following chemical equation determine which species is the strongest acid and which is the strongest base, using the Brønsted–Lowry definition. At equilibrium, is there a greater concentration of reactants or products present?

a. $$\mathrm{HIO_{3\ (aq)} + HCOO^-_{(aq)} \rightleftharpoons HCOOH_{(aq)} + IO^-_{3\ (aq)}}$$

b. $$\left(\mathrm{HIO_{3\ (aq)} \rightleftharpoons IO^-_{3\ (aq)}} \qquad \mathrm{K_a} = 1 \cdot 6 \times 10^{-1}\right)$$

c. $$\left(\mathrm{HCOOH_{(aq)} \rightleftharpoons HCOO^-_{(aq)}} \qquad \mathrm{K_a} = 1 \cdot 8 \times 10^{-4}\right)$$

Solution

A Brønsted–Lowry acid is the species that donates protons in a solution. When comparing two different weak acids in solution, like:

$$\mathrm{HIO_{3\ (aq)} + HCOO^-_{(aq)} \rightleftharpoons HCOOH_{(aq)} + IO^-_{3\ (aq)}}$$

We can compare their abilities to donate protons to see which one is the stronger of the two weak acids.

$$\mathrm{HIO_{3\ (aq)} + H_2O_{(aq)} \rightleftharpoons IO^-_{3\ (aq)} + H_3O^+_{(aq)} \qquad K_a = 1 \cdot 6 \times 10^{-1}}$$

$$\mathrm{HCOOH_{(aq)} + H_2O_{(aq)} \rightleftharpoons HCOO^-_{(aq)} + H_3O^+_{(aq)} \qquad K_a = 1 \cdot 8 \times 10^{-4}}$$

Seeing that $\mathrm{K_a = 1 \cdot 6 \times 10^{-1} > K_a = 1 \cdot 8 \times 10^{-4}}$, we know $\mathrm{HIO_3}$ is the stronger acid.

A Brønsted–Lowry base is the species that accepts protons. So in this case, we must examine which of the two weak acids has a stronger conjugate base, which means we must find the $\mathrm{K_b}$ for the reactions of the conjugate bases.

We know that:

$$\mathrm{K_w = K_a \times K_b}$$

and

$$\mathrm{K_w = 1.0 \times 10^{-7}}$$

So we can find $\mathrm{K_b}$ by dividing $\mathrm{K_w}$ by $\mathrm{K_a}$ which ultimately gives us:

$$\mathrm{IO^-_{3\ (aq)} + H_2O_{(aq)} \rightleftharpoons HIO_{3\ (aq)} + OH^-_{(aq)} \qquad K_b = 6 \cdot 3 \times 10^{-14}}$$

$$\mathrm{HCOO^-_{(aq)} + H_2O_{(aq)} \rightleftharpoons HCOOH_{(aq)} + OH^-_{(aq)} \qquad K_b = 5 \cdot 6 \times 10^{-11}}$$

Seeing that $\mathrm{K_b = 5 \cdot 6 \times 10^{-11} > K_a = 6 \cdot 3 \times 10^{-14}}$, we know $\mathrm{HCOO^-}$ is the stronger base.

To determine whether there is a greater concentration of reactants or products present, the K value for the overall reaction must be determined. The overall reaction is the product of the first given reaction and the reverse of the second given reaction. Dividing the first value for $\mathrm{K_a}$ by the second gives

$$K = 888$$

$$K > 1$$

which indicates that at equilibrium, there is a greater concentration of products than reactants.

Q27

Acetic acid gives vinegar a sour taste and strong aroma. Its K_a value is 1.75 x 10^{-5}. What is the pH of the solution if 0.59 grams of acetic acid is dissolved in 40 mL of water?

Solution

First, convert grams of acetic acid to moles.

$$(0.59\ g\ CH_3COOH)\left(\frac{1\ mol}{60.05\ g\ CH_3COOH}\right) = 0.0098\ mol$$

Then, find the molarity of acetic acid by dividing the number of moles of acetic acid by the number of liters of water.

$$\frac{0.0098\ mol}{0.04\ L\ water} = 0.246\ M$$

Using the molarity and $\mathrm{K_a}$, construct and solve an ICE table to find out how much the acetic acid dissociates.

$\mathrm{CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}}$

	CH_3COOH	H_2O	CH_3COO^-	H_3O^+

I	0.246	---	0	0
C	-x	---	+x	+x
E	0.246-x	---	x	x

The acid dissociation constant works in the below equation:

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

Plug in the final concentration values from the ICE table and solve for x.

$$1.75 \times 10^{-5} = \frac{x^2}{0.246 - x}$$

$$x = 0.0021$$

Use the calculated value of x to calculate the concentration of H_3O+, which in this case is equal to x. Then, plug this concentration into the equation for pH.

$$pH = -log[0.0021]$$

$$pH = 2.6848$$

Q29

a. A student prepares a solution of 0.60M of formic acid carefully in a water bath that remains constant at 25°C, determine the pH of the solution. (Ka of formic acid: 1.8 x 10^{-4})
b. How many grams of trichloroacetic acid should be dissolved per liter of deionized water so that the solution of trichloroacetic acid would have the same pH as that of the formic acid solution in a)? (Ka of trichloroacetic acid is 2.2 x 10^{-1})

Solution

Construct an ICE table based on the equation:

$$\mathrm{HCOOH + H_2O \rightleftharpoons HCO_2^- + H_3O^+}$$

	$HCOOH$	H_2O	HCO_2^-	H_3O^+
I	0.6	-	0	0
C	-x	-	+x	+x
E	0.6-x	-	x	x

Ka can then be equated to an algebraic expression:

$$\mathrm{Ka} = \frac{\mathrm{x}^2}{0.6 - \mathrm{x}}$$

$$1.8 \times 10^{-4} = \frac{\mathrm{x}^2}{0.6 - \mathrm{x}}$$

$$\mathrm{x} = 0.0103026$$

or

$$\mathrm{x} = -0.0104$$

x must be postive. Thus, x = 0.0103026.

$$[H_3O^+]$$

$$pH = -\log(0.0103026) = 1.987$$

Because we know the pH we want to attain (1.987), we have start by first finding $[H_3O^+]$:

$$-\log[H_3O^+] = 1.987$$

$$[H_3O^+] = 10^{-1.987}$$

$$[H_3O^+] = 0.0103026$$

An ICE table can also be constructed for the reaction:

$$CCl_3CO_2H + H_2O \rightleftharpoons CCl_3CO_2^- + H_3O^+$$

	CCl_3CO_2H	H_2O	$CCl_3CO_2^-$	H_3O^+
I	x	-	0	0
C	-0.010303	-	+0.010303	+0.010303
E	x-0.010303	-	0.010303	0.010303

$$K_a = \frac{(0.010303)^2}{(x - 0.010303)}$$

$$2.2 \times 10^{-1} = \frac{(0.010303)^2}{(x - 0.010303)}$$

$$x = 0.0107855 M$$

To calculate the mass of trichloroacetic acid, we can calculate the molarity of trichloroacetic acid by its molar mass.

$$\text{Mass of trichloroacetic acid} = 0.0107855 \text{ M} \times (35.5 \frac{g}{mol} \times 3 + 12 \frac{g}{mol} \times 2 + 16 \frac{g}{mol} \times 2 + 1 \frac{g}{mol}) = 1.76 \text{ g}$$

Q41

Rank each of the 0.2 M solution below in an order of increasing pH: NH_4I, KF, HCl, KCl, KOH.

Solution

$$HCl < NH_4I < KF < KCl < KOH$$

Q43

0.040 mol of Diethylamine ($C_4H_{11}N$, pK_b =11.09) is titrated with 0.015 mol of HCl in a 1.00L wash bottle, calculate the pH value of the solution.

Solution

Because equivalence point is not reached yet, we can employ Henderson-Hasselbalch equation.

$$pOH \approx pK_b + \log \frac{[BH^+]}{[B]}$$

$$pOH \approx (11.09) + \log \frac{[C_4H_{12}N^+]}{[C_4H_{11}N]}$$

$$pOH \approx (11.09) + \log \frac{0.015}{0.040 - 15}$$

$$pOH \approx 10.87$$

At room temperature $K_w = 14$ and

$$\begin{aligned} pH &= pK_w - pOH \\ &= 14.00 - 10.87 \\ &= 3.13 \end{aligned}$$

Q45

Prepare a Hypochlorous acid/Hypochlorite buffer at pH 7.

a. Suppose you only have 0.5 mol of lithium hypochlorite, but an infinite supply of hypochlorous acid (pKa = 7.53) and water. How many moles of hypochlorous acid should you use, assuming you use all 0.5 mol of lithium hypochlorite, and dilute the buffer to 100 mL?
b. Suppose Professor Güntherfœrd's arm was doused in about 0.12 moles total HCl. Will this buffer be enough to bring her arm up to a pH over 6.5?

Solution

Using the Henderson–Hasselbalch approximation:

$$\mathrm{pH} \approx \mathrm{pK_a} + \log \frac{[\mathrm{ClO^-}]_o}{[\mathrm{HClO}]_o}$$

It's easy to re-arrange the equation to solve for $[\mathrm{HClO}]_\circ$. Multiplying by 100 mL yields the moles of acid added.

$$\mathrm{pH} \approx \mathrm{pK_a} + \log \frac{[\mathrm{ClO^-}]_o}{[\mathrm{HClO}]_o}$$

$$7 \approx \mathrm{pK_a} + \log \frac{[\mathrm{ClO^-}]_o}{[\mathrm{HClO}]_o}$$

$$7 \approx 7.53 + \log \frac{5}{[\mathrm{HClO}]_o}$$

$$[\mathrm{HClO}]_\circ \approx 16.94$$

$$\text{Moles HClO} \approx 1.694$$

Q49

A student is given 500 mL of a 0.500 M acetic acid solution and wants to create a pH 5.0 buffer. How many mL of 1 M NaOH must be added to the original solution? Acetic acid has a $\mathrm{pK_a}$ of 4.756.

Solution

We first use the Henderson-Hasselbach approximation to determine the required ratio of base to acid in the solution:

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right)$$

$$5.00 = 4.756 + \log\left(\frac{[base]}{[acid]}\right)$$

$$0.244 = \log\left(\frac{[base]}{[acid]}\right)$$

$$1.75 = \frac{[base]}{[acid]}$$

Next, we will determine the molar amount of base required to get a pH of 5.00. In order to simplify things we will first solve for the molar quantities as of each using the simple ratio above in relation to 1.75:

$$\text{Acetic Acid in 500 mL solution} = (0.5\ M) \times (0.5\ L)$$

$$= 0.25\ mol$$

$$NaOH\ in\ 500\ mL\ solution = (0.25\ mol) \times (1.75) + 0.25 = 0.6875 +\ mol$$

Now we'll determine the volume of 1M NaOH needed to raise the pH:

$$\left(\frac{1\ mol}{1\ L}\right) = \left(\frac{0.6875\ mol}{x}\right)$$

$$s = 0.6875\ L\ NaOH$$

Now we'll check to make sure everything is right:

$$Acetic\ Acid\ = \left(\frac{0.25}{0.9375}\right) = 0.2667M$$

$$NaOH\ = \left(\frac{0.6875 - 0.25}{0.9375}\right) = 0.4667M$$

$$5.00 = 4.756 + \log\left(\frac{[base]}{[acid]}\right)$$

$$pH = 4.756 + \log\left(\frac{[0.4667]}{[0.2667]}\right)$$

$$pH = 4.756 + 0.243 = 4.999$$

We get a pH of 4.999 which is about 5.00 and isn't exactly 5.00 due to rounding early in the problem, so the problem was done correctly.

Q51

0.15M of HBr is added into 50mL of 0.1M $Ca(OH)_2$ for the titration.

a. What is the pH of the solution before HBr is added?
b. What is the pH of the solution at the point when it needs 1 mL of HBr to neutralize the solution?
c. What is the pH of the solution when it is titrated 1 mL past neutralization?

Solution

$$2HBr + Ca(OH)_2 \rightleftharpoons 2H_2O + CaBr_2 \tag{14.1.E.1}$$

a) $Ca(OH)_2$ is strong base. They dissociate completely.

$$[\mathrm{OH^-}] = 2[\mathrm{Ca(OH)_2}] = 0.2\mathrm{M}$$

$$\mathrm{pH} = \mathrm{pK_w} - \mathrm{pOH}$$

$$\mathrm{pH} = 14 + \log(0.2\ \mathrm{M})$$

$$\mathrm{pH} = 13.3$$

b) Because $Ca(OH)_2$ and HBr are both strong base and strong acid, at equilibrium, the pH is 7.00.

$$\mathrm{mole}_{\mathrm{Ca(OH)_2}} = (\mathrm{Volume})(\mathrm{Molarity}) \tag{14.1.E.2}$$

$$\mathrm{mole}_{\mathrm{Ca(OH)_2}} = (0.05\mathrm{L})(0.1\mathrm{M}) \tag{14.1.E.3}$$

$$\mathrm{mole}_{\mathrm{Ca(OH)_2}} = 0.005\ \mathrm{mol} \tag{14.1.E.4}$$

@ equilibrium;

$$\mathrm{mole}_{\mathrm{HBr}} = 2\ \mathrm{mole}_{\mathrm{Ca(OH)_2}} \tag{14.1.E.5}$$

$$\mathrm{mole}_{\mathrm{HBr}} = 2(0.005\ \mathrm{mol}) = 0.01\ \mathrm{mol} \tag{14.1.E.6}$$

$$\mathrm{Volume}_{\mathrm{HBr}} = \frac{\mathrm{mole}_{\mathrm{HBr}}}{\mathrm{molarity}_{\mathrm{HBr}}} = \frac{0.01\ \mathrm{mol}}{0.15\mathrm{M}} = 0.0667\ \mathrm{L} = 66.7\ \mathrm{mL} \tag{14.1.E.7}$$

$$\mathrm{Total\ Volume\ at\ equilibrium} = 66.7\mathrm{mL} + 50\mathrm{mL} = 116.7\mathrm{mL} \tag{14.1.E.8}$$

$$\mathrm{Total\ Volume\ 1mL\ short\ of\ equilibrium} = 116.7\mathrm{mL} - 1\mathrm{mL} = 115.7\mathrm{mL} \tag{14.1.E.9}$$

$$\mathrm{Volume}_{\mathrm{HBr}}\ 1\mathrm{mL\ short\ of\ equilibrium} = 66.7\mathrm{mL} - 1\mathrm{mL} = 65.7\ \mathrm{mL} \tag{14.1.E.10}$$

$$\mathrm{mols\ of\ OH^-\ not\ neutralized\ by\ HBr} = 0.01\ \mathrm{mol} - 0.0657\ \mathrm{L} \times (0.15\ \mathrm{M}) = 1.45 \times 10^{-4}\ \mathrm{mol} \tag{14.1.E.11}$$

$$\mathrm{pH} = 14 + \log(\frac{1.45^{-4}\ \mathrm{mol}}{0.1157\ \mathrm{L}}) = 11.1 \tag{14.1.E.12}$$

c)

At 1mL after equilibrium, $Ca(OH)_2$ has been neutralized by HBr. Only HBr exists in the solution.

$$\mathrm{mole}_{\mathrm{HBr}} = (0.001\mathrm{L})(0.15\mathrm{M}) = 1.5 \times 10^{-4}\ \mathrm{mol} \tag{14.1.E.13}$$

$$\mathrm{Volume} = \mathrm{Total\ Volume} + 1\mathrm{mL} = 117.7\mathrm{mL} = 0.1177\ \mathrm{L} \tag{14.1.E.14}$$

$$\mathrm{M_{HBr}\ in\ the\ solution} = \frac{1.5 \times 10^{-4}\ \mathrm{mol}}{0.1177\ \mathrm{L}} = 1.274 \times 10^{-3}\mathrm{M} \tag{14.1.E.15}$$

$$\mathrm{M_{HBr}\ in\ the\ solution} = \mathrm{M_{H^+}\ in\ the\ solution} \tag{14.1.E.16}$$

$$\mathrm{pH} = -\log[\mathrm{H^+}] = -\log(1.274 \times 10^{-3}\mathrm{M}) = 2.89 \tag{14.1.E.17}$$

Q55

K_b at 25°C for Diethylamine ($(C_2H_5)_2NH$) is 1.3×10^{-3}. Consider the titration of 50.00 mL of a 0.1000 M solution of Diethylamine with 0.100 M HCl added with the following volumes: 0, 10.00, 50.00 mL. Calculate pH for each solutions. At an unknown volume beyond 50.00 mL, the pH is 3.90. Find the corresponding amount volume of HCl needed to obtain that pH.

Solution

When HCl volume = 0.00 mL.

$$DiEtNH_{(aq)} + H_2O_{(l)} \rightleftharpoons DiEtNH^+_{2(aq)} + OH^-_{aq} \tag{14.1.E.18}$$

$$\frac{[DiEtNH_2^+][OH^-]}{[DiEtNH]} = 1.3 \times 10^{-3} \tag{14.1.E.19}$$

$$[OH^-] = [DiEtNH_2^+] = y$$

$$[DiEtNH] = 0.1000 - y$$

$$\frac{y^2}{0.1000-y} = 1.3 \times 10^{-3} \tag{14.1.E.20}$$

$$\mathrm{y = 0.01077 M = [OH^-]}$$

$$\mathrm{pOH = 1.97}$$

$$\mathrm{pH = 12.03}$$

When HCl volume = 10.00 mL.

$$\mathrm{[DiEtNH_2^+]} = \frac{(0.1000\mathrm{M})(0.01\mathrm{L})}{(0.050+0.010)\mathrm{L}} = 0.0167 \text{ M} \tag{14.1.E.21}$$

$$\mathrm{[DiEtNH]} = \frac{(0.1000\mathrm{M}(0.050\mathrm{L}) - (0.1000\mathrm{M})(0.01\mathrm{L})}{(0.050+0.010)\mathrm{L}} = 0.0667 \text{ M} \tag{14.1.E.22}$$

Plug it back to Henerson Hasselbalch equation

$$\mathrm{pOH = pK_b + \log(\frac{[BH^+]}{[B]})} \tag{14.1.E.23}$$

\[\mathrm{pOH = -\log(1.3 \times 10^{-3}) +\log(\dfrac{[0.0167 \; M]}{[0.0667 \; M]})}$$

$$\mathrm{pH = pH - pOH = 14.00 - 2.28 = 11.72} \tag{14.1.E.24}$$

When HCl volume = 50 mL.

The titration is at the equivalence point. At equivalence, the reaction consists of 100 mL of 0.050 mol $\mathrm{DiEtNH_2^+}$

$$\mathrm{DiEtNH^+_{2(aq)} + H_2O_{(l)} \rightleftharpoons DiEtNH_{(aq)} + H_3O^+_{(aq)}} \tag{14.1.E.25}$$

$$\mathrm{K_a} = \frac{1.00 \times 10^{-14}}{1.3 \times 10^{-3}} = 7.69 \times 10^{-12}$$

$$\mathrm{K_a} = 7.69 \times 10^{-12} = \frac{\mathrm{x}^2}{(0.5000-\mathrm{x})}; \mathrm{x = [H_3O^+]} \tag{14.1.E.26}$$

$$\mathrm{x} = 1.96 \times 10^{-6}; \mathrm{pH} = 5.71$$

Beyond the equivalence point

Beyond the equivalence point, solution behaves like *HCl*.

Given pH = 3.90.

$$10^{-3.90} = \frac{(\mathrm{z} - 0.050 \text{ L})}{0.100 \text{ L} + \mathrm{z}} \times 0.1000 \text{ M} \tag{14.1.E.27}$$

$\mathrm{z} = 0.0502 \text{ L}$

Q57

Sodium Bicarbonate ($\mathrm{NaHCO_3}$) is a very weak base when dissolved in water. Some amount of sodium bicarbonate is dissolved in 125 mL of a 0.25 M solution of $\mathrm{HNO_3}$. The 168 mL of 0.15 M NaOH was used to titrate the solution. How many grams of sodium bicarbonate were added?

Solution

We are titrating an acid with two bases so solve for the amount of acid the NaOH neutralizes and the remaining moles of acid will be the number of moles of sodium bicarbonate.

$$\text{Moles } \mathrm{HNO_3} = \frac{0.25 \text{ moles}}{1 \text{ L}} \times 0.125 \text{ L} = 0.03125 \text{ moles}$$

$$\text{Moles NaOH} = \frac{0.15 \text{ moles}}{1 \text{ L}} \times 0.168 \text{ L} = 0.0252 \text{ moles}$$

$$0.03125 - 0.0252 = 0.00605 \text{ moles sodium bicarbonate}$$

Now just multiply by sodium bicarbonate's molar mass (84.007 $\frac{g}{mol}$) to find the mass of sodium bicarbonate added

$$0.00605 \times 84.007 = 0.51\text{g}$$

Q59

What is the molarity of a HNO_3 water solution if it requires 31.80 mL of such solution to titrate 0.0662 g Aniline in 100 mL aqueous solution to equivalence point? What will the pH value be at the equivalence point if $\text{K}_\text{b}(\text{Aniline}) = 3.8 \times 10^{-10}$?

Solution

Aniline and HNO_3 react with a one-to-one stoichiometry

$$\text{C}_6\text{H}_5\text{NH}_2(\text{aq}) + \text{HNO}_3(\text{aq}) \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+(\text{aq}) + \text{NO}_3^-(\text{aq})$$

Therefore

$$M(HNO_3) = \frac{0.0662\ g}{93.13\ g/mol} \times \frac{1}{0.03180\ L} = 0.0224\ M$$

Suppose at the equivalence point all Aniline is converted to its conjugate acid, then its concentration equals

$$[\text{C}_6\text{H}_5\text{NH}_3^+] = \frac{0.0662\,g}{(93.13\,g/mol)\ 0.1318\,L} = 0.00539\,M$$

Also as some Aniline's conjugate acid reacts with water,

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{3.8 \times 10^{-10}} = 2.63 \times 10^{-5} = \frac{[H_3O^+][C_6H_5NH_2]}{[C_6H_5NH_3^+]} = \frac{x^2}{0.00539 - x}$$

Therefore,

$$x = [H_3O^+] = 3.636 \times 10^{-4} M$$

so $\text{pH} = 3.44$.

14.1.E: Acid-Base Equilibria (Exercises) is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

SECTION OVERVIEW

14.2: Electrochemistry

An General Chemistry Libretexts Textmap organized around the textbook

Principles of Modern Chemistry

by Oxtoby, Gillis, and Campion

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XVII XVIII XIX XX XXI XXII XXIII • **Homework Exercises**

Template:HideTOC

Electrochemistry is the study of electricity and how it relates to chemical reactions. In electrochemistry, electricity can be generated by movements of electrons from one element to another in a reaction known as redox reaction, or oxidation-reduction reaction.

Topic hierarchy

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14.2.1: Electrochemical Cells

Learning Objectives

- To understand the basics of voltaic cells
- To connect voltage from a voltaic cell to underlying redox chemistry

In any electrochemical process, electrons flow from one chemical substance to another, driven by an oxidation–reduction (redox) reaction. A redox reaction occurs when electrons are transferred from a substance that is oxidized to one that is being reduced. The **reductant** is the substance that loses electrons and is oxidized in the process; the **oxidant** is the species that gains electrons and is reduced in the process. The associated potential energy is determined by the potential difference between the valence electrons in atoms of different elements.

Because it is impossible to have a reduction without an oxidation and vice versa, a redox reaction can be described as two **half-reactions**, one representing the oxidation process and one the reduction process. For the reaction of zinc with bromine, the overall chemical reaction is as follows:

$$\mathrm{Zn(s) + Br_2(aq) \rightarrow Zn^{2+}(aq) + 2\,Br^-(aq)}$$

The half-reactions are as follows:

reduction half-reaction:

$$\mathrm{Br_2(aq) + 2\,e^- \rightarrow 2\,Br^-(aq)}$$

oxidation half-reaction:

$$\mathrm{Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^-}$$

Each half-reaction is written to show what is actually occurring in the system; Zn is the *reductant* in this reaction (it loses electrons), and $\mathrm{Br_2}$ is the *oxidant* (it gains electrons). Adding the two half-reactions gives the overall chemical reaction (Equation 14.2.1.1). A redox reaction is balanced when the number of electrons lost by the reductant equals the number of electrons gained by the oxidant. Like any balanced chemical equation, the overall process is electrically neutral; that is, the net charge is the same on both sides of the equation.

> *In any redox reaction, the number of electrons lost by the oxidation reaction(s) equals the number of electrons gained by the reduction reaction(s).*

In most of our discussions of chemical reactions, we have assumed that the reactants are in intimate physical contact with one another. Acid–base reactions, for example, are usually carried out with the acid and the base dispersed in a single phase, such as a liquid solution. With redox reactions, however, it is possible to physically separate the oxidation and reduction half-reactions in space, as long as there is a complete circuit, including an external electrical connection, such as a wire, between the two half-reactions. As the reaction progresses, the electrons flow from the reductant to the oxidant over this electrical connection, producing an electric current that can be used to do work. An apparatus that is used to generate electricity from a spontaneous redox reaction or, conversely, that uses electricity to drive a nonspontaneous redox reaction is called an **electrochemical cell**.

There are two types of electrochemical cells: galvanic cells and electrolytic cells. Galvanic cells are named for the Italian physicist and physician Luigi Galvani (1737–1798), who observed that dissected frog leg muscles twitched when a small electric shock was applied, demonstrating the electrical nature of nerve impulses. A **galvanic (voltaic) cell** uses the energy released during a spontaneous redox reaction ($\Delta G < 0$) to generate electricity. This type of electrochemical cell is often called a voltaic cell after its inventor, the Italian physicist Alessandro Volta (1745–1827). In contrast, an **electrolytic cell** consumes electrical energy from an external source, using it to cause a nonspontaneous redox reaction to occur ($\Delta G > 0$). Both types contain two **electrodes**, which are solid metals connected to an external circuit that provides an electrical connection between the two parts of the system (Figure 14.2.1.1). The oxidation half-reaction occurs at one electrode (the **anode**), and the reduction half-reaction occurs at the other (the **cathode**). When the circuit is closed, electrons flow from the anode to the cathode. The electrodes are also connected by an electrolyte, an ionic substance or solution that allows ions to transfer between the electrode compartments, thereby maintaining the system's electrical neutrality. In this section, we focus on reactions that occur in galvanic cells.

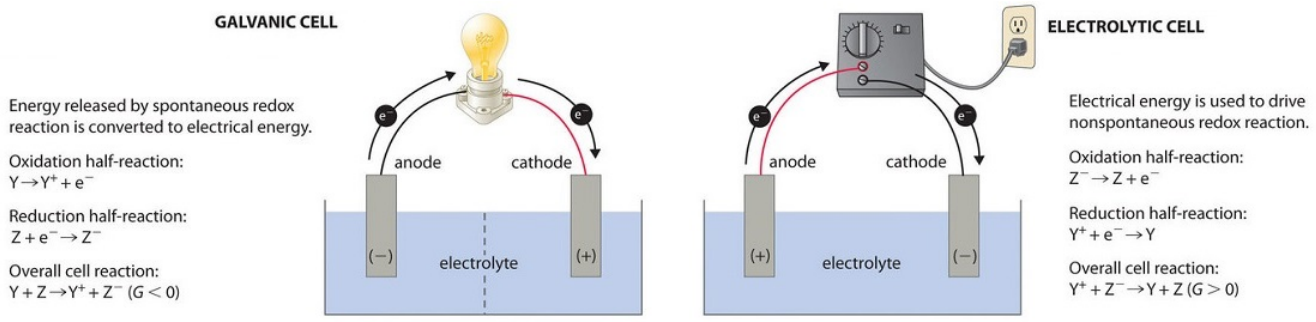


Figure 14.2.1.1: Electrochemical Cells. A galvanic cell (left) transforms the energy released by a spontaneous redox reaction into electrical energy that can be used to perform work. The oxidative and reductive half-reactions usually occur in separate compartments that are connected by an external electrical circuit; in addition, a second connection that allows ions to flow between the compartments (shown here as a vertical dashed line to represent a porous barrier) is necessary to maintain electrical neutrality. The potential difference between the electrodes (voltage) causes electrons to flow from the reductant to the oxidant through the external circuit, generating an electric current. In an electrolytic cell (right), an external source of electrical energy is used to generate a potential difference between the electrodes that forces electrons to flow, driving a nonspontaneous redox reaction; only a single compartment is employed in most applications. In both kinds of electrochemical cells, the anode is the electrode at which the oxidation half-reaction occurs, and the cathode is the electrode at which the reduction half-reaction occurs.

Voltaic (Galvanic) Cells

To illustrate the basic principles of a galvanic cell, let's consider the reaction of metallic zinc with cupric ion (Cu^{2+}) to give copper metal and Zn^{2+} ion. The balanced chemical equation is as follows:

$$\mathrm{Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)} \tag{14.2.1.1}$$

We can cause this reaction to occur by inserting a zinc rod into an aqueous solution of copper(II) sulfate. As the reaction proceeds, the zinc rod dissolves, and a mass of metallic copper forms. These changes occur spontaneously, but all the energy released is in the form of heat rather than in a form that can be used to do work.



Figure 14.2.1.2: The Reaction of Metallic Zinc with Aqueous Copper(II) Ions in a Single Compartment. When a zinc rod is inserted into a beaker that contains an aqueous solution of copper(II) sulfate, a spontaneous redox reaction occurs: the zinc electrode dissolves to give $\mathrm{Zn^{2+}(aq)}$ ions, while $\mathrm{Cu^{2+}(aq)}$ ions are simultaneously reduced to metallic copper. The reaction occurs so rapidly that the copper is deposited as very fine particles that appear black, rather than the usual reddish color of copper. (youtu.be/2gPRK0HmYu4)

This same reaction can be carried out using the galvanic cell illustrated in Figure $14.2.1.3a$ To assemble the cell, a copper strip is inserted into a beaker that contains a 1 M solution of $\mathrm{Cu^{2+}}$ ions, and a zinc strip is inserted into a different beaker that contains a 1 M solution of $\mathrm{Zn^{2+}}$ ions. The two metal strips, which serve as electrodes, are connected by a wire, and the compartments are connected by a **salt bridge**, a U-shaped tube inserted into both solutions that contains a concentrated liquid or gelled electrolyte. The ions in the salt bridge are selected so that they do not interfere with the electrochemical reaction by being oxidized or reduced themselves or by forming a precipitate or complex; commonly used cations and anions are $\mathrm{Na^+}$ or $\mathrm{K^+}$ and $\mathrm{NO_3^-}$ or $\mathrm{SO_4^{2-}}$, respectively. (The ions in the salt bridge do not have to be the same as those in the redox couple in either compartment.) When the

circuit is closed, a spontaneous reaction occurs: zinc metal is oxidized to Zn^{2+} ions at the zinc electrode (the anode), and Cu^{2+} ions are reduced to Cu metal at the copper electrode (the cathode). As the reaction progresses, the zinc strip dissolves, and the concentration of Zn^{2+} ions in the solution increases; simultaneously, the copper strip gains mass, and the concentration of Cu^{2+} ions in the solution decreases (Figure 14.2.1.3*b*). Thus we have carried out the same reaction as we did using a single beaker, but this time the oxidative and reductive half-reactions are physically separated from each other. The electrons that are released at the anode flow through the wire, producing an electric current. Galvanic cells therefore transform chemical energy into electrical energy that can then be used to do work.

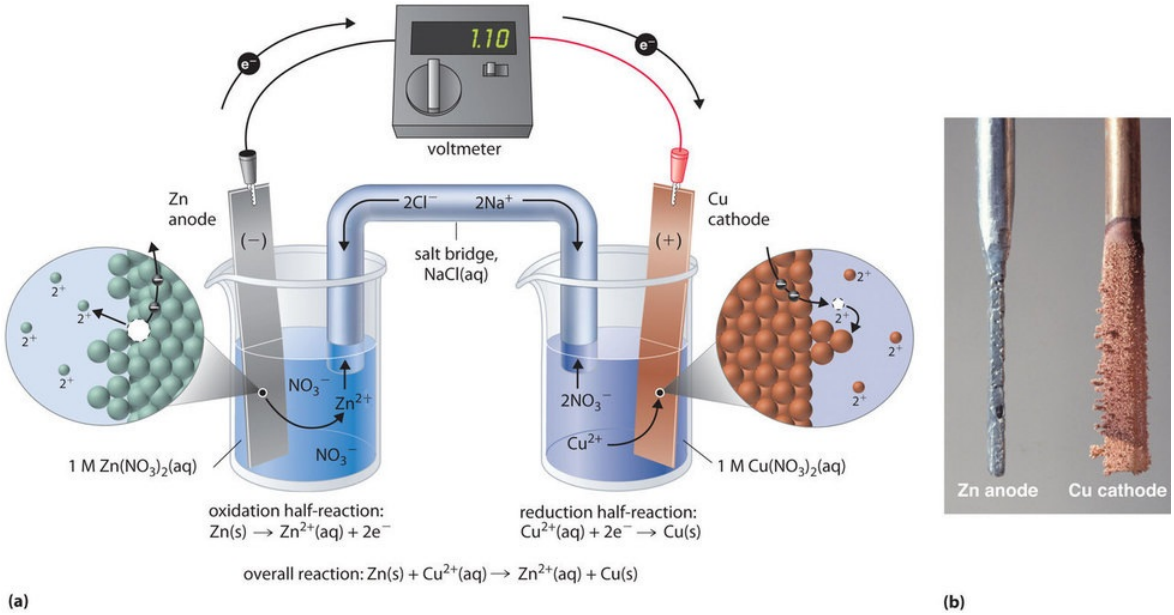


Figure 14.2.1.3: The Reaction of Metallic Zinc with Aqueous Copper(II) Ions in a Galvanic Cell. (a) A galvanic cell can be constructed by inserting a copper strip into a beaker that contains an aqueous 1 M solution of Cu^{2+} ions and a zinc strip into a different beaker that contains an aqueous 1 M solution of Zn^{2+} ions. The two metal strips are connected by a wire that allows electricity to flow, and the beakers are connected by a salt bridge. When the switch is closed to complete the circuit, the zinc electrode (the anode) is spontaneously oxidized to Zn^{2+} ions in the left compartment, while Cu^{2+} ions are simultaneously reduced to copper metal at the copper electrode (the cathode). (b) As the reaction progresses, the Zn anode loses mass as it dissolves to give Zn^{2+}(aq) ions, while the Cu cathode gains mass as Cu^{2+}(aq) ions are reduced to copper metal that is deposited on the cathode. (CC BY-SA-NC; anonymous)

The electrolyte in the salt bridge serves two purposes: it completes the circuit by carrying electrical charge and maintains electrical neutrality in both solutions by allowing ions to migrate between them. The identity of the salt in a salt bridge is unimportant, as long as the component ions do not react or undergo a redox reaction under the operating conditions of the cell. Without such a connection, the total positive charge in the Zn^{2+} solution would increase as the zinc metal dissolves, and the total positive charge in the Cu^{2+} solution would decrease. The salt bridge allows charges to be neutralized by a flow of anions into the Zn^{2+} solution and a flow of cations into the Cu^{2+} solution. In the absence of a salt bridge or some other similar connection, the reaction would rapidly cease because electrical neutrality could not be maintained.

A voltmeter can be used to measure the difference in electrical potential between the two compartments. Opening the switch that connects the wires to the anode and the cathode prevents a current from flowing, so no chemical reaction occurs. With the switch closed, however, the external circuit is closed, and an electric current can flow from the anode to the cathode. The **potential** (E_{cell}) of the cell, measured in volts, is the difference in electrical potential between the two half-reactions and is related to the energy needed to move a charged particle in an electric field. In the cell we have described, the voltmeter indicates a potential of 1.10 V (Figure 14.2.1.3*a*). Because electrons from the oxidation half-reaction are released at the anode, the anode in a galvanic cell is negatively charged. The cathode, which attracts electrons, is positively charged.

Not all electrodes undergo a chemical transformation during a redox reaction. The electrode can be made from an inert, highly conducting metal such as platinum to prevent it from reacting during a redox process, where it does not appear in the overall electrochemical reaction. This phenomenon is illustrated in Example 14.2.1.1.

> *A galvanic (voltaic) cell converts the energy released by a **spontaneous** chemical reaction to electrical energy. An electrolytic cell consumes electrical energy from an external source to drive a **nonspontaneous** chemical reaction.*

Example 14.2.1.1

A chemist has constructed a galvanic cell consisting of two beakers. One beaker contains a strip of tin immersed in aqueous sulfuric acid, and the other contains a platinum electrode immersed in aqueous nitric acid. The two solutions are connected by a salt bridge, and the electrodes are connected by a wire. Current begins to flow, and bubbles of a gas appear at the platinum electrode. The spontaneous redox reaction that occurs is described by the following balanced chemical equation:

$$3\,\mathrm{Sn(s)} + 2\,\mathrm{NO_3^-(aq)} + 8\,\mathrm{H^+(aq)} \rightarrow 3\,\mathrm{Sn^{2+}(aq)} + 2\,\mathrm{NO(g)} + 4\,\mathrm{H_2O(l)}$$

For this galvanic cell,

a. write the half-reaction that occurs at each electrode.
b. indicate which electrode is the cathode and which is the anode.
c. indicate which electrode is the positive electrode and which is the negative electrode.

Given: galvanic cell and redox reaction

Asked for: half-reactions, identity of anode and cathode, and electrode assignment as positive or negative

Strategy:

A. Identify the oxidation half-reaction and the reduction half-reaction. Then identify the anode and cathode from the half-reaction that occurs at each electrode.
B. From the direction of electron flow, assign each electrode as either positive or negative.

Solution

A In the reduction half-reaction, nitrate is reduced to nitric oxide. (The nitric oxide would then react with oxygen in the air to form NO_2, with its characteristic red-brown color.) In the oxidation half-reaction, metallic tin is oxidized. The half-reactions corresponding to the actual reactions that occur in the system are as follows:

reduction:

$$\mathrm{NO_3^-(aq)} + 4\,\mathrm{H^+(aq)} + 3\,\mathrm{e^-} \rightarrow \mathrm{NO(g)} + 2\,\mathrm{H_2O(l)}$$

oxidation:

$$\mathrm{Sn(s)} \rightarrow \mathrm{Sn^{2+}(aq)} + 2\,\mathrm{e^-}$$

Thus nitrate is reduced to NO, while the tin electrode is oxidized to Sn^{2+}.

Because the reduction reaction occurs at the Pt electrode, it is the cathode. Conversely, the oxidation reaction occurs at the tin electrode, so it is the anode.

B Electrons flow from the tin electrode through the wire to the platinum electrode, where they transfer to nitrate. The electric circuit is completed by the salt bridge, which permits the diffusion of cations toward the cathode and anions toward the anode. Because electrons flow from the tin electrode, it must be electrically negative. In contrast, electrons flow toward the Pt electrode, so that electrode must be electrically positive.

Exercise 14.2.1.1

Consider a simple galvanic cell consisting of two beakers connected by a salt bridge. One beaker contains a solution of $\mathrm{MnO_4^-}$ in dilute sulfuric acid and has a Pt electrode. The other beaker contains a solution of $\mathrm{Sn^{2+}}$ in dilute sulfuric acid, also with a Pt electrode. When the two electrodes are connected by a wire, current flows and a spontaneous reaction occurs that is described by the following balanced chemical equation:

$$2\,\mathrm{MnO_4^-(aq)} + 5\,\mathrm{Sn^{2+}(aq)} + 16\,\mathrm{H^+(aq)} \rightarrow 2\,\mathrm{Mn^{2+}(aq)} + 5\,\mathrm{Sn^{4+}(aq)} + 8\,\mathrm{H_2O(l)}$$

For this galvanic cell,

a. write the half-reaction that occurs at each electrode.
b. indicate which electrode is the cathode and which is the anode.
c. indicate which electrode is positive and which is negative.

Answer a

$$\mathrm{MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \rightarrow Mn^{2+}(aq) + 4\,H_2O(l)}$$
$$\mathrm{Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2\,e^-}$$

Answer b

The Pt electrode in the permanganate solution is the cathode; the one in the tin solution is the anode.

Answer c

The cathode (electrode in beaker that contains the permanganate solution) is positive, and the anode (electrode in beaker that contains the tin solution) is negative.



Electrochemical Cells: Electrochemical Cells(opens in new window) [youtu.be]

Constructing Cell Diagrams (Cell Notation)

Because it is somewhat cumbersome to describe any given galvanic cell in words, a more convenient notation has been developed. In this line notation, called a cell diagram, the identity of the electrodes and the chemical contents of the compartments are indicated by their chemical formulas, with the anode written on the far left and the cathode on the far right. Phase boundaries are shown by single vertical lines, and the salt bridge, which has two phase boundaries, by a double vertical line. Thus the cell diagram for the $\mathrm{Zn/Cu}$ cell shown in Figure $14.2.1.3a$is written as follows:

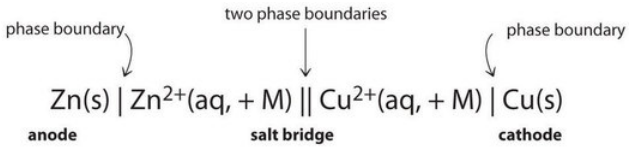


Figure 14.2.1.4: A cell diagram includes solution concentrations when they are provided. The + M term is meant to indicate the applicable concentration of the species. If the species is a gas, then you substitute the pressure instead.

At the anode is solid zinc. after the phase boundary is aq Zinc two plus and plus M. After the two phase boundary is aq copper two plus and plus M. At the cathode is solid copper.

Galvanic cells can have arrangements other than the examples we have seen so far. For example, the voltage produced by a redox reaction can be measured more accurately using two electrodes immersed in a single beaker containing an electrolyte that completes the circuit. This arrangement reduces errors caused by resistance to the flow of charge at a boundary, called the **junction potential**. One example of this type of galvanic cell is as follows:

$$\mathrm{Pt(s)\,|\,H_2(g)|HCl(aq,\ 1\ M)\,|\,AgCl(s)\,Ag(s)}$$

This cell diagram does not include a double vertical line representing a salt bridge because there is no salt bridge providing a junction between two dissimilar solutions. Moreover, solution concentrations have not been specified, so they are not included in the cell diagram. The half-reactions and the overall reaction for this cell are as follows:

cathode reaction:

$$\mathrm{AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)}$$

anode reaction:

$$\mathrm{\tfrac{1}{2}H_2(g) \longrightarrow H^+(aq) + e^-}$$

overall:

$$\mathrm{AgCl(s) + \tfrac{1}{2}H_2(g) \longrightarrow Ag(s) + Cl^- + H^+(aq)}$$

A single-compartment galvanic cell will initially exhibit the same voltage as a galvanic cell constructed using separate compartments, but it will discharge rapidly because of the direct reaction of the reactant at the anode with the oxidized member of the cathodic redox couple. Consequently, cells of this type are not particularly useful for producing electricity.

Example 14.2.1.2

Draw a cell diagram for the galvanic cell described in Example 14.2.1.1 The balanced chemical reaction is as follows:

$$\mathrm{3\,Sn(s) + 2\,NO_3^-(aq) + 8\,H^+(aq) \rightarrow 3\,Sn^{2+}(aq) + 2\,NO(g) + 4\,H_2O(l)}$$

Given: galvanic cell and redox reaction

Asked for: cell diagram

Strategy:

Using the symbols described, write the cell diagram beginning with the oxidation half-reaction on the left.

Solution

The anode is the tin strip, and the cathode is the Pt electrode. Beginning on the left with the anode, we indicate the phase boundary between the electrode and the tin solution by a vertical bar. The anode compartment is thus $\mathrm{Sn(s)\,|\,Sn^{2+}(aq)}$. We could include $\mathrm{H_2SO_4(aq)}$ with the contents of the anode compartment, but the sulfate ion (as $\mathrm{HSO_4^-}$) does not participate in the overall reaction, so it does not need to be specifically indicated. The cathode compartment contains aqueous nitric acid, which does participate in the overall reaction, together with the product of the reaction (NO) and the Pt electrode. These are written as $\mathrm{HNO_3(aq)\,|\,NO(g)\,|\,Pt(s)}$, with single vertical bars indicating the phase boundaries. Combining the two compartments and using a double vertical bar to indicate the salt bridge,

$$\mathrm{Sn(s)\,|\,Sn^{2+}(aq)\,||\,HNO_3(aq)\,|\,NO(g)\,|\,Pt(s)}$$

The solution concentrations were not specified, so they are not included in this cell diagram.

Exercise 14.2.1.2

Draw the cell diagram for the following reaction, assuming the concentration of $\mathrm{Ag^+}$ and $\mathrm{Mg^{2+}}$ are each 1 M:

$$\mathrm{Mg(s) + 2\,Ag^+(aq) \rightarrow Mg^{2+}(aq) + 2\,Ag(s)}$$

Answer

$$\mathrm{Mg(s)\,|\,Mg^{2+}(aq,\ 1\ M)\,||\,Ag^+(aq,\ 1\ M)\,|\,Ag(s)}$$



Cell Diagrams: Cell Diagrams(opens in new window) [youtu.be]

Summary

A galvanic (voltaic) cell uses the energy released during a spontaneous redox reaction to generate electricity, whereas an electrolytic cell consumes electrical energy from an external source to force a reaction to occur. Electrochemistry is the study of the relationship between electricity and chemical reactions. The oxidation–reduction reaction that occurs during an electrochemical process consists of two half-reactions, one representing the oxidation process and one the reduction process. The sum of the half-reactions gives the overall chemical reaction. The overall redox reaction is balanced when the number of electrons lost by the reductant equals the number of electrons gained by the oxidant. An electric current is produced from the flow of electrons from the reductant to the oxidant. An electrochemical cell can either generate electricity from a spontaneous redox reaction or consume electricity to drive a nonspontaneous reaction. In a galvanic (voltaic) cell, the energy from a spontaneous reaction generates electricity, whereas in an electrolytic cell, electrical energy is consumed to drive a nonspontaneous redox reaction. Both types of cells use two electrodes that provide an electrical connection between systems that are separated in space. The oxidative half-reaction occurs at the anode, and the reductive half-reaction occurs at the cathode. A salt bridge connects the separated solutions, allowing ions to migrate to either solution to ensure the system's electrical neutrality. A voltmeter is a device that measures the flow of electric current between two half-reactions. The potential of a cell, measured in volts, is the energy needed to move a charged particle in an electric field. An electrochemical cell can be described using line notation called a cell diagram, in which vertical lines indicate phase boundaries and the location of the salt bridge. Resistance to the flow of charge at a boundary is called the junction potential.

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14.2.2: The Gibbs Free Energy and Cell Voltage

Learning Objectives

- To understand the relationship between cell potential and the equilibrium constant.
- To use cell potentials to calculate solution concentrations.

Changes in reaction conditions can have a tremendous effect on the course of a redox reaction. For example, under standard conditions, the reaction of $\mathrm{Co(s)}$ with $\mathrm{Ni^{2+}(aq)}$ to form $\mathrm{Ni(s)}$ and $\mathrm{Co^{2+}(aq)}$ occurs spontaneously, but if we reduce the concentration of $\mathrm{Ni^{2+}}$ by a factor of 100, so that $[\mathrm{Ni^{2+}}]$ is 0.01 M, then the reverse reaction occurs spontaneously instead. The relationship between voltage and concentration is one of the factors that must be understood to predict whether a reaction will be spontaneous.

The Relationship between Cell Potential & Gibbs Energy

Electrochemical cells convert chemical energy to electrical energy and vice versa. The total amount of energy produced by an electrochemical cell, and thus the amount of energy available to do electrical work, depends on both the cell potential and the total number of electrons that are transferred from the reductant to the oxidant during the course of a reaction. The resulting electric current is measured in **coulombs (C)**, an SI unit that measures the number of electrons passing a given point in 1 s. A coulomb relates energy (in joules) to electrical potential (in volts). Electric current is measured in **amperes (A)**; 1 A is defined as the flow of 1 C/s past a given point (1 C = 1 A·s):

$$\frac{1\ \mathrm{J}}{1\ \mathrm{V}} = 1\ \mathrm{C} = \mathrm{A \cdot s}$$

In chemical reactions, however, we need to relate the coulomb to the charge on a mole of electrons. Multiplying the charge on the electron by Avogadro's number gives us the charge on 1 mol of electrons, which is called the **faraday (F)**, named after the English physicist and chemist Michael Faraday (1791–1867):

$$\begin{aligned} F &= (1.60218 \times 10^{-19}\ \mathrm{C}) \left(\frac{6.02214 \times 10^{23}\ J}{1\ \mathrm{mol\ e^-}} \right) \\ &= 9.64833212 \times 10^{4}\ \mathrm{C/mol\ e^-} \\ &\simeq 96,485\ J/(\mathrm{V \cdot mol\ e^-}) \end{aligned}$$

The total charge transferred from the reductant to the oxidant is therefore nF, where n is the number of moles of electrons.

Michael Faraday (1791–1867)

Faraday was a British physicist and chemist who was arguably one of the greatest experimental scientists in history. The son of a blacksmith, Faraday was self-educated and became an apprentice bookbinder at age 14 before turning to science. His experiments in electricity and magnetism made electricity a routine tool in science and led to both the electric motor and the electric generator. He discovered the phenomenon of electrolysis and laid the foundations of electrochemistry. In fact, most of the specialized terms introduced in this chapter (electrode, anode, cathode, and so forth) are due to Faraday. In addition, he discovered benzene and invented the system of oxidation state numbers that we use today. Faraday is probably best known for "The Chemical History of a Candle," a series of public lectures on the chemistry and physics of flames.

The maximum amount of work that can be produced by an electrochemical cell (w_{max}) is equal to the product of the cell potential (E°_{cell}) and the total charge transferred during the reaction (nF):

$$w_{max} = nFE_{cell}$$

Work is expressed as a negative number because work is being done by a system (an electrochemical cell with a positive potential) on its surroundings.

The change in free energy (ΔG) is also a measure of the maximum amount of work that can be performed during a chemical process ($\Delta G = w_{max}$). Consequently, there must be a relationship between the potential of an electrochemical cell and ΔG; this

relationship is as follows:

$$\Delta G = -nFE_{cell}$$

A spontaneous redox reaction is therefore characterized by a negative value of ΔG and a positive value of E°_{cell}, consistent with our earlier discussions. When both reactants and products are in their standard states, the relationship between ΔG° and E°_{cell} is as follows:

$$\Delta G^\circ = -nFE^\circ_{cell} \tag{14.2.2.1}$$

A spontaneous redox reaction is characterized by a negative value of ΔG°, which corresponds to a positive value of E°_{cell}.

Example 14.2.2.1

Suppose you want to prepare elemental bromine from bromide using the dichromate ion as an oxidant. Using the data in Table P2, calculate the free-energy change (ΔG°) for this redox reaction under standard conditions. Is the reaction spontaneous?

Given: redox reaction

Asked for: ΔG^o for the reaction and spontaneity

Strategy:

A. From the relevant half-reactions and the corresponding values of E^o, write the overall reaction and calculate E°_{cell}.

B. Determine the number of electrons transferred in the overall reaction. Then use Equation 14.2.2.1 to calculate ΔG^o. If ΔG^o is negative, then the reaction is spontaneous.

Solution

A

As always, the first step is to write the relevant half-reactions and use them to obtain the overall reaction and the magnitude of E^o. From Table P2, we can find the reduction and oxidation half-reactions and corresponding E^o values:

cathode:	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	$E^\circ_{cathode} = 1.36\ V$
anode:	$2Br^-(aq) \rightarrow Br_2(aq) + 2e^-$	$E^\circ_{anode} = 1.09\ V$

To obtain the overall balanced chemical equation, we must multiply both sides of the oxidation half-reaction by 3 to obtain the same number of electrons as in the reduction half-reaction, remembering that the magnitude of E^o is not affected:

cathode:	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	$E^\circ_{cathode} = 1.36\ V$
anode:	$6Br^-(aq) \rightarrow 3Br_2(aq) + 6e^-$	$E^\circ_{anode} = 1.09\ V$
overall:	$Cr_2O_7^{2-}(aq) + 6Br^-(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 3Br_2(aq) + 7H_2O(l)$	$E^\circ_{cell} = 0.27\ V$

B

We can now calculate ΔG° using Equation 14.2.2.1. Because six electrons are transferred in the overall reaction, the value of n is 6:

$$\begin{aligned}\Delta G^\circ &= -(n)(F)(E^\circ_{cell}) \\ &= -(6\ \text{mole})[96,485\ \text{J}/(\text{V}\cdot\text{mol})(0.27\ \text{V})] \\ &= -15.6\ \times 10^4\ \text{J} \\ &= -156\ \text{kJ/mol}\ Cr_2O_7^{2-}\end{aligned}$$

Thus ΔG^o is −168 kJ/mol for the reaction as written, and the reaction is spontaneous.

Exercise 14.2.2.1

Use the data in Table P2 to calculate ΔG^o for the reduction of ferric ion by iodide:

$$2\,Fe^{3+}(aq) + 2\,I^-(aq) \rightarrow 2\,Fe^{2+}(aq) + I_2(s)$$

Is the reaction spontaneous?

Answer

−44 kJ/mol I_2; yes

Potentials for the Sums of Half-Reactions

Although Table P2 list several half-reactions, many more are known. When the standard potential for a half-reaction is not available, we can use relationships between standard potentials and free energy to obtain the potential of any other half-reaction that can be written as the sum of two or more half-reactions whose standard potentials are available. For example, the potential for the reduction of $\mathrm{Fe}^{3+}(\mathrm{aq})$ to $\mathrm{Fe}(\mathrm{s})$ is not listed in the table, but two related reductions are given:

$$\mathrm{Fe}^{3+}(\mathrm{aq}) + \mathrm{e}^- \longrightarrow \mathrm{Fe}^{2+}(\mathrm{aq}) \quad E^\circ = +0.77V$$

$$\mathrm{Fe}^{2+}(\mathrm{aq}) + 2\,\mathrm{e}^- \longrightarrow \mathrm{Fe}(\mathrm{s}) \quad E^\circ = -0.45V$$

Although the sum of these two half-reactions gives the desired half-reaction, we cannot simply add the potentials of two reductive half-reactions to obtain the potential of a third reductive half-reaction because E^o is not a state function. However, because ΔG^o is a state function, the sum of the ΔG^o values for the individual reactions gives us ΔG^o for the overall reaction, which is proportional to both the potential and the number of electrons (n) transferred. To obtain the value of E^o for the overall half-reaction, we first must add the values of $\Delta G^o (= -nFE^o)$ for each individual half-reaction to obtain ΔG^o for the overall half-reaction:

$$\begin{aligned}
\mathrm{Fe}^{3+}(\mathrm{aq}) + \mathrm{e}^- &\rightarrow \mathrm{Fe}^{2+}(\mathrm{aq}) & \Delta G^\circ &= -(1)(F)(0.77\ \mathrm{V}) \\
\mathrm{Fe}^{2+}(\mathrm{aq}) + 2\,\mathrm{e}^- &\rightarrow \mathrm{Fe}(\mathrm{s}) & \Delta G^\circ &= -(2)(F)(-0.45\ \mathrm{V}) \\
\mathrm{Fe}^{3+}(\mathrm{aq}) + 3\,\mathrm{e}^- &\rightarrow \mathrm{Fe}(\mathrm{s}) & \Delta G^\circ &= [-(1)(F)(0.77\ \mathrm{V})] + [-(2)(F)(-0.45\ \mathrm{V})]
\end{aligned}$$

Solving the last expression for ΔG° for the overall half-reaction,

$$\Delta G^\circ = F[(-0.77V) + (-2)(-0.45V)] = F(0.13V)$$

Three electrons ($n = 3$) are transferred in the overall reaction, so substituting into Equation 14.2.2.1 and solving for E^o gives the following:

$$\begin{aligned}
\Delta G^\circ &= -nFE^\circ_{\text{cell}} \\
F(0.13\ \mathrm{V}) &= -(3)(F)(E^\circ_{\text{cell}}) \\
E^\circ &= -\frac{0.13\ \mathrm{V}}{3} = -0.043\ \mathrm{V}
\end{aligned}$$

This value of E^o is very different from the value that is obtained by simply adding the potentials for the two half-reactions (0.32 V) and even has the opposite sign.

> *Values of E^o for half-reactions cannot be added to give E^o for the sum of the half-reactions; only values of $\Delta G^o = -nFE^\circ_{cell}$ for half-reactions can be added.*

The Relationship between Cell Potential & the Equilibrium Constant

We can use the relationship between ΔG° and the equilibrium constant K, to obtain a relationship between E°_{cell} and K. Recall that for a general reaction of the type $aA + bB \rightarrow cC + dD$, the standard free-energy change and the equilibrium constant are related by the following equation:

$$\Delta G^\circ = -RT \ln K$$

Given the relationship between the standard free-energy change and the standard cell potential (Equation 14.2.2.1), we can write

$$-nFE^\circ_{cell} = -RT \ln K$$

Rearranging this equation,

$$E^\circ_{\text{cell}} = \left(\frac{RT}{nF}\right) \ln K \tag{14.2.2.2}$$

For $T = 298\ K$, Equation 14.2.2.2 can be simplified as follows:

$$\begin{aligned} E^\circ_{\text{cell}} &= \left(\frac{RT}{nF}\right) \ln K \\ &= \left[\frac{[8.314\ \text{J/(mol}\cdot\text{K)(298 K)}]}{n[96,485\ \text{J/(V}\cdot\text{mol)}]}\right] 2.303 \log K \\ &= \left(\frac{0.0592\ \text{V}}{n}\right) \log K \end{aligned} \tag{14.2.2.3}$$

Thus E°_{cell} is directly proportional to the logarithm of the equilibrium constant. This means that large equilibrium constants correspond to large positive values of E°_{cell} and vice versa.

Example 14.2.2.2

Use the data in Table P2 to calculate the equilibrium constant for the reaction of metallic lead with PbO_2 in the presence of sulfate ions to give $PbSO_4$ under standard conditions. (This reaction occurs when a car battery is discharged.) Report your answer to two significant figures.

Given: redox reaction

Asked for: K

Strategy:

A. Write the relevant half-reactions and potentials. From these, obtain the overall reaction and E^o_{cell}.

B. Determine the number of electrons transferred in the overall reaction. Use Equation 14.2.2.3 to solve for $\log K$ and then K.

Solution

A The relevant half-reactions and potentials from Table P2 are as follows:

cathode:	$\text{PbO}_2(\text{s}) + \text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l})$	$E^\circ_{\text{cathode}} = 1.69\ \text{V}$
anode:	$\text{Pb}(\text{s}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{PbSO}_4(\text{s}) + 2\text{e}^-$	$E^\circ_{\text{anode}} = -0.36\ \text{V}$
overall:	$\text{Pb}(\text{s}) + \text{PbO}_2(\text{s}) + 2\text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) \rightarrow 2\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l})$	$E^\circ_{\text{cell}} = 2.05\ \text{V}$

B Two electrons are transferred in the overall reaction, so $n = 2$. Solving Equation 14.2.2.3 for log K and inserting the values of n and E^o,

$$\log K = \frac{nE^\circ}{0.0591\ \text{V}} = \frac{2(2.05\ \text{V})}{0.0591\ \text{V}} = 69.37$$

$$K = 2.3 \times 10^{69}$$

Thus the equilibrium lies far to the right, favoring a discharged battery (as anyone who has ever tried unsuccessfully to start a car after letting it sit for a long time will know).

Exercise 14.2.2.2

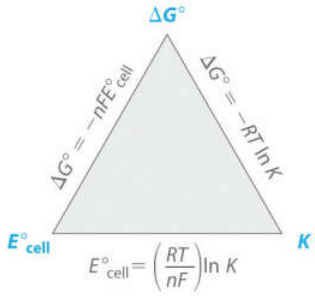
Use the data in Table P2 to calculate the equilibrium constant for the reaction of $\text{Sn}^{2+}(\text{aq})$ with oxygen to produce $\text{Sn}^{4+}(\text{aq})$ and water under standard conditions. Report your answer to two significant figures. The reaction is as follows:

$$2\,\text{Sn}^{2+}(\text{aq}) + \text{O}_2(\text{g}) + 4\,\text{H}^+(\text{aq}) \rightleftharpoons 2\,\text{Sn}^{4+}(\text{aq}) + 2\,\text{H}_2\text{O}(\text{l})$$

Answer

5.7×10^{72}

Figure 14.2.2.1 summarizes the relationships that we have developed based on properties of the system—that is, based on the equilibrium constant, standard free-energy change, and standard cell potential—and the criteria for spontaneity (ΔG° < 0). Unfortunately, these criteria apply only to systems in which all reactants and products are present in their standard states, a situation that is seldom encountered in the real world. A more generally useful relationship between cell potential and reactant and product concentrations, as we are about to see, uses the relationship between ΔG and the reaction quotient Q.



ΔG°	$E°_{cell}$	K	Direction of Reaction
< 0	> 0	>1	spontaneous in forward direction
> 0	< 0	< 1	spontaneous in reverse direction
0	0	1	no net reaction: system at equilibrium

Figure 14.2.2.1: The Relationships among Criteria for Thermodynamic Spontaneity. The three properties of a system that can be used to predict the spontaneity of a redox reaction under standard conditions are K, ΔG°, and $E°_{cell}$. If we know the value of one of these quantities, then these relationships enable us to calculate the value of the other two. The signs of ΔG° and $E°_{cell}$ and the magnitude of K determine the direction of spontaneous reaction under standard conditions. (CC BY-NC-SA; Anonymous by request)

If ΔG is less than zero, E^o is greater than zero and K is greater than 1 then the direction of the reaction is spontaneous in forward direction. If ΔG is greater than zero, E^o is less than zero and K is less than one then the direction of reaction is spontaneous in reverse direction. If ΔG is zero, E is zero and K is one that there is no net reaction and the system is at equilibrium .

Summary

A coulomb (C) relates electrical potential, expressed in volts, and energy, expressed in joules. The current generated from a redox reaction is measured in amperes (A), where 1 A is defined as the flow of 1 C/s past a given point. The faraday (F) is Avogadro's number multiplied by the charge on an electron and corresponds to the charge on 1 mol of electrons. The product of the cell potential and the total charge is the maximum amount of energy available to do work, which is related to the change in free energy that occurs during the chemical process. Adding together the ΔG values for the half-reactions gives ΔG for the overall reaction, which is proportional to both the potential and the number of electrons (n) transferred. Spontaneous redox reactions have a negative ΔG and therefore a positive E_{cell}. Because the equilibrium constant K is related to ΔG, $E°_{cell}$ and K are also related. Large equilibrium constants correspond to large positive values of E°.

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14.2.3: Concentration Effects and the Nernst Equation

Learning Objectives

- Relate cell potentials to Gibbs energy changes
- Use the Nernst equation to determine cell potentials at nonstandard conditions
- Perform calculations that involve converting between cell potentials, free energy changes, and equilibrium constants

The *Nernst Equation* enables the determination of cell potential under non-standard conditions. It relates the measured cell potential to the reaction quotient and allows the accurate determination of equilibrium constants (including solubility constants).

The Effect of Concentration on Cell Potential: The Nernst Equation

Recall that the actual free-energy change for a reaction under nonstandard conditions, ΔG, is given as follows:

$$\Delta G = \Delta G^{\circ} + RT \ln Q \tag{14.2.3.1}$$

We also know that $\Delta G = -nFE_{cell}$ (under non-standard conditions) and $\Delta G^{o} = -nFE^{o}_{cell}$ (under standard conditions). Substituting these expressions into Equation 14.2.3.1, we obtain

$$-nFE_{cell} = -nFE^{o}_{cell} + RT \ln Q \tag{14.2.3.2}$$

Dividing both sides of this equation by $-nF$,

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \left(\frac{RT}{nF}\right) \ln Q \tag{14.2.3.3}$$

Equation 14.2.3.3 is called the **Nernst equation**, after the German physicist and chemist Walter Nernst (1864–1941), who first derived it. The Nernst equation is arguably the most important relationship in electrochemistry. When a redox reaction is at equilibrium ($\Delta G = 0$), then Equation 14.2.3.3 reduces to Equation 14.2.3.4 and 14.2.3.5 because $Q = K$, and there is no net transfer of electrons (i.e., E_{cell} = 0).

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \left(\frac{RT}{nF}\right) \ln K = 0 \tag{14.2.3.4}$$

since

$$E^{\circ}_{\text{cell}} = \left(\frac{RT}{nF}\right) \ln K \tag{14.2.3.5}$$

Substituting the values of the constants into Equation 14.2.3.3 with $T = 298\ K$ and converting to base-10 logarithms give the relationship of the actual cell potential (E_{cell}), the standard cell potential ($E°_{cell}$), and the reactant and product concentrations at room temperature (contained in Q):

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right) \log Q \tag{14.2.3.6}$$

The Power of the Nernst Equation

The Nernst Equation (14.2.3.3) can be used to determine the value of E_{cell}, and thus the direction of spontaneous reaction, for any redox reaction under any conditions.

Equation 14.2.3.6 allows us to calculate the potential associated with any electrochemical cell at 298 K for any combination of reactant and product concentrations under any conditions. We can therefore determine the spontaneous direction of any redox reaction under any conditions, as long as we have tabulated values for the relevant standard electrode potentials. Notice in Equation 14.2.3.6 that the cell potential changes by 0.0591/n V for each 10-fold change in the value of Q because log 10 = 1.

Example 14.2.3.1

The following reaction proceeds spontaneously under standard conditions because $E°_{cell} > 0$ (which means that $\Delta G° < 0$):

$$2\,Ce^{4+}(aq) + 2\,Cl^-(aq) \longrightarrow 2\,Ce^{3+}(aq) + Cl_2(g) \qquad E^\circ_{cell} = 0.25\ V$$

Calculate E_{cell} for this reaction under the following nonstandard conditions and determine whether it will occur spontaneously: $[Ce^{4+}] = 0.013$ M, $[Ce^{3+}] = 0.60$ M, $[Cl^-] = 0.0030$ M, $P_{Cl_2} = 1.0$ atm, and T = 25°C.

Given: balanced redox reaction, standard cell potential, and nonstandard conditions

Asked for: cell potential

Strategy:

Determine the number of electrons transferred during the redox process. Then use the Nernst equation to find the cell potential under the nonstandard conditions.

Solution

We can use the information given and the Nernst equation to calculate E_{cell}. Moreover, because the temperature is 25°C (298 K), we can use Equation 14.2.3.6 instead of Equation 14.2.3.3. The overall reaction involves the net transfer of two electrons:

$$2Ce^{4+}_{(aq)} + 2e^- \rightarrow 2Ce^{3+}_{(aq)}$$

$$2Cl^-_{(aq)} \rightarrow Cl_{2(g)} + 2e^-$$

so n = 2. Substituting the concentrations given in the problem, the partial pressure of Cl_2, and the value of $E°_{cell}$ into Equation 14.2.3.6,

$$\begin{aligned} E_{cell} &= E^\circ_{cell} - \left(\frac{0.0591\ \text{V}}{n}\right)\log Q \\ &= 0.25\ \text{V} - \left(\frac{0.0591\ \text{V}}{2}\right)\log\left(\frac{[Ce^{3+}]^2 P_{Cl_2}}{[Ce^{4+}]^2[Cl^-]^2}\right) \\ &= 0.25\ \text{V} - [(0.0296\ \text{V})(8.37)] = 0.00\ \text{V} \end{aligned}$$

Thus the reaction will not occur spontaneously under these conditions (because E = 0 V and $\Delta G = 0$). The composition specified is that of an equilibrium mixture

Exercise 14.2.3.1

Molecular oxygen will not oxidize MnO_2 to permanganate via the reaction

$$4\,MnO_2(s) + 3\,O_2(g) + 4\,OH^-(aq) \longrightarrow 4\,MnO_4^-(aq) + 2\,H_2O(l) \quad E^\circ_{cell} = -0.20\ V$$

Calculate E_{cell} for the reaction under the following nonstandard conditions and decide whether the reaction will occur spontaneously: pH 10, $P_{O_2} = 0.20$ atm, $[MNO_4^-] = 1.0 \times 10^{-4}$ M, and T = 25°C.

Answer

$E_{cell} = -0.22$ V; the reaction will not occur spontaneously.

Applying the Nernst equation to a simple electrochemical cell such as the Zn/Cu cell allows us to see how the cell voltage varies as the reaction progresses and the concentrations of the dissolved ions change. Recall that the overall reaction for this cell is as follows:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s) \quad E^\circ cell = 1.10V \tag{14.2.3.7}$$

The reaction quotient is therefore $Q = [Zn^{2+}]/[Cu^{2+}]$. Suppose that the cell initially contains 1.0 M Cu^{2+} and 1.0×10^{-6} M Zn^{2+}. The initial voltage measured when the cell is connected can then be calculated from Equation 14.2.3.6:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right)\log\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \tag{14.2.3.8}$$

$$= 1.10\ \text{V} - \left(\frac{0.0591\ \text{V}}{2}\right)\log\left(\frac{1.0\times10^{-6}}{1.0}\right) = 1.28\ \text{V} \tag{14.2.3.9}$$

Thus the initial voltage is greater than E° because $Q < 1$. As the reaction proceeds, [Zn^{2+}] in the anode compartment increases as the zinc electrode dissolves, while [Cu^{2+}] in the cathode compartment decreases as metallic copper is deposited on the electrode. During this process, the ratio Q = [Zn^{2+}]/[Cu^{2+}] steadily increases, and the cell voltage therefore steadily decreases. Eventually, [Zn^{2+}] = [Cu^{2+}], so Q = 1 and E_{cell} = $E°_{cell}$. Beyond this point, [Zn^{2+}] will continue to increase in the anode compartment, and [Cu^{2+}] will continue to decrease in the cathode compartment. Thus the value of Q will increase further, leading to a further decrease in E_{cell}. When the concentrations in the two compartments are the opposite of the initial concentrations (i.e., 1.0 M Zn^{2+} and 1.0 × 10^{-6} M Cu^{2+}), Q = 1.0 × 10^6, and the cell potential will be reduced to 0.92 V.

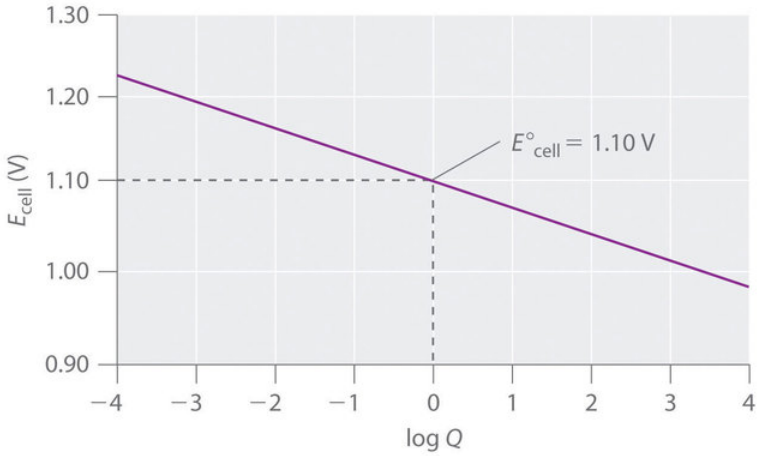


Figure 14.2.3.1: The Variation of E_{cell} with Log Q for a Zn/Cu Cell. Initially, log Q < 0, and the voltage of the cell is greater than $E°_{cell}$. As the reaction progresses, log Q increases, and E_{cell} decreases. When [Zn^{2+}] = [Cu^{2+}], log Q = 0 and E_{cell} = $E°_{cell}$ = 1.10 V. As long as the electrical circuit remains intact, the reaction will continue, and log Q will increase until Q = K and the cell voltage reaches zero. At this point, the system will have reached equilibrium.

The variation of E_{cell} with $\log Q$ over this range is linear with a slope of −0.0591/n, as illustrated in Figure 14.2.3.1. As the reaction proceeds still further, Q continues to increase, and E_{cell} continues to decrease. If neither of the electrodes dissolves completely, thereby breaking the electrical circuit, the cell voltage will eventually reach zero. This is the situation that occurs when a battery is "dead." The value of Q when E_{cell} = 0 is calculated as follows:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right)\log Q = 0 \tag{14.2.3.10}$$

$$E^\circ = \left(\frac{0.0591\ \text{V}}{n}\right)\log Q \tag{14.2.3.11}$$

$$\log Q = \frac{E^\circ n}{0.0591\ \text{V}} = \frac{(1.10\ \text{V})(2)}{0.0591\ \text{V}} = 37.23 \tag{14.2.3.12}$$

$$Q = 10^{37.23} = 1.7\times10^{37} \tag{14.2.3.13}$$

Recall that at equilibrium, $Q = K$. Thus the equilibrium constant for the reaction of Zn metal with Cu^{2+} to give Cu metal and Zn^{2+} is 1.7 × 10^{37} at 25°C.



The Nernst Equation: The Nernst Equation (opens in new window) [youtu.be]

Concentration Cells

A voltage can also be generated by constructing an electrochemical cell in which each compartment contains the same redox active solution but at different concentrations. The voltage is produced as the concentrations equilibrate. Suppose, for example, we have a cell with 0.010 M $AgNO_3$ in one compartment and 1.0 M $AgNO_3$ in the other. The cell diagram and corresponding half-reactions are as follows:

$$\mathrm{Ag(s)\,|\,Ag^+}(aq, 0.010\ M)\,||\,\mathrm{Ag^+}(aq, 1.0\ M)\,|\,\mathrm{Ag(s)} \tag{14.2.3.14}$$

cathode:

$$\mathrm{Ag^+}(aq, 1.0\ M) + \mathrm{e^-} \rightarrow \mathrm{Ag(s)} \tag{14.2.3.15}$$

anode:

$$\mathrm{Ag(s)} \rightarrow \mathrm{Ag^+}(aq, 0.010\ M) + \mathrm{e^-} \tag{14.2.3.16}$$

Overall

$$\mathrm{Ag^+}(aq, 1.0\ M) \rightarrow \mathrm{Ag^+}(aq, 0.010\ M) \tag{14.2.3.17}$$

As the reaction progresses, the concentration of Ag^+ will increase in the left (oxidation) compartment as the silver electrode dissolves, while the Ag^+ concentration in the right (reduction) compartment decreases as the electrode in that compartment gains mass. The total mass of $Ag(s)$ in the cell will remain constant, however. We can calculate the potential of the cell using the Nernst equation, inserting 0 for $E°_{cell}$ because $E°_{cathode} = -E°_{anode}$:

$$\begin{aligned} E_{\text{cell}} &= E^\circ_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right)\log Q \\ &= 0 - \left(\frac{0.0591\ \text{V}}{1}\right)\log\left(\frac{0.010}{1.0}\right) \\ &= 0.12\ \text{V} \end{aligned}$$

An electrochemical cell of this type, in which the anode and cathode compartments are identical except for the concentration of a reactant, is called a **concentration cell**. As the reaction proceeds, the difference between the concentrations of Ag^+ in the two compartments will decrease, as will E_{cell}. Finally, when the concentration of Ag^+ is the same in both compartments, equilibrium will have been reached, and the measured potential difference between the two compartments will be zero ($E_{cell} = 0$).

Example 14.2.3.2

Calculate the voltage in a galvanic cell that contains a manganese electrode immersed in a 2.0 M solution of $MnCl_2$ as the cathode, and a manganese electrode immersed in a 5.2×10^{-2} M solution of $MnSO_4$ as the anode (T = 25°C).

Given: galvanic cell, identities of the electrodes, and solution concentrations

Asked for: voltage

Strategy:

A. Write the overall reaction that occurs in the cell.

B. Determine the number of electrons transferred. Substitute this value into the Nernst equation to calculate the voltage.

Solution

A This is a concentration cell, in which the electrode compartments contain the same redox active substance but at different concentrations. The anions (Cl^- and SO_4^{2-}) do not participate in the reaction, so their identity is not important. The overall reaction is as follows:

$$Mn^{2+}(aq, 2.0\ M) \rightarrow Mn^{2+}(aq, 5.2 \times 10^{-2}\ M)$$

B For the reduction of $Mn^{2+}(aq)$ to Mn(s), n = 2. We substitute this value and the given Mn^{2+} concentrations into Equation 14.2.3.6:

$$\begin{aligned} E_{cell} &= E^\circ_{cell} - \left(\frac{0.0591\ V}{n}\right) \log Q \\ &= 0\ V - \left(\frac{0.0591\ V}{2}\right) \log\left(\frac{5.2 \times 10^{-2}}{2.0}\right) \\ &= 0.047\ V \end{aligned}$$

Thus manganese will dissolve from the electrode in the compartment that contains the more dilute solution and will be deposited on the electrode in the compartment that contains the more concentrated solution.

? Exercise 14.2.3.2

Suppose we construct a galvanic cell by placing two identical platinum electrodes in two beakers that are connected by a salt bridge. One beaker contains 1.0 M HCl, and the other a 0.010 M solution of Na_2SO_4 at pH 7.00. Both cells are in contact with the atmosphere, with P_{O_2} = 0.20 atm. If the relevant electrochemical reaction in both compartments is the four-electron reduction of oxygen to water:

$$O_2(g) + 4\,H^+(aq) + 4\,e^- \rightarrow 2\,H_2O(l)$$

What will be the potential when the circuit is closed?

Answer

0.41 V

Using Cell Potentials to Measure Solubility Products

Because voltages are relatively easy to measure accurately using a voltmeter, electrochemical methods provide a convenient way to determine the concentrations of very dilute solutions and the solubility products (K_{sp}) of sparingly soluble substances. As you learned previously, solubility products can be very small, with values of less than or equal to 10^{-30}. Equilibrium constants of this magnitude are virtually impossible to measure accurately by direct methods, so we must use alternative methods that are more sensitive, such as electrochemical methods.

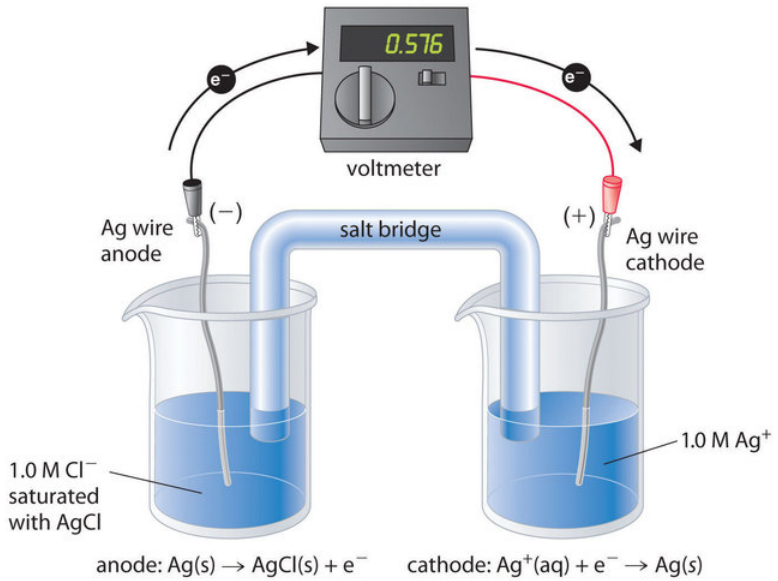


Figure 14.2.3.1: A Galvanic ("Concentration") Cell for Measuring the Solubility Product of AgCl. One compartment contains a silver wire inserted into a 1.0 M solution of Ag^+, and the other compartment contains a silver wire inserted into a 1.0 M Cl^- solution saturated with AgCl. The potential due to the difference in $[Ag^+]$ between the two cells can be used to determine K_{sp}. (CC BY-NC-SA; Anonymous by request)

To understand how an electrochemical cell is used to measure a solubility product, consider the cell shown in Figure 14.2.3.1, which is designed to measure the solubility product of silver chloride:

$$K_{sp} = [\mathrm{Ag^+}][\mathrm{Cl^-}].$$

In one compartment, the cell contains a silver wire inserted into a 1.0 M solution of Ag^+; the other compartment contains a silver wire inserted into a 1.0 M Cl^- solution saturated with AgCl. In this system, the Ag^+ ion concentration in the first compartment equals K_{sp}. We can see this by dividing both sides of the equation for K_{sp} by $[Cl^-]$ and substituting:

$$\begin{aligned}[\mathrm{Ag^+}] &= \frac{K_{sp}}{[\mathrm{Cl^-}]} \\ &= \frac{K_{sp}}{1.0} = K_{sp}.\end{aligned}$$

The overall cell reaction is as follows:

$$\mathrm{Ag^+(aq,\ concentrated)} \rightarrow \mathrm{Ag^+(aq,\ dilute)}$$

Thus the voltage of the concentration cell due to the difference in $[Ag^+]$ between the two cells is as follows:

$$\begin{aligned}E_{\text{cell}} &= 0\ \text{V} - \left(\frac{0.0591\ \text{V}}{1}\right)\log\left(\frac{[\mathrm{Ag^+}]_{\text{dilute}}}{[\mathrm{Ag^+}]_{\text{concentrated}}}\right) \\ &= -0.0591\ \text{V}\ \log\left(\frac{K_{\text{sp}}}{1.0}\right) \\ &= -0.0591\ \text{V}\ \log K_{\text{sp}} \qquad (14.2.3.18)\end{aligned}$$

By closing the circuit, we can measure the potential caused by the difference in [Ag+] in the two cells. In this case, the experimentally measured voltage of the concentration cell at 25°C is 0.580 V. Solving Equation 14.2.3.18for K_{sp},

$$\begin{aligned}\log K_{\text{sp}} &= \frac{-E_{\text{cell}}}{0.0591\ \text{V}} = \frac{-0.580\ \text{V}}{0.0591\ \text{V}} = -9.81 \\ K_{\text{sp}} &= 1.5 \times 10^{-10}\end{aligned}$$

Thus a single potential measurement can provide the information we need to determine the value of the solubility product of a sparingly soluble salt.

Example 14.2.3.3: Solubility of lead(II) sulfate

To measure the solubility product of lead(II) sulfate ($PbSO_4$) at 25°C, you construct a galvanic cell like the one shown in Figure 14.2.3.1, which contains a 1.0 M solution of a very soluble Pb^{2+} salt [lead(II) acetate trihydrate] in one compartment that is connected by a salt bridge to a 1.0 M solution of Na_2SO_4 saturated with $PbSO_4$ in the other. You then insert a Pb electrode into each compartment and close the circuit. Your voltmeter shows a voltage of 230 mV. What is K_{sp} for $PbSO_4$? Report your answer to two significant figures.

Given: galvanic cell, solution concentrations, electrodes, and voltage

Asked for: K_{sp}

Strategy:

A. From the information given, write the equation for K_{sp}. Express this equation in terms of the concentration of Pb^{2+}.

B. Determine the number of electrons transferred in the electrochemical reaction. Substitute the appropriate values into Equation ??? and solve for K_{sp}.

Solution

A You have constructed a concentration cell, with one compartment containing a 1.0 M solution of Pb^{2+} and the other containing a dilute solution of Pb^{2+} in 1.0 M Na_2SO_4. As for any concentration cell, the voltage between the two compartments can be calculated using the Nernst equation. The first step is to relate the concentration of Pb^{2+} in the dilute solution to K_{sp}:

$$[Pb^{2+}][SO_4^{2-}] = K_{sp}$$

$$[Pb^{2+}] = \frac{K_{sp}}{[SO_4^{2-}]} = \frac{K_{sp}}{1.0\ M} = K_{sp}$$

B The reduction of Pb^{2+} to Pb is a two-electron process and proceeds according to the following reaction:

$$Pb^{2+}(aq, concentrated) \rightarrow Pb^{2+}(aq, dilute)$$

so

$$E_{cell} = E^{\circ}_{cell} - \left(\frac{0.0591}{n}\right) \log Q$$

$$0.230\ V = 0\ V - \left(\frac{0.0591\ V}{2}\right) \log\left(\frac{[Pb^{2+}]_{dilute}}{[Pb^{2+}]_{concentrated}}\right) = -0.0296\ V \log\left(\frac{K_{sp}}{1.0}\right)$$

$$-7.77 = \log K_{sp}$$

$$1.7 \times 10^{-8} = K_{sp}$$

Exercise 14.2.3.3

A concentration cell similar to the one described in Example 14.2.3.3 contains a 1.0 M solution of lanthanum nitrate [$La(NO_3)_3$] in one compartment and a 1.0 M solution of sodium fluoride saturated with LaF_3 in the other. A metallic La strip is inserted into each compartment, and the circuit is closed. The measured potential is 0.32 V. What is the K_{sp} for LaF_3? Report your answer to two significant figures.

Answer

5.7×10^{-17}

Using Cell Potentials to Measure Concentrations

Another use for the Nernst equation is to calculate the concentration of a species given a measured potential and the concentrations of all the other species. We saw an example of this in Example 14.2.3.3, in which the experimental conditions were defined in such a way that the concentration of the metal ion was equal to K_{sp}. Potential measurements can be used to obtain the concentrations of dissolved species under other conditions as well, which explains the widespread use of electrochemical cells in many analytical devices. Perhaps the most common application is in the determination of $[H^+]$ using a pH meter, as illustrated below.

Example 14.2.3.4: Measuring pH

Suppose a galvanic cell is constructed with a standard Zn/Zn^{2+} couple in one compartment and a modified hydrogen electrode in the second compartment. The pressure of hydrogen gas is 1.0 atm, but $[H^+]$ in the second compartment is unknown. The cell diagram is as follows:

$$Zn(s)|Zn^{2+}(aq, 1.0\ M)||H^+(aq, ?\ M)|H_2(g, 1.0\ atm)|Pt(s)$$

What is the pH of the solution in the second compartment if the measured potential in the cell is 0.26 V at 25°C?

Given: galvanic cell, cell diagram, and cell potential

Asked for: pH of the solution

Strategy:

A. Write the overall cell reaction.
B. Substitute appropriate values into the Nernst equation and solve for $-\log[H^+]$ to obtain the pH.

Solution

A Under standard conditions, the overall reaction that occurs is the reduction of protons by zinc to give H_2 (note that Zn lies below H_2 in Table P2):

$$Zn(s) + 2H^{2+}(aq) \rightarrow Zn^{2+}(aq) + H_2(g) \quad E°=0.76\ V$$

B By substituting the given values into the simplified Nernst equation (Equation 14.2.3.6), we can calculate $[H^+]$ under nonstandard conditions:

$$\begin{aligned} E_{cell} &= E^\circ_{cell} - \left(\frac{0.0591\ V}{n}\right)\log\left(\frac{[Zn^{2+}]P_{H_2}}{[H^+]^2}\right) \\ 0.26\ V &= 0.76\ V - \left(\frac{0.0591\ V}{2}\right)\log\left(\frac{(1.0)(1.0)}{[H^+]^2}\right) \\ 16.9 &= \log\left(\frac{1}{[H^+]^2}\right) = \log[H^+]^{-2} = (-2)\log[H^+] \\ 8.46 &= -\log[H^+] \\ 8.5 &= pH \end{aligned}$$

Thus the potential of a galvanic cell can be used to measure the pH of a solution.

Exercise 14.2.3.4

Suppose you work for an environmental laboratory and you want to use an electrochemical method to measure the concentration of Pb^{2+} in groundwater. You construct a galvanic cell using a standard oxygen electrode in one compartment ($E°_{cathode}$ = 1.23 V). The other compartment contains a strip of lead in a sample of groundwater to which you have added sufficient acetic acid, a weak organic acid, to ensure electrical conductivity. The cell diagram is as follows:

$$Pb_{(s)} \mid Pb^{2+}(aq, ?M) \parallel H^+(aq), 1.0M \mid O_2(g, 1.0atm) \mid Pt_{(s)}$$

When the circuit is closed, the cell has a measured potential of 1.62 V. Use Table P2 to determine the concentration of Pb^{2+} in the groundwater.

Answer

$1.2 \times 10^{-9}\ M$

Summary

The Nernst equation can be used to determine the direction of spontaneous reaction for any redox reaction in aqueous solution. The Nernst equation allows us to determine the spontaneous direction of any redox reaction under any reaction conditions from values of the relevant standard electrode potentials. Concentration cells consist of anode and cathode compartments that are identical

except for the concentrations of the reactant. Because $\Delta G = 0$ at equilibrium, the measured potential of a concentration cell is zero at equilibrium (the concentrations are equal). A galvanic cell can also be used to measure the solubility product of a sparingly soluble substance and calculate the concentration of a species given a measured potential and the concentrations of all the other species.

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14.2.4: Batteries and Fuel Cells

Because galvanic cells can be self-contained and portable, they can be used as batteries and fuel cells. A **battery (storage cell)** is a galvanic cell (or a series of galvanic cells) that contains all the reactants needed to produce electricity. In contrast, a **fuel cell** is a galvanic cell that requires a constant external supply of one or more reactants to generate electricity. In this section, we describe the chemistry behind some of the more common types of batteries and fuel cells.

Batteries

There are two basic kinds of batteries: disposable, or primary, batteries, in which the electrode reactions are effectively irreversible and which cannot be recharged; and rechargeable, or secondary, batteries, which form an insoluble product that adheres to the electrodes. These batteries can be recharged by applying an electrical potential in the reverse direction. The recharging process temporarily converts a rechargeable battery from a galvanic cell to an electrolytic cell.

Batteries are cleverly engineered devices that are based on the same fundamental laws as galvanic cells. The major difference between batteries and the galvanic cells we have previously described is that commercial batteries use solids or pastes rather than solutions as reactants to maximize the electrical output per unit mass. The use of highly concentrated or solid reactants has another beneficial effect: the concentrations of the reactants and the products do not change greatly as the battery is discharged; consequently, the output voltage remains remarkably constant during the discharge process. This behavior is in contrast to that of the Zn/Cu cell, whose output decreases logarithmically as the reaction proceeds (Figure 14.2.4.1). When a battery consists of more than one galvanic cell, the cells are usually connected in series—that is, with the positive (+) terminal of one cell connected to the negative (−) terminal of the next, and so forth. The overall voltage of the battery is therefore the sum of the voltages of the individual cells.

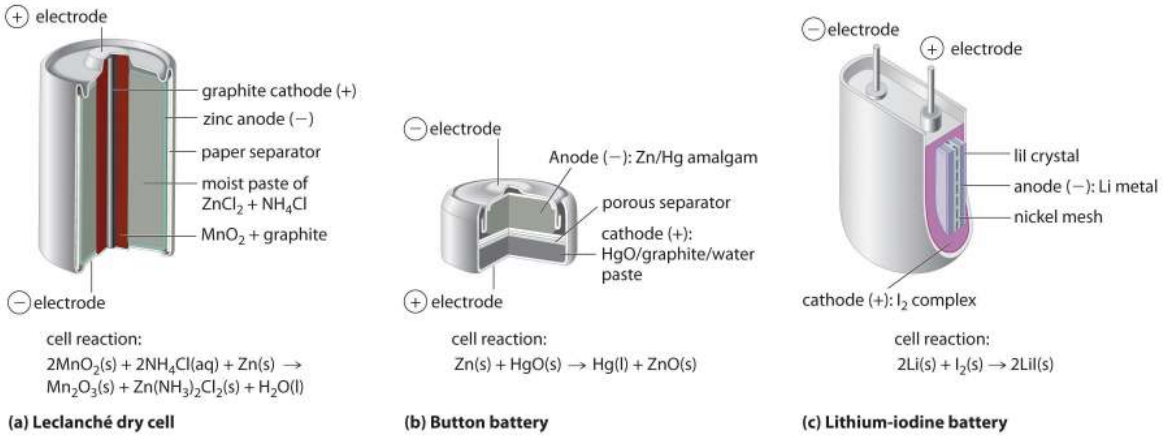


Figure 14.2.4.1: Three Kinds of Primary (Nonrechargeable) Batteries. (a) A Leclanché dry cell is actually a "wet cell," in which the electrolyte is an acidic water-based paste containing MnO_2, NH_4Cl, $ZnCl_2$, graphite, and starch. Though inexpensive to manufacture, the cell is not very efficient in producing electrical energy and has a limited shelf life. (b) In a button battery, the anode is a zinc–mercury amalgam, and the cathode can be either HgO (shown here) or Ag_2O as the oxidant. Button batteries are reliable and have a high output-to-mass ratio, which allows them to be used in applications such as calculators and watches, where their small size is crucial. (c) A lithium–iodine battery consists of two cells separated by a metallic nickel mesh that collects charge from the anodes. The anode is lithium metal, and the cathode is a solid complex of I_2. The electrolyte is a layer of solid LiI that allows Li^+ ions to diffuse from the cathode to the anode. Although this type of battery produces only a relatively small current, it is highly reliable and long-lived.

> The major difference between batteries and the galvanic cells is that commercial typically batteries use solids or pastes rather than solutions as reactants to maximize the electrical output per unit mass. An obvious exception is the standard car battery which used solution phase chemistry.

Leclanché Dry Cell

The dry cell, by far the most common type of battery, is used in flashlights, electronic devices such as the Walkman and Game Boy, and many other devices. Although the dry cell was patented in 1866 by the French chemist Georges Leclanché and more than 5 billion such cells are sold every year, the details of its electrode chemistry are still not completely understood. In spite of its name, the **Leclanché dry cell** is actually a "wet cell": the electrolyte is an acidic water-based paste containing MnO_2, NH_4Cl, $ZnCl_2$, graphite, and starch (part (a) in Figure 14.2.4.1). The half-reactions at the anode and the cathode can be summarized as follows:

- cathode (reduction):

$$2\,MnO_2(s) + 2\,NH_4^+(aq) + 2\,e^- \longrightarrow Mn_2O_3(s) + 2\,NH_3(aq) + H_2O(l)$$

- anode (oxidation):

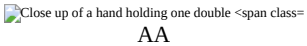
$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^-$$

The Zn^{2+} ions formed by the oxidation of $Zn(s)$ at the anode react with NH_3 formed at the cathode and Cl^- ions present in solution, so the overall cell reaction is as follows:

- overall reaction:

$$2\,MnO_2(s) + 2\,NH_4Cl(aq) + Zn(s) \longrightarrow Mn_2O_3(s) + Zn(NH_3)_2Cl_2(s) + H_2O(l) \tag{14.2.4.1}$$

The dry cell produces about 1.55 V and is inexpensive to manufacture. It is not, however, very efficient in producing electrical energy because only the relatively small fraction of the MnO_2 that is near the cathode is actually reduced and only a small fraction of the zinc cathode is actually consumed as the cell discharges. In addition, dry cells have a limited shelf life because the Zn anode reacts spontaneously with NH_4Cl in the electrolyte, causing the case to corrode and allowing the contents to leak out.



AA

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Source: Photo courtesy of Mitchclanky2008, www.flickr.com/photos/25597837@N05/2422765479/.

The **alkaline battery** is essentially a Leclanché cell adapted to operate under alkaline, or basic, conditions. The half-reactions that occur in an alkaline battery are as follows:

- cathode (reduction)

$$2\,MnO_2(s) + H_2O(l) + 2\,e^- \longrightarrow Mn_2O_3(s) + 2\,OH^-(aq)$$

- anode (oxidation):

$$Zn(s) + 2\,OH^-(aq) \longrightarrow ZnO(s) + H_2O(l) + 2\,e^-$$

- overall reaction:

$$Zn(s) + 2\,MnO_2(s) \longrightarrow ZnO(s) + Mn_2O_3(s)$$

This battery also produces about 1.5 V, but it has a longer shelf life and more constant output voltage as the cell is discharged than the Leclanché dry cell. Although the alkaline battery is more expensive to produce than the Leclanché dry cell, the improved performance makes this battery more cost-effective.

Button Batteries

Although some of the small button batteries used to power watches, calculators, and cameras are miniature alkaline cells, most are based on a completely different chemistry. In these "button" batteries, the anode is a zinc–mercury amalgam rather than pure zinc, and the cathode uses either HgO or Ag_2O as the oxidant rather than MnO_2 in Figure 14.2.4.1*b*.



Button batteries. (Gerhard H Wrodnigg via Wikipedia)

The cathode, anode and overall reactions and cell output for these two types of button batteries are as follows (two half-reactions occur at the anode, but the overall oxidation half-reaction is shown):

- cathode (mercury battery):

$$HgO(s) + H_2O(l) + 2\,e^- \longrightarrow Hg(l) + 2\,OH^-(aq)$$

- Anode (mercury battery):

$$Zn + 2\,OH^- \longrightarrow ZnO + H_2O + 2\,e^-$$

- overall reaction (mercury battery):

$$Zn(s) + 2\,HgO(s) \longrightarrow 2\,Hg(l) + ZnO(s)$$

  with $E_{cell} = 1.35\,V$.
- cathode reaction (silver battery):

$$Ag_2O(s) + H_2O(l) + 2\,e^- \longrightarrow 2\,Ag(s) + 2\,OH^-(aq)$$

- anode (silver battery):

$$\mathrm{Zn + 2\,OH^- \longrightarrow ZnO + H_2O + 2\,e^-}$$

- Overall reaction (silver battery):

$$\mathrm{Zn(s) + 2\,Ag_2O(s) \longrightarrow 2\,Ag(s) + ZnO(s)}$$

with $E_{cell} = 1.6\,V$.

The major advantages of the mercury and silver cells are their reliability and their high output-to-mass ratio. These factors make them ideal for applications where small size is crucial, as in cameras and hearing aids. The disadvantages are the expense and the environmental problems caused by the disposal of heavy metals, such as Hg and Ag.

Lithium–Iodine Battery

None of the batteries described above is actually "dry." They all contain small amounts of liquid water, which adds significant mass and causes potential corrosion problems. Consequently, substantial effort has been expended to develop water-free batteries. One of the few commercially successful water-free batteries is the **lithium–iodine battery**. The anode is lithium metal, and the cathode is a solid complex of I_2. Separating them is a layer of solid LiI, which acts as the electrolyte by allowing the diffusion of Li^+ ions. The electrode reactions are as follows:

- cathode (reduction):

$$I_{2(s)} + 2e^- \rightarrow 2I^-_{(LiI)} \tag{14.2.4.2}$$

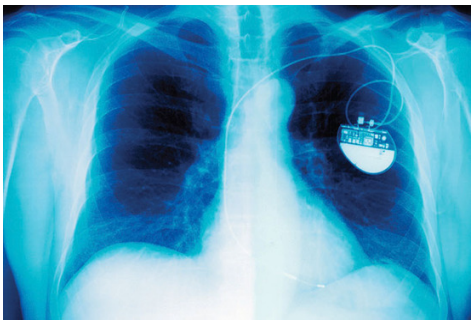
- anode (oxidation):

$$2Li_{(s)} \rightarrow 2Li^+_{(LiI)} + 2e^- \tag{14.2.4.3}$$

- overall:

$$2Li_{(s)} + I_{2(s)} \rightarrow 2LiI_{(s)} \tag{14.2.4.4}$$

with $E_{cell} = 3.5\,V$



Cardiac pacemaker: An x-ray of a patient showing the location and size of a pacemaker powered by a lithium–iodine battery.

As shown in part (c) in Figure 14.2.4.1, a typical lithium–iodine battery consists of two cells separated by a nickel metal mesh that collects charge from the anode. Because of the high internal resistance caused by the solid electrolyte, only a low current can be drawn. Nonetheless, such batteries have proven to be long-lived (up to 10 yr) and reliable. They are therefore used in applications where frequent replacement is difficult or undesirable, such as in cardiac pacemakers and other medical implants and in computers for memory protection. These batteries are also used in security transmitters and smoke alarms. Other batteries based on lithium anodes and solid electrolytes are under development, using TiS_2, for example, for the cathode.

Dry cells, button batteries, and lithium–iodine batteries are disposable and cannot be recharged once they are discharged. Rechargeable batteries, in contrast, offer significant economic and environmental advantages because they can be recharged and discharged numerous times. As a result, manufacturing and disposal costs drop dramatically for a given number of hours of battery usage. Two common rechargeable batteries are the nickel–cadmium battery and the lead–acid battery, which we describe next.

Nickel–Cadmium (NiCad) Battery

The **nickel–cadmium**, or NiCad, battery is used in small electrical appliances and devices like drills, portable vacuum cleaners, and AM/FM digital tuners. It is a water-based cell with a cadmium anode and a highly oxidized nickel cathode that is usually described as the nickel(III) oxo-hydroxide, NiO(OH). As shown in Figure 14.2.4.2 the design maximizes the surface area of the electrodes and minimizes the distance between them, which decreases internal resistance and makes a rather high discharge current possible.

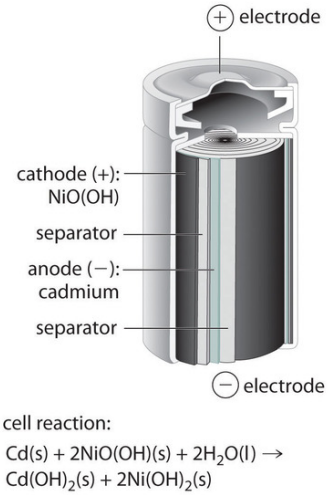


Figure 14.2.4.2: The Nickel–Cadmium (NiCad) Battery, a Rechargeable Battery. NiCad batteries contain a cadmium anode and a highly oxidized nickel cathode. This design maximizes the surface area of the electrodes and minimizes the distance between them, which gives the battery both a high discharge current and a high capacity.

The electrode reactions during the discharge of a $NiCad$ battery are as follows:

- cathode (reduction):

$$2NiO(OH)_{(s)} + 2H_2O_{(l)} + 2e^- \rightarrow 2Ni(OH)_{2(s)} + 2OH^-_{(aq)} \tag{14.2.4.5}$$

- anode (oxidation):

$$Cd_{(s)} + 2OH^-_{(aq)} \rightarrow Cd(OH)_{2(s)} + 2e^- \tag{14.2.4.6}$$

- overall:

$$Cd_{(s)} + 2NiO(OH)_{(s)} + 2H_2O_{(l)} \rightarrow Cd(OH)_{2(s)} + 2Ni(OH)_{2(s)} \tag{14.2.4.7}$$

$$E_{cell} = 1.4V$$

Because the products of the discharge half-reactions are solids that adhere to the electrodes [$Cd(OH)_2$ and $2Ni(OH)_2$], the overall reaction is readily reversed when the cell is recharged. Although NiCad cells are lightweight, rechargeable, and high capacity, they have certain disadvantages. For example, they tend to lose capacity quickly if not allowed to discharge fully before recharging, they do not store well for long periods when fully charged, and they present significant environmental and disposal problems because of the toxicity of cadmium.

A variation on the NiCad battery is the nickel–metal hydride battery (NiMH) used in hybrid automobiles, wireless communication devices, and mobile computing. The overall chemical equation for this type of battery is as follows:

\[NiO(OH)_{(s)} + MH \rightarrow Ni(OH)_{2(s)} + M_{(s)} \label{Eq16} \]

The NiMH battery has a 30%–40% improvement in capacity over the NiCad battery; it is more environmentally friendly so storage, transportation, and disposal are not subject to environmental control; and it is not as sensitive to recharging memory. It is, however, subject to a 50% greater self-discharge rate, a limited service life, and higher maintenance, and it is more expensive than the NiCad battery.

> Directive 2006/66/EC of the European Union prohibits the placing on the market of portable batteries that contain more than 0.002% of cadmium by weight. The aim of this directive was to improve "the environmental performance of batteries and accumulators"

Lead–Acid (Lead Storage) Battery

The **lead–acid battery** is used to provide the starting power in virtually every automobile and marine engine on the market. Marine and car batteries typically consist of multiple cells connected in series. The total voltage generated by the battery is the potential per cell ($E°_{cell}$) times the number of cells.

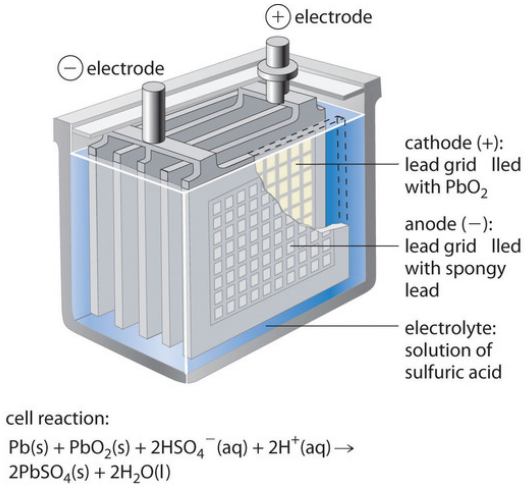


Figure 14.2.4.3: One Cell of a Lead–Acid Battery. The anodes in each cell of a rechargeable battery are plates or grids of lead containing spongy lead metal, while the cathodes are similar grids containing powdered lead dioxide (PbO_2). The electrolyte is an aqueous solution of sulfuric acid. The value of E° for such a cell is about 2 V. Connecting three such cells in series produces a 6 V battery, whereas a typical 12 V car battery contains six cells in series. When treated properly, this type of high-capacity battery can be discharged and recharged many times over.

As shown in Figure 14.2.4.3, the anode of each cell in a lead storage battery is a plate or grid of spongy lead metal, and the cathode is a similar grid containing powdered lead dioxide (PbO_2). The electrolyte is usually an approximately 37% solution (by mass) of sulfuric acid in water, with a density of 1.28 g/mL (about 4.5 M H_2SO_4). Because the redox active species are solids, there is no need to separate the electrodes. The electrode reactions in each cell during discharge are as follows:

- cathode (reduction):

\[PbO_{2(s)} + HSO^-_{4(aq)} + 3H^+_{(aq)} + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O_{(l)} \label{Eq17} \]

with $E^\circ_{cathode} = 1.685\ V$

- anode (oxidation):

$$Pb_{(s)} + HSO^-_{4(aq)} \rightarrow PbSO_{4(s)} + H^+_{(aq)} + 2e^- \tag{14.2.4.8}$$

with $E^\circ_{anode} = -0.356\ V$

- overall:

$$Pb_{(s)} + PbO_{2(s)} + 2HSO^-_{4(aq)} + 2H^+_{(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(l)} \tag{14.2.4.9}$$

and $E^\circ_{cell} = 2.041\ V$

As the cell is discharged, a powder of $PbSO_4$ forms on the electrodes. Moreover, sulfuric acid is consumed and water is produced, decreasing the density of the electrolyte and providing a convenient way of monitoring the status of a battery by simply measuring the density of the electrolyte. This is often done with the use of a hydrometer.



A hydrometer can be used to test the specific gravity of each cell as a measure of its state of charge (www.youtube.com/watch?v=SRcOqfL6GqQ).

When an external voltage in excess of 2.04 V per cell is applied to a lead–acid battery, the electrode reactions reverse, and $PbSO_4$ is converted back to metallic lead and PbO_2. If the battery is recharged too vigorously, however, electrolysis of water can occur:

$$2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2(g)} \tag{14.2.4.10}$$

This results in the evolution of potentially explosive hydrogen gas. The gas bubbles formed in this way can dislodge some of the $PbSO_4$ or PbO_2 particles from the grids, allowing them to fall to the bottom of the cell, where they can build up and cause an internal short circuit. Thus the recharging process must be carefully monitored to optimize the life of the battery. With proper care, however, a lead–acid battery can be discharged and recharged thousands of times. In automobiles, the alternator supplies the electric current that causes the discharge reaction to reverse.

Fuel Cells

A fuel cell is a galvanic cell that requires a constant external supply of reactants because the products of the reaction are continuously removed. Unlike a battery, it does not store chemical or electrical energy; a fuel cell allows electrical energy to be extracted directly from a chemical reaction. In principle, this should be a more efficient process than, for example, burning the fuel to drive an internal combustion engine that turns a generator, which is typically less than 40% efficient, and in fact, the efficiency of a fuel cell is generally between 40% and 60%. Unfortunately, significant cost and reliability problems have hindered the wide-scale adoption of fuel cells. In practice, their use has been restricted to applications in which mass may be a significant cost factor, such as US manned space vehicles.

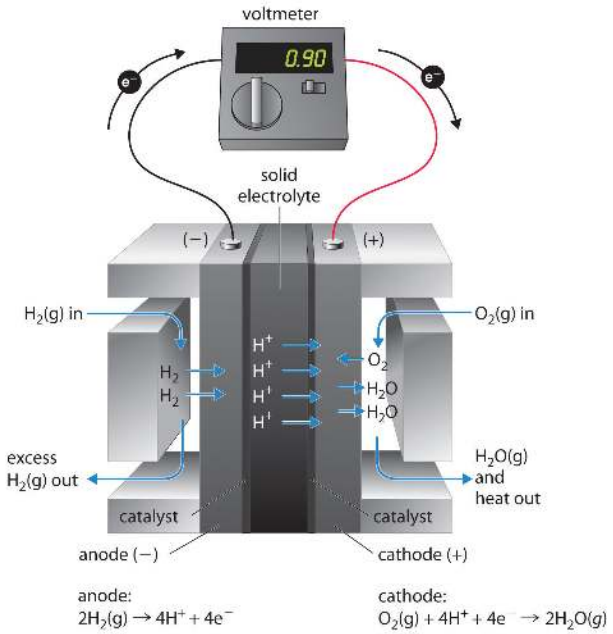


Figure 14.2.4.4: A Hydrogen Fuel Cell Produces Electrical Energy Directly from a Chemical Reaction. Hydrogen is oxidized to protons at the anode, and the electrons are transferred through an external circuit to the cathode, where oxygen is reduced and combines with H^+ to form water. A solid electrolyte allows the protons to diffuse from the anode to the cathode. Although fuel cells are an essentially pollution-free means of obtaining electrical energy, their expense and technological complexity have thus far limited their applications.

These space vehicles use a hydrogen/oxygen fuel cell that requires a continuous input of $H_2(g)$ and $O_2(g)$, as illustrated in Figure 14.2.4.4 The electrode reactions are as follows:

- cathode (reduction):

$$O_{2(g)} + 4H^+ + 4e^- \rightarrow 2H_2O_{(g)} \tag{14.2.4.11}$$

- anode (oxidation):

$$2H_{2(g)} \rightarrow 4H^+ + 4e^- \tag{14.2.4.12}$$

- overall:

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)} \tag{14.2.4.13}$$

The overall reaction represents an essentially pollution-free conversion of hydrogen and oxygen to water, which in space vehicles is then collected and used. Although this type of fuel cell should produce 1.23 V under standard conditions, in practice the device achieves only about 0.9 V. One of the major barriers to achieving greater efficiency is the fact that the four-electron reduction of $O_2(g)$ at the cathode is intrinsically rather slow, which limits current that can be achieved. All major automobile manufacturers have major research programs involving fuel cells: one of the most important goals is the development of a better catalyst for the reduction of $O_2(g)$.

Summary

Commercial batteries are galvanic cells that use solids or pastes as reactants to maximize the electrical output per unit mass. A battery is a contained unit that produces electricity, whereas a fuel cell is a galvanic cell that requires a constant external supply of one or more reactants to generate electricity. One type of battery is the Leclanché dry cell, which contains an electrolyte in an acidic water-based paste. This battery is called an alkaline battery when adapted to operate under alkaline conditions. Button batteries have a high output-to-mass ratio; lithium–iodine batteries consist of a solid electrolyte; the nickel–cadmium (NiCad) battery is rechargeable; and the lead–acid battery, which is also rechargeable, does not require the electrodes to be in separate compartments. A fuel cell requires an external supply of reactants as the products of the reaction are continuously removed. In a fuel cell, energy is not stored; electrical energy is provided by a chemical reaction.

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14.2.5: Corrosion and Its Prevention

Learning Objectives

- To understand the process of corrosion.

Corrosion is a galvanic process by which metals deteriorate through oxidation—usually but not always to their oxides. For example, when exposed to air, iron rusts, silver tarnishes, and copper and brass acquire a bluish-green surface called a patina. Of the various metals subject to corrosion, iron is by far the most important commercially. An estimated $100 billion per year is spent in the United States alone to replace iron-containing objects destroyed by corrosion. Consequently, the development of methods for protecting metal surfaces from corrosion constitutes a very active area of industrial research. In this section, we describe some of the chemical and electrochemical processes responsible for corrosion. We also examine the chemical basis for some common methods for preventing corrosion and treating corroded metals.

> *Corrosion is a REDOX process.*

Under ambient conditions, the oxidation of most metals is thermodynamically spontaneous, with the notable exception of gold and platinum. Hence it is actually somewhat surprising that any metals are useful at all in Earth's moist, oxygen-rich atmosphere. Some metals, however, are resistant to corrosion for kinetic reasons. For example, aluminum in soft-drink cans and airplanes is protected by a thin coating of metal oxide that forms on the surface of the metal and acts as an impenetrable barrier that prevents further destruction. Aluminum cans also have a thin plastic layer to prevent reaction of the oxide with acid in the soft drink. Chromium, magnesium, and nickel also form protective oxide films. Stainless steels are remarkably resistant to corrosion because they usually contain a significant proportion of chromium, nickel, or both.

In contrast to these metals, when iron corrodes, it forms a red-brown hydrated metal oxide ($\mathrm{Fe_2O_3 \cdot xH_2O}$), commonly known as rust, that does not provide a tight protective film (Figure 14.2.5.1). Instead, the rust continually flakes off to expose a fresh metal surface vulnerable to reaction with oxygen and water. Because both oxygen and water are required for rust to form, an iron nail immersed in deoxygenated water will not rust—even over a period of several weeks. Similarly, a nail immersed in an organic solvent such as kerosene or mineral oil will not rust because of the absence of water even if the solvent is saturated with oxygen.

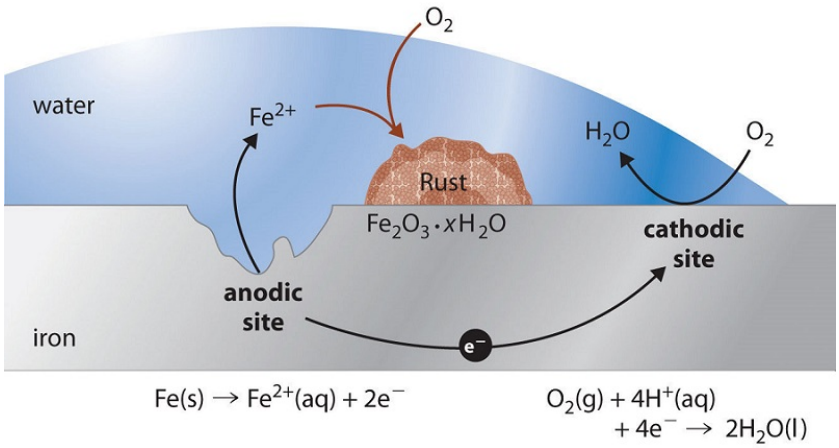


Figure 14.2.5.1: Rust, the Result of Corrosion of Metallic Iron. Iron is oxidized to Fe^{2+}(aq) at an anodic site on the surface of the iron, which is often an impurity or a lattice defect. Oxygen is reduced to water at a different site on the surface of the iron, which acts as the cathode. Electrons are transferred from the anode to the cathode through the electrically conductive metal. Water is a solvent for the Fe^{2+} that is produced initially and acts as a salt bridge. Rust (Fe_2O_3•xH_2O) is formed by the subsequent oxidation of Fe^{2+} by atmospheric oxygen. (CC BY-NC-SA; anonymous)

In the corrosion process, iron metal acts as the anode in a galvanic cell and is oxidized to Fe^{2+}; oxygen is reduced to water at the cathode. The relevant reactions are as follows:

- at cathode:

$$\mathrm{O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(l)}$$

with $E^o_{SRP} = 1.23\ V$.

- at anode:

$$\mathrm{Fe(s) \longrightarrow Fe^{2+}(aq) + 2\,e^-}$$

with $E^o_{SRP} = -0.45\ V$.

- overall:

$$\mathrm{2\,Fe(s) + O_2(g) + 4\,H^+(aq) \longrightarrow 2\,Fe^{2+}(aq) + 2\,H_2O(l)} \qquad (14.2.5.1)$$

with $E^o_{cell} = 1.68\ V$.

The $\mathrm{Fe^{2+}}$ ions produced in the initial reaction are then oxidized by atmospheric oxygen to produce the insoluble hydrated oxide containing $\mathrm{Fe^{3+}}$, as represented in the following equation:

$$\mathrm{4\,Fe^{2+}(aq) + O_2(g) + (2 + 4\,x)H_2O \rightarrow 2\,Fe_2O_3 \cdot xH_2O + 4\,H^+(aq)} \qquad (14.2.5.2)$$

The sign and magnitude of E^o_{cell} for the corrosion process (Equation 14.2.5.1) indicate that there is a strong driving force for the oxidation of iron by O_2 under standard conditions (1 M H^+). Under neutral conditions, the driving force is somewhat less but still appreciable (E = 1.25 V at pH 7.0). Normally, the reaction of atmospheric CO_2 with water to form H^+ and HCO_3^- provides a low enough pH to enhance the reaction rate, as does acid rain. Automobile manufacturers spend a great deal of time and money developing paints that adhere tightly to the car's metal surface to prevent oxygenated water, acid, and salt from coming into contact with the underlying metal. Unfortunately, even the best paint is subject to scratching or denting, and the electrochemical nature of the corrosion process means that two scratches relatively remote from each other can operate together as anode and cathode, leading to sudden mechanical failure (Figure 14.2.5.2).

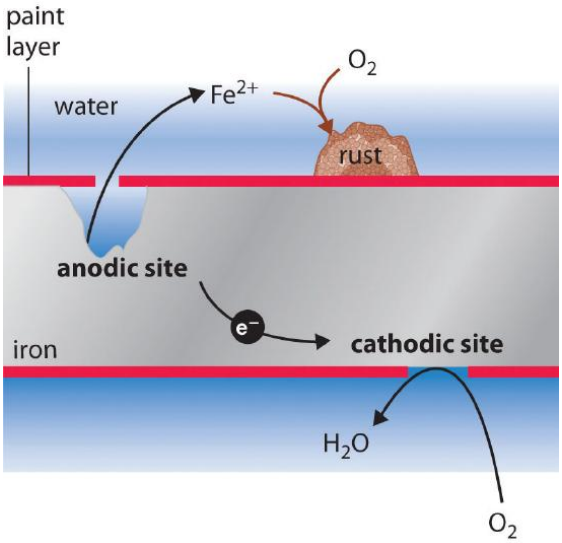


Figure 14.2.5.2: Small Scratches in a Protective Paint Coating Can Lead to the Rapid Corrosion of Iron. Holes in a protective coating allow oxygen to be reduced at the surface with the greater exposure to air (the cathode), while metallic iron is oxidized to Fe^{2+}(aq) at the less exposed site (the anode). Rust is formed when Fe^{2+}(aq) diffuses to a location where it can react with atmospheric oxygen, which is often remote from the anode. The electrochemical interaction between cathodic and anodic sites can cause a large pit to form under a painted surface, eventually resulting in sudden failure with little visible warning that corrosion has occurred.

Prophylactic Protection

One of the most common techniques used to prevent the corrosion of iron is applying a protective coating of another metal that is more difficult to oxidize. Faucets and some external parts of automobiles, for example, are often coated with a thin layer of chromium using an electrolytic process. With the increased use of polymeric materials in cars, however, the use of chrome-plated steel has diminished in recent years. Similarly, the "tin cans" that hold soups and other foods are actually consist of steel container that is coated with a thin layer of tin. While neither chromium nor tin metals are intrinsically resistant to corrosion, they both form protective oxide coatings that hinder access of oxygen and water to the underlying steel (iron alloy).

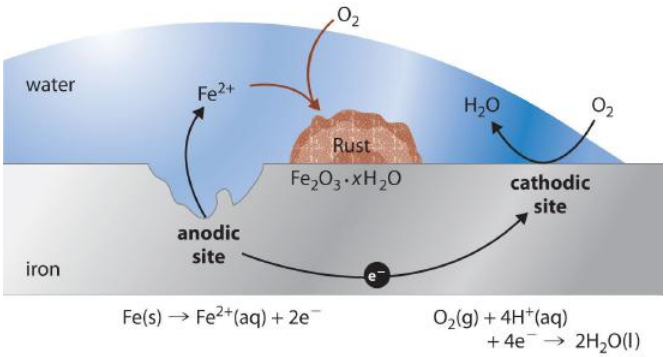


Figure 14.2.5.3: Galvanic Corrosion. If iron is in contact with a more corrosion-resistant metal such as tin, copper, or lead, the other metal can act as a large cathode that greatly increases the rate of reduction of oxygen. Because the reduction of oxygen is coupled to the oxidation of iron, this can result in a dramatic increase in the rate at which iron is oxidized at the anode. Galvanic corrosion is likely to occur whenever two dissimilar metals are connected directly, allowing electrons to be transferred from one to the other.

As with a protective paint, scratching a protective metal coating will allow corrosion to occur. In this case, however, the presence of the second metal can actually increase the rate of corrosion. The values of the standard electrode potentials for Sn^{2+} ($E° = -0.14$ V) and Fe^{2+} ($E° = -0.45$ V) in Table P2 show that Fe is more easily oxidized than Sn. As a result, the more corrosion-resistant metal (in this case, tin) accelerates the corrosion of iron by acting as the cathode and providing a large surface area for the reduction of oxygen (Figure 14.2.5.3). This process is seen in some older homes where copper and iron pipes have been directly connected to each other. The less easily oxidized copper acts as the cathode, causing iron to dissolve rapidly near the connection and occasionally resulting in a catastrophic plumbing failure.

Cathodic Protection

One way to avoid these problems is to use a more easily oxidized metal to protect iron from corrosion. In this approach, called cathodic protection, a more reactive metal such as Zn ($E° = -0.76$ V for $Zn^{2+} + 2\,e^- \longrightarrow Zn$) becomes the anode, and iron becomes the cathode. This prevents oxidation of the iron and protects the iron object from corrosion. The reactions that occur under these conditions are as follows:

$$\underbrace{O_{2(g)} + 4e^- + 4H^+_{(aq)} \rightarrow 2H_2O_{(l)}}_{\text{reduction at cathode}} \tag{14.2.5.3}$$

$$\underbrace{Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-}_{\text{oxidation at anode}} \tag{14.2.5.4}$$

$$\underbrace{2Zn_{(s)} + O_{2(g)} + 4H^+_{(aq)} \rightarrow 2Zn^{2+}_{(aq)} + 2H_2O_{(l)}}_{\text{overall}} \tag{14.2.5.5}$$

The more reactive metal reacts with oxygen and will eventually dissolve, “sacrificing” itself to protect the iron object. Cathodic protection is the principle underlying galvanized steel, which is steel protected by a thin layer of zinc. Galvanized steel is used in objects ranging from nails to garbage cans.



Crystalline surface of a hot-dip galvanized steel surface. This served both as prophylactic protection (protecting the underlying steel from the oxygen in the air) and cathodic protection (once exposed, the zinc will oxidize before the underlying steel).

In a similar strategy, **sacrificial electrodes** using magnesium, for example, are used to protect underground tanks or pipes (Figure 14.2.5.4). Replacing the sacrificial electrodes is more cost-effective than replacing the iron objects they are protecting.

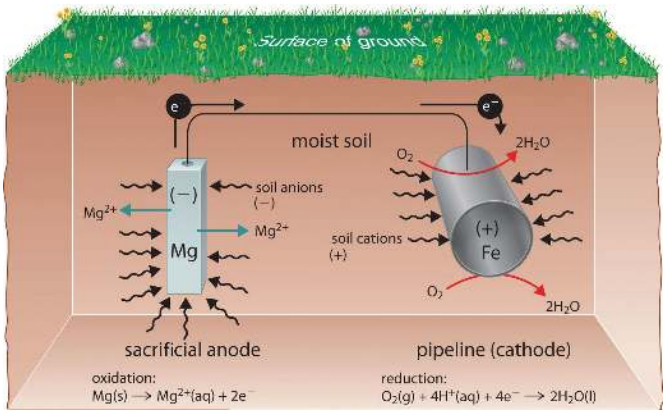


Figure 14.2.5.4: The Use of a Sacrificial Electrode to Protect Against Corrosion. Connecting a magnesium rod to an underground steel pipeline protects the pipeline from corrosion. Because magnesium (E° = −2.37 V) is much more easily oxidized than iron (E° = −0.45 V), the Mg rod acts as the anode in a galvanic cell. The pipeline is therefore forced to act as the cathode at which oxygen is reduced. The soil between the anode and the cathode acts as a salt bridge that completes the electrical circuit and maintains electrical neutrality. As Mg(s) is oxidized to Mg^{2+} at the anode, anions in the soil, such as nitrate, diffuse toward the anode to neutralize the positive charge. Simultaneously, cations in the soil, such as H^+ or NH_4^+, diffuse toward the cathode, where they replenish the protons that are consumed as oxygen is reduced. A similar strategy uses many miles of somewhat less reactive zinc wire to protect the Alaska oil pipeline.

Example 14.2.5.1

Suppose an old wooden sailboat, held together with iron screws, has a bronze propeller (recall that bronze is an alloy of copper containing about 7%–10% tin).

a. If the boat is immersed in seawater, what corrosion reaction will occur? What is $E^{o\,\circ}{}_{cell}$?
b. How could you prevent this corrosion from occurring?

Given: identity of metals

Asked for: corrosion reaction, $E^{o\,\circ}{}_{cell}$, and preventive measures

Strategy:

A. Write the reactions that occur at the anode and the cathode. From these, write the overall cell reaction and calculate $E^{o\,\circ}{}_{cell}$.
B. Based on the relative redox activity of various substances, suggest possible preventive measures.

Solution

a. **A** According to Table P2, both copper and tin are less active metals than iron (i.e., they have higher positive values of $E^{o\,\circ}{}_{cell}$ than iron). Thus if tin or copper is brought into electrical contact by seawater with iron in the presence of oxygen, corrosion will occur. We therefore anticipate that the bronze propeller will act as the cathode at which O_2 is reduced, and the iron screws will act as anodes at which iron dissolves:

$$\begin{aligned}
&\text{cathode:} && \mathrm{O_2(s) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)} && E^\circ_{\text{cathode}} = 1.23\ \text{V}\\
&\text{anode:} && \mathrm{Fe(s) \rightarrow Fe^{2+} + 2e^-} && E^\circ_{\text{anode}} = -0.45\ \text{V}\\
&\text{overall:} && \mathrm{2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l)} && E^\circ_{\text{overall}} = 1.68\ \text{V}
\end{aligned}$$

Over time, the iron screws will dissolve, and the boat will fall apart.

b. **B** Possible ways to prevent corrosion, in order of decreasing cost and inconvenience, are as follows: disassembling the boat and rebuilding it with bronze screws; removing the boat from the water and storing it in a dry place; or attaching an inexpensive piece of zinc metal to the propeller shaft to act as a sacrificial electrode and replacing it once or twice a year. Because zinc is a more active metal than iron, it will act as the sacrificial anode in the electrochemical cell and dissolve (Equation 14.2.5.5).



Zinc sacrificial anode (rounded object screwed to underside of hull) used to prevent corrosion on the screw in a boat via cathodic protection. Image by Rémi Kaupp and used with permission.

? Exercise 14.2.5.1

Suppose the water pipes leading into your house are made of lead, while the rest of the plumbing in your house is iron. To eliminate the possibility of lead poisoning, you call a plumber to replace the lead pipes. He quotes you a very low price if he can use up his existing supply of copper pipe to do the job.

a. Do you accept his proposal?
b. What else should you have the plumber do while at your home?

Answer a

Not unless you plan to sell the house very soon because the $\mathrm{Cu/Fe}$ pipe joints will lead to rapid corrosion.

Answer b

Any existing $\mathrm{Pb/Fe}$ joints should be examined carefully for corrosion of the iron pipes due to the $\mathrm{Pb–Fe}$ junction; the less active Pb will have served as the cathode for the reduction of $\mathrm{O_2}$, promoting oxidation of the more active Fe nearby.

Summary

Corrosion is a galvanic process that can be prevented using cathodic protection. The deterioration of metals through oxidation is a galvanic process called corrosion. Protective coatings consist of a second metal that is more difficult to oxidize than the metal being protected. Alternatively, a more easily oxidized metal can be applied to a metal surface, thus providing cathodic protection of the surface. A thin layer of zinc protects galvanized steel. Sacrificial electrodes can also be attached to an object to protect it.

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14.2.6: A Deeper Look- Electrolysis of Water and Aqueous Solutions

Learning Objectives

- To understand electrolysis and describe it quantitatively.

In this chapter, we have described various galvanic cells in which a spontaneous chemical reaction is used to generate electrical energy. In an electrolytic cell, however, the opposite process, called **electrolysis**, occurs: an external voltage is applied to drive a nonspontaneous reaction. In this section, we look at how electrolytic cells are constructed and explore some of their many commercial applications.

Electrolytic Cells

If we construct an electrochemical cell in which one electrode is copper metal immersed in a 1 M Cu^{2+} solution and the other electrode is cadmium metal immersed in a $1\ M\ Cd^{2+}$ solution and then close the circuit, the potential difference between the two compartments will be 0.74 V. The cadmium electrode will begin to dissolve (Cd is oxidized to Cd^{2+}) and is the anode, while metallic copper will be deposited on the copper electrode (Cu^{2+} is reduced to Cu), which is the cathode (Figure $14.2.6.1a$).

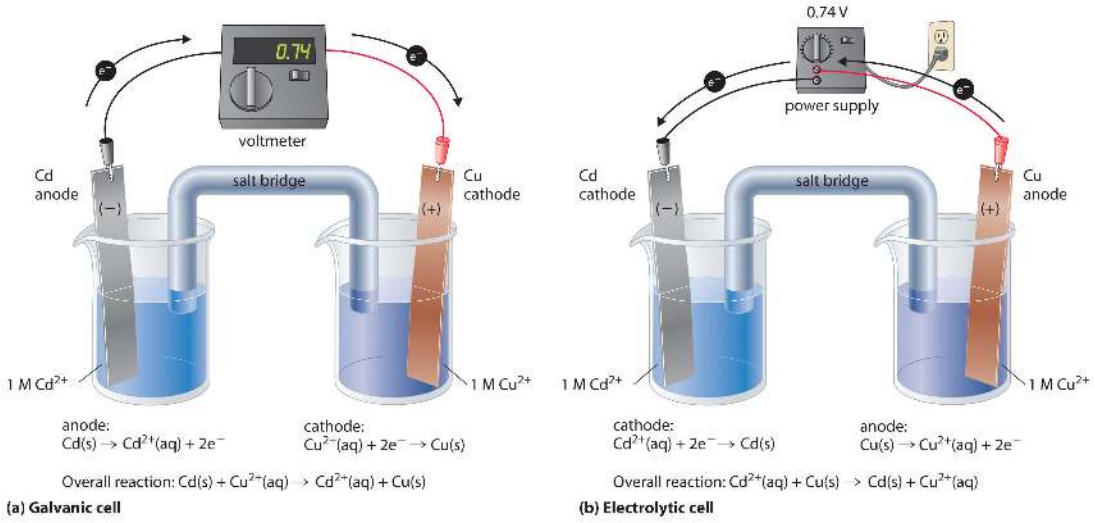


Figure 14.2.6.1: An Applied Voltage Can Reverse the Flow of Electrons in a Galvanic Cd/Cu Cell. (a) When compartments that contain a Cd electrode immersed in 1 M Cd^{2+}(aq) and a Cu electrode immersed in 1 M Cu^{2+}(aq) are connected to create a galvanic cell, Cd(s) is spontaneously oxidized to Cd^{2+}(aq) at the anode, and Cu^{2+}(aq) is spontaneously reduced to Cu(s) at the cathode. The potential of the galvanic cell is 0.74 V. (b) Applying an external potential greater than 0.74 V in the reverse direction forces electrons to flow from the Cu electrode [which is now the anode, at which metallic Cu(s) is oxidized to Cu^{2+}(aq)] and into the Cd electrode [which is now the cathode, at which Cd^{2+}(aq) is reduced to Cd(s)]. The anode in an electrolytic cell is positive because electrons are flowing from it, whereas the cathode is negative because electrons are flowing into it. (CC BY-SA-NC; anonymous)

The overall reaction is as follows:

$$\mathrm{Cd(s) + Cu^{2+}(aq) \rightarrow Cd^{2+}(aq) + Cu(s)}$$

with $E^{\circ}_{cell} = 0.74\ V$

This reaction is thermodynamically spontaneous as written ($\Delta G^{o} < 0$):

$$\begin{aligned}\Delta G^{\circ} &= -nFE^{\circ}_{\text{cell}} \\ &= -(2\ \text{mol e}^{-})[96,485\ \text{J}/(\text{V}\cdot\text{mol})](0.74\ \text{V}) \\ &= -140\ \text{kJ (per mole Cd)}\end{aligned}$$

In this direction, the system is acting as a galvanic cell.

> *In an electrolytic cell, an external voltage is applied to drive a nonspontaneous reaction.*

The reverse reaction, the reduction of Cd^{2+} by Cu, is thermodynamically nonspontaneous and will occur only with an input of 140 kJ. We can force the reaction to proceed in the reverse direction by applying an electrical potential greater than 0.74 V from an external power supply. The applied voltage forces electrons through the circuit in the reverse direction, converting a galvanic cell to an electrolytic cell. Thus the copper electrode is now the anode (Cu is oxidized), and the cadmium electrode is now the cathode (Cd^{2+} is reduced) (Figure 14.2.6.1*b*). The signs of the cathode and the anode have switched to reflect the flow of electrons in the circuit. The half-reactions that occur at the cathode and the anode are as follows:

- half-reaction at the cathode:

$$\mathrm{Cd^{2+}(aq) + 2\,e^- \rightarrow Cd(s)} \tag{14.2.6.1}$$

with $E^\circ_{cathode} = -0.40\,V$

- half-reaction at the anode:

$$\mathrm{Cu(s) \rightarrow Cu^{2+}(aq) + 2\,e^-} \tag{14.2.6.2}$$

with $E^\circ_{anode} = 0.34\,V$

- Overall Reaction:

$$\mathrm{Cd^{2+}(aq) + Cu(s) \rightarrow Cd(s) + Cu^{2+}(aq)} \tag{14.2.6.3}$$

with $E^\circ_{cell} = -0.74\,V$

Because $E^\circ_{cell} < 0$, the overall reaction—the reduction of Cd^{2+} by Cu—clearly **cannot** occur spontaneously and proceeds only when sufficient electrical energy is applied. The differences between galvanic and electrolytic cells are summarized in Table 14.2.6.1.

Table 14.2.6.1: Comparison of Galvanic and Electrolytic Cells

Property	Galvanic Cell	Electrolytic Cell
ΔG	< 0	> 0
E_{cell}	> 0	< 0
Electrode Process		
anode	oxidation	oxidation
cathode	reduction	reduction
Sign of Electrode		
anode	−	+
cathode	+	−

Electrolytic Reactions

At sufficiently high temperatures, ionic solids melt to form liquids that conduct electricity extremely well due to the high concentrations of ions. If two inert electrodes are inserted into molten NaCl, for example, and an electrical potential is applied, Cl^- is oxidized at the anode, and Na^+ is reduced at the cathode. The overall reaction is as follows:

$$\mathrm{2\,NaCl(l) \rightarrow 2\,Na(l) + Cl_2(g)} \tag{14.2.6.4}$$

This is the reverse of the formation of NaCl from its elements. The product of the reduction reaction is liquid sodium because the melting point of sodium metal is 97.8°C, well below that of NaCl (801°C). Approximately 20,000 tons of sodium metal are produced commercially in the United States each year by the electrolysis of molten NaCl in a Downs cell (Figure 14.2.6.2). In this specialized cell, $CaCl_2$ (melting point = 772°C) is first added to the NaCl to lower the melting point of the mixture to about 600°C, thereby lowering operating costs.

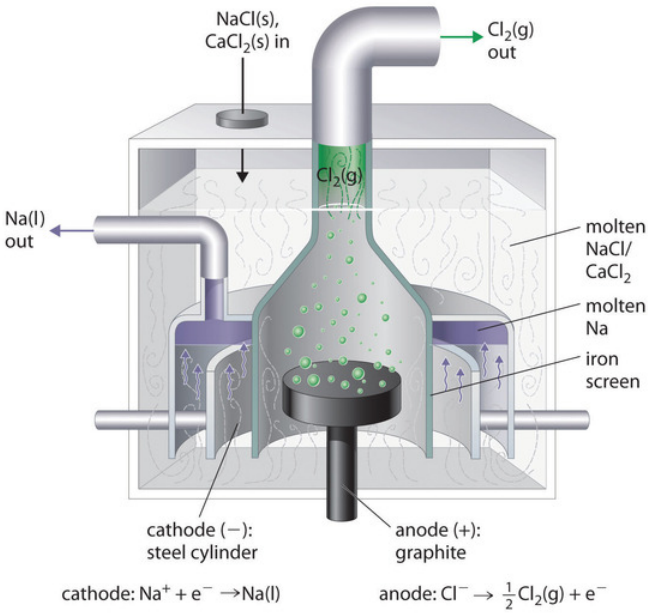


Figure 14.2.6.2: A Downs Cell for the Electrolysis of Molten NaCl. The electrolysis of a molten mixture of NaCl and $CaCl_2$ results in the formation of elemental sodium and chlorine gas. Because sodium is a liquid under these conditions and liquid sodium is less dense than molten sodium chloride, the sodium floats to the top of the melt and is collected in concentric capped iron cylinders surrounding the cathode. Gaseous chlorine collects in the inverted cone over the anode. An iron screen separating the cathode and anode compartments ensures that the molten sodium and gaseous chlorine do not come into contact. (CC BY-SA-NC; anonymous)

Similarly, in the Hall–Heroult process used to produce aluminum commercially, a molten mixture of about 5% aluminum oxide (Al_2O_3; melting point = 2054°C) and 95% cryolite (Na_3AlF_6; melting point = 1012°C) is electrolyzed at about 1000°C, producing molten aluminum at the cathode and CO_2 gas at the carbon anode. The overall reaction is as follows:

$$2\,Al_2O_3(l) + 3\,C(s) \longrightarrow 4\,Al(l) + 3\,CO_2(g) \tag{14.2.6.5}$$

Oxide ions react with oxidized carbon at the anode, producing $CO_2(g)$.

There are two important points to make about these two commercial processes and about the electrolysis of molten salts in general.

1. The electrode potentials for molten salts are likely to be very different from the standard cell potentials listed in Table P2, which are compiled for the reduction of the hydrated ions in aqueous solutions under standard conditions.
2. Using a mixed salt system means there is a possibility of competition between different electrolytic reactions. When a mixture of NaCl and $CaCl_2$ is electrolyzed, Cl^- is oxidized because it is the only anion present, but either Na^+ or Ca^{2+} can be reduced. Conversely, in the Hall–Heroult process, only one cation is present that can be reduced (Al^{3+}), but there are three species that can be oxidized: C, O^{2-}, and F^-.

In the Hall–Heroult process, C is oxidized instead of O^{2-} or F^- because oxygen and fluorine are more electronegative than carbon, which means that C is a weaker oxidant than either O_2 or F_2. Similarly, in the Downs cell, we might expect electrolysis of a NaCl/$CaCl_2$ mixture to produce calcium rather than sodium because Na is slightly less electronegative than Ca (χ = 0.93 versus 1.00, respectively), making Na easier to oxidize and, conversely, Na^+ more difficult to reduce. In fact, the reduction of Na^+ to Na is the observed reaction. In cases where the electronegativities of two species are similar, other factors, such as the formation of complex ions, become important and may determine the outcome.

Example 14.2.6.1

If a molten mixture of $MgCl_2$ and KBr is electrolyzed, what products will form at the cathode and the anode, respectively?

Given: identity of salts

Asked for: electrolysis products

Strategy:

A. List all the possible reduction and oxidation products. Based on the electronegativity values shown in Figure 7.5, determine which species will be reduced and which species will be oxidized.
B. Identify the products that will form at each electrode.

Solution

A The possible reduction products are Mg and K, and the possible oxidation products are Cl_2 and Br_2. Because Mg is more electronegative than K (χ = 1.31 versus 0.82), it is likely that Mg will be reduced rather than K. Because Cl is more electronegative than Br (3.16 versus 2.96), Cl_2 is a stronger oxidant than Br_2.

B Electrolysis will therefore produce Br_2 at the anode and Mg at the cathode.

? Exercise 14.2.6.1

Predict the products if a molten mixture of $AlBr_3$ and LiF is electrolyzed.

Answer

Br_2 and Al

Electrolysis can also be used to drive the thermodynamically nonspontaneous decomposition of water into its constituent elements: H_2 and O_2. However, because pure water is a very poor electrical conductor, a small amount of an ionic solute (such as H_2SO_4 or Na_2SO_4) must first be added to increase its electrical conductivity. Inserting inert electrodes into the solution and applying a voltage between them will result in the rapid evolution of bubbles of H_2 and O_2 (Figure 14.2.6.3).

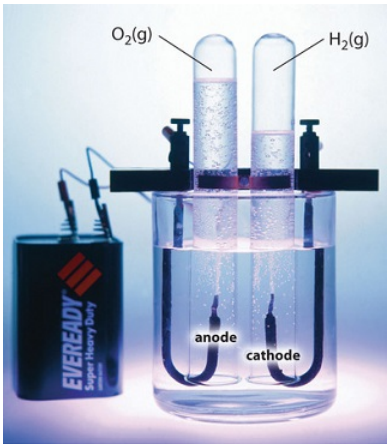


Figure 14.2.6.3: The Electrolysis of Water. Applying an external potential of about 1.7–1.9 V to two inert electrodes immersed in an aqueous solution of an electrolyte such as H_2SO_4 or Na_2SO_4 drives the thermodynamically nonspontaneous decomposition of water into H_2 at the cathode and O_2 at the anode. (CC BY-SA-NC; anonymous)

The reactions that occur are as follows:

- cathode:

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} \qquad E^\circ_{cathode} = 0V \tag{14.2.6.6}$$

- anode:

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^- \qquad E^\circ_{anode} = 1.23\ V \tag{14.2.6.7}$$

- overall:

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 2H_{2(g)} \qquad E^\circ_{cell} = -1.23\ V \tag{14.2.6.8}$$

For a system that contains an electrolyte such as Na_2SO_4, which has a negligible effect on the ionization equilibrium of liquid water, the pH of the solution will be 7.00 and $[H^+] = [OH^-] = 1.0 \times 10^{-7}$. Assuming that $P_{O_2} = P_{H_2} = 1$ atm, we can use the standard potentials to calculate E for the overall reaction:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right)\log(P_{O_2}P^2_{H_2}) \tag{14.2.6.9}$$

$$= -1.23\ \text{V} - \left(\frac{0.0591\ \text{V}}{4}\right)\log(1) = -1.23\ \text{V} \tag{14.2.6.10}$$

Thus E_{cell} is −1.23 V, which is the value of $E°_{cell}$ if the reaction is carried out in the presence of 1 M H^+ rather than at pH 7.0.

In practice, a voltage about 0.4–0.6 V greater than the calculated value is needed to electrolyze water. This added voltage, called an **overvoltage**, represents the additional driving force required to overcome barriers such as the large activation energy for the formation of a gas at a metal surface. Overvoltages are needed in all electrolytic processes, which explain why, for example, approximately 14 V must be applied to recharge the 12 V battery in your car.

In general, any metal that does not react readily with water to produce hydrogen can be produced by the electrolytic reduction of an aqueous solution that contains the metal cation. The p-block metals and most of the transition metals are in this category, but metals in high oxidation states, which form oxoanions, cannot be reduced to the metal by simple electrolysis. Active metals, such as aluminum and those of groups 1 and 2, react so readily with water that they can be prepared only by the electrolysis of molten salts. Similarly, any nonmetallic element that does not readily oxidize water to O_2 can be prepared by the electrolytic oxidation of an aqueous solution that contains an appropriate anion. In practice, among the nonmetals, only F_2 cannot be prepared using this method. Oxoanions of nonmetals in their highest oxidation states, such as NO_3^-, SO_4^{2-}, PO_4^{3-}, are usually difficult to reduce electrochemically and usually behave like spectator ions that remain in solution during electrolysis.

> *In general, any metal that does not react readily with water to produce hydrogen can be produced by the electrolytic reduction of an aqueous solution that contains the metal cation.*

Electroplating

In a process called **electroplating**, a layer of a second metal is deposited on the metal electrode that acts as the cathode during electrolysis. Electroplating is used to enhance the appearance of metal objects and protect them from corrosion. Examples of electroplating include the chromium layer found on many bathroom fixtures or (in earlier days) on the bumpers and hubcaps of cars, as well as the thin layer of precious metal that coats silver-plated dinnerware or jewelry. In all cases, the basic concept is the same. A schematic view of an apparatus for electroplating silverware and a photograph of a commercial electroplating cell are shown in Figure 14.2.6.4

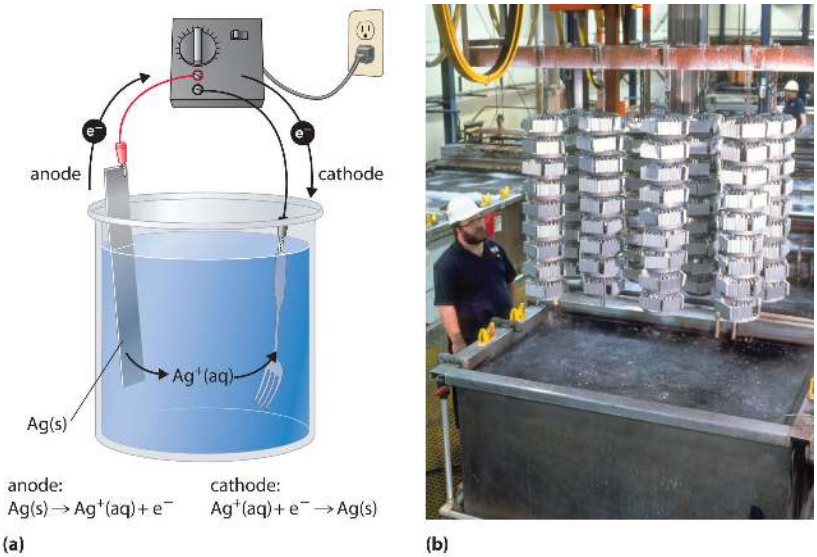


Figure 14.2.6.3: Electroplating. (a) Electroplating uses an electrolytic cell in which the object to be plated, such as a fork, is immersed in a solution of the metal to be deposited. The object being plated acts as the cathode, on which the desired metal is deposited in a thin layer, while the anode usually consists of the metal that is being deposited (in this case, silver) that maintains the solution concentration as it dissolves. (b) In this commercial electroplating apparatus, a large number of objects can be plated simultaneously by lowering the rack into the Ag^+ solution and applying the correct potential. (CC BY-SA-NC; anonymous)

The half-reactions in electroplating a fork, for example, with silver are as follows:

- cathode (fork):

$$\mathrm{Ag^+(aq) + e^- \longrightarrow Ag(s)} \qquad E^\circ_{cathode} = 0.80V$$

- anode (silver bar):

$$\mathrm{Ag(s) \longrightarrow Ag^+(aq) + e^-} \qquad E^\circ_{anode} = 0.80V$$

The overall reaction is the transfer of silver metal from one electrode (a silver bar acting as the anode) to another (a fork acting as the cathode). Because $E^o_{cell} = 0\,V$, it takes only a small applied voltage to drive the electroplating process. In practice, various other substances may be added to the plating solution to control its electrical conductivity and regulate the concentration of free metal ions, thus ensuring a smooth, even coating.

Quantitative Considerations

If we know the stoichiometry of an electrolysis reaction, the amount of current passed, and the length of time, we can calculate the amount of material consumed or produced in a reaction. Conversely, we can use stoichiometry to determine the combination of current and time needed to produce a given amount of material.

The quantity of material that is oxidized or reduced at an electrode during an electrochemical reaction is determined by the stoichiometry of the reaction and the amount of charge that is transferred. For example, in the reaction

$$\mathrm{Ag^+(aq) + e^- \rightarrow Ag(s)}$$

1 mol of electrons reduces 1 mol of $\mathrm{Ag^+}$ to Ag metal. In contrast, in the reaction

$$\mathrm{Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)}$$

1 mol of electrons reduces only 0.5 mol of $\mathrm{Cu^{2+}}$ to Cu metal. Recall that the charge on 1 mol of electrons is 1 faraday (1 F), which is equal to 96,485 C. We can therefore calculate the number of moles of electrons transferred when a known current is passed through a cell for a given period of time. The total charge (q in coulombs) transferred is the product of the current (I in amperes) and the time (t, in seconds):

$$q = I \times t \tag{14.2.6.11}$$

The stoichiometry of the reaction and the total charge transferred enable us to calculate the amount of product formed during an electrolysis reaction or the amount of metal deposited in an electroplating process.

For example, if a current of 0.60 A passes through an aqueous solution of $\mathrm{CuSO_4}$ for 6.0 min, the total number of coulombs of charge that passes through the cell is as follows:

$$\begin{aligned} q &= (0.60\text{ A})(6.0\text{ min})(60\text{ s/min}) \\ &= 220\text{ A}\cdot\text{s} \\ &= 220\text{ C} \end{aligned}$$

The number of moles of electrons transferred to $\mathrm{Cu^{2+}}$ is therefore

$$\begin{aligned} \text{moles e}^- &= \frac{220\text{ C}}{96{,}485\text{ C/mol}} \\ &= 2.3 \times 10^{-3}\text{ mol e}^- \end{aligned}$$

Because two electrons are required to reduce a single Cu^{2+} ion, the total number of moles of Cu produced is half the number of moles of electrons transferred, or 1.2 × 10^{-3} mol. This corresponds to 76 mg of Cu. In commercial electrorefining processes, much higher currents (greater than or equal to 50,000 A) are used, corresponding to approximately 0.5 F/s, and reaction times are on the order of 3–4 weeks.

Example 14.2.6.2

A silver-plated spoon typically contains about 2.00 g of Ag. If 12.0 h are required to achieve the desired thickness of the Ag coating, what is the average current per spoon that must flow during the electroplating process, assuming an efficiency of 100%?

Given: mass of metal, time, and efficiency

Asked for: current required

Strategy:

A. Calculate the number of moles of metal corresponding to the given mass transferred.
B. Write the reaction and determine the number of moles of electrons required for the electroplating process.
C. Use the definition of the faraday to calculate the number of coulombs required. Then convert coulombs to current in amperes.

Solution

A We must first determine the number of moles of Ag corresponding to 2.00 g of Ag:

$$\text{moles Ag} = \frac{2.00\ \text{g}}{107.868\ \text{g/mol}} = 1.85 \times 10^{-2}\ \text{mol Ag}$$

B The reduction reaction is $Ag^+(aq) + e^- \rightarrow Ag(s)$, so 1 mol of electrons produces 1 mol of silver.

C Using the definition of the faraday,

$$\text{coulombs} = (1.85 \times 10^{-2}\text{mol e}^-)(96{,}485\ \text{C/mol e}^-) = 1.78 \times 10^3\ \text{C / mole}$$

The current in amperes needed to deliver this amount of charge in 12.0 h is therefore

$$\begin{aligned}\text{amperes} &= \frac{1.78 \times 10^3\ \text{C}}{(12.0\ \text{h})(60\ \text{min/h})(60\ \text{s/min})} \\ &= 4.12 \times 10^{-2}\ \text{C/s} = 4.12 \times 10^{-2}\ \text{A}\end{aligned}$$

Because the electroplating process is usually much less than 100% efficient (typical values are closer to 30%), the actual current necessary is greater than 0.1 A.

Exercise 14.2.6.2

A typical aluminum soft-drink can weighs about 29 g. How much time is needed to produce this amount of Al(s) in the Hall–Heroult process, using a current of 15 A to reduce a molten Al_2O_3/Na_3AlF_6 mixture?

Answer

5.8 h



Electroplating: Electroplating(opens in new window) [youtu.be]

Summary

In electrolysis, an external voltage is applied to drive a **nonspontaneous** reaction. The quantity of material oxidized or reduced can be calculated from the stoichiometry of the reaction and the amount of charge transferred. Relationship of charge, current and time:

$$q = I \times t$$

In electrolysis, an external voltage is applied to drive a nonspontaneous reaction. Electrolysis can also be used to produce H_2 and O_2 from water. In practice, an additional voltage, called an overvoltage, must be applied to overcome factors such as a large activation energy and a junction potential. Electroplating is the process by which a second metal is deposited on a metal surface, thereby enhancing an object's appearance or providing protection from corrosion. The amount of material consumed or produced in a reaction can be calculated from the stoichiometry of an electrolysis reaction, the amount of current passed, and the duration of the electrolytic reaction.

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SECTION OVERVIEW

14.3: Solubility and Precipitation Equilibria

An General Chemistry Libretexts Textmap organized around the textbook

Principles of Modern Chemistry

by Oxtoby, Gillis, and Campion

I II III IV V VI VII VIII IX X XI XII XIII XIV XV XVI
XVII XVIII XIX XX XXI XXII XXIII • **Homework Exercises**

Template:HideTOC

Solubility equilibrium is a type of dynamic equilibrium. It exists when a chemical compound in the solid state is in chemical equilibrium with a solution of that compound. The solid may dissolve unchanged, with dissociation or with chemical reaction with another constituent of the solvent, such as acid or alkali. Each type of equilibrium is characterized by a temperature-dependent equilibrium constant. Solubility equilibria are important in pharmaceutical, environmental and many other scenarios.

14.3.1: The Nature of Solubility Equilibria

14.3.2: Ionic Equilibria between Solids and Solutions

14.3.3: Precipitation and the Solubility Product

14.3.4: The Effects of pH on Solubility

14.3.5: Complex Ions and Solubility

14.3.6: A Deeper Look- Selective Precipitation of Ions

14.3.E: Solubility and Precipitation (Exercises)

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14.3.1: The Nature of Solubility Equilibria

Learning Objectives

- Understand the qualitative nature of dissolving a salt in water

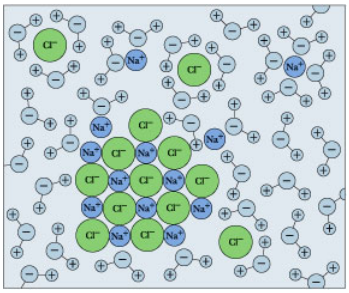
Dissolution of a salt in water is a chemical process that is governed by the same laws of chemical equilibrium that apply to any other reaction. There are, however, a number of special aspects of of these equilibria that set them somewhat apart from the more general ones that are covered in the lesson set devoted specifically to chemical equilibrium. These include such topics as the common ion effect, the influence of pH on solubility, supersaturation, and some special characteristics of particularly important solubility systems... all explained in what follows.

The Dissolution of Salts in Water

Drop some ordinary table salt into a glass of water, and watch it "disappear". We refer to this as *dissolution*, and we explain it as a process in which the sodium and chlorine units break away from the crystal surface, get surrounded by H_2O molecules, and become *hydrated ions*.

$$\mathrm{NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)}$$

The designation *(aq)* means "aqueous" and comes from *aqua*, the Latin word for water. It is used whenever we want to emphasize that the ions are hydrated — that H_2O molecules are attached to them.



Remember that solubility equilibrium and the calculations that relate to it are only meaningful when *both* sides (solids and dissolved ions) are simultaneously present. But if you keep adding salt, there will come a point at which it no longer seems to dissolve. If this condition persists, we say that the salt has reached its *solubility limit*, and the solution is *saturated* in NaCl. The situation is now described by

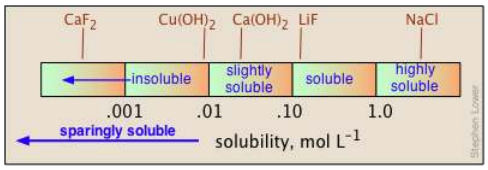
$$\mathrm{NaCl(s) \rightleftharpoons Na^+(aq) + Cl^-(aq)}$$

in which the solid and its ions are *in equilibrium*.

Salt solutions that have reached or exceeded their solubility limits (usually 36-39 g per 100 mL of water) are responsible for prominent features of the earth's geochemistry. They typically form when NaCl leaches from soils into waters that flow into salt lakes in arid regions that have no natural outlets; subsequent evaporation of these brines force the above equilibrium to the left, forming natural salt deposits. These are often admixed with other salts, but in some cases are almost pure NaCl. Many parts of the world contain buried deposits of NaCl (known as halite) that formed from the evaporation of ancient seas, and which are now mined.

Expressing solubilities

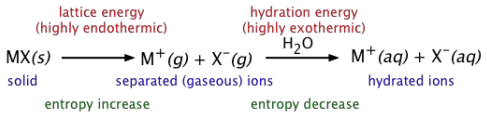
Solubilities are most fundamentally expressed in molar (mol L^{-1} of solution) or molal (mol kg^{-1} of water) units. But for practical use in preparing stock solutions, chemistry handbooks usually express solubilities in terms of grams-per-100 ml of water at a given temperature, frequently noting the latter in a superscript. Thus 6.9^{20} means 6.9 g of solute will dissolve in 100 mL of water at 20° C.



When quantitative data are lacking, the designations "soluble", "insoluble", "slightly soluble", and "highly soluble" are used. There is no agreed-on standard for these classifications, but a useful guideline might be that shown below.

What determines solubility?

The solubilities of salts in water span a remarkably large range of values, from almost completely insoluble to highly soluble. Moreover, there is no simple way of predicting these values, or even of explaining the trends that are observed for the solubilities of different anions within a given group of the periodic table.



Ultimately, the driving force for dissolution (and for *all* chemical processes) is determined by the Gibbs free energy change. Dissolution of a salt is conceptually understood as a sequence of the two processes depicted above:

1. breakup of the ionic lattice of the solid (i.e., lattice energy)
2. followed by attachment of water molecules to the released ions (Solvation or Hydration Energy).

The first step consumes a large quantity of energy, something that by itself would strongly discourage solubility. But the second step *releases* a large amount of energy and thus has the opposite effect. Thus the net energy change depends on the sum of two large energy terms (often approaching 1000 kJ/mol) having opposite signs. Each of these terms will to some extent be influenced by the size, charge, and polarizability of the particular ions involved, and on the lattice structure of the solid. This large number of variables makes it impossible to predict the solubility of a given salt.

Nevertheless, there are some clear trends for how the solubilities of a series of salts of a given anion (such as hydroxides, sulfates, etc.) change with a periodic table group. And of course, there are a number of general *solubility rules*.

Solubility Rules

1. Salts containing Group I elements are soluble (Li^+, Na^+, K^+, Cs^+, Rb^+). Exceptions to this rule are rare. Salts containing the ammonium ion (NH_4^+) are also soluble.
2. Salts containing nitrate ion (NO_3^-) are generally soluble.
3. Salts containing Cl^-, Br^-, I^- are generally soluble. Important exceptions to this rule are halide salts of Ag^+, Pb^{2+}, and $(Hg_2)^{2+}$. Thus, AgCl, $PbBr_2$, and Hg_2Cl_2 are all insoluble.
4. Most silver salts are insoluble. $AgNO_3$ and $Ag(C_2H_3O_2)$ are common soluble salts of silver; virtually anything else is insoluble.
5. Most sulfate salts are soluble. Important exceptions to this rule include $BaSO_4$, $PbSO_4$, Ag_2SO_4 and $SrSO_4$.
6. Most hydroxide salts are only slightly soluble. Hydroxide salts of Group I elements are soluble. Hydroxide salts of Group II elements (Ca, Sr, and Ba) are slightly soluble. Hydroxide salts of transition metals and Al^{3+} are insoluble. Thus, $Fe(OH)_3$, $Al(OH)_3$, $Co(OH)_2$ are not soluble.
7. Most sulfides of transition metals are highly insoluble. Thus, CdS, FeS, ZnS, Ag_2S are all insoluble. Arsenic, antimony, bismuth, and lead sulfides are also insoluble.
8. Carbonates are frequently insoluble. Group II carbonates (Ca, Sr, and Ba) are insoluble. Some other insoluble carbonates include $FeCO_3$ and $PbCO_3$.
9. Chromates are frequently insoluble. Examples: $PbCrO_4$, $BaCrO_4$
10. Phosphates are frequently insoluble. Examples: $Ca_3(PO_4)_2$, Ag_3PO_4
11. Fluorides are frequently insoluble. Examples: BaF_2, MgF_2 PbF_2.

A solution must be saturated to be in equilibrium with the solid. This is a *necessary* condition for solubility equilibrium, but it is not by itself *sufficient*. True chemical equilibrium can only occur when all components are simultaneously present. A solubility

system can be in equilibrium only when some of the solid is in contact with a saturated solution of its ions. Failure to appreciate this is a very common cause of errors in solving solubility problems.

Undersaturated and supersaturated solutions

If the ion product is smaller than the solubility product, the system is not in equilibrium and no solid can be present. Such a solution is said to be *undersaturated*. A *supersaturated* solution is one in which the ion product exceeds the solubility product. A supersaturated solution is not at equilibrium, and no solid can ordinarily be present in such a solution. If some of the solid is added, the excess ions precipitate out and until solubility equilibrium is achieved.

Solubility and Temperature

Solubility usually increases with temperature - but not always. This is very apparent from the solubility-vs.-temperature plots shown in Figure 14.3.1.1. (Some of the plots are colored differently in order to make it easier to distinguish them where they crowd together.) The temperature dependence of any process depends on its entropy change — that is, on the degree to which thermal kinetic energy can spread throughout the system. When a solid dissolves, its component molecules or ions diffuse into the much greater volume of the solution, carrying their thermal energy along with them. So we would normally expect the entropy to increase — something that makes any process take place to a greater extent at a higher temperature.

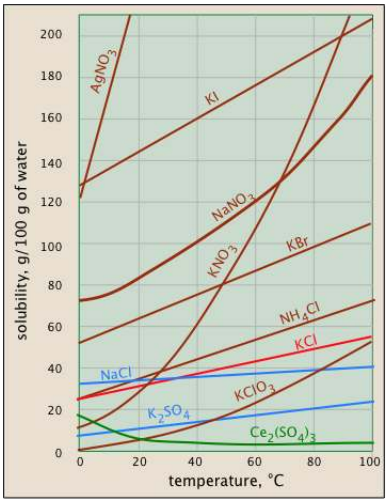


Figure 14.3.1.1: Solubility of select salts in water as a function of temperature.

So why does the solubility of cerium sulfate (green plot) diminish with temperature? Dispersal of the Ce^{3+} and SO_4^{2-} ions themselves is still associated with an entropy increase, but in this case the entropy of the *water*decreases even more owing to the ordering of the H_2O molecules that attach to the Ce^{3+} ions as they become hydrated. It's difficult to predict these effects, or explain why they occur in individual cases — but they do happen.

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14.3.2: Ionic Equilibria between Solids and Solutions

Learning Objectives

- To calculate the solubility of an ionic compound from its K_{sp}

We begin our discussion of solubility and complexation equilibria—those associated with the formation of complex ions—by developing quantitative methods for describing dissolution and precipitation reactions of ionic compounds in aqueous solution. Just as with acid–base equilibria, we can describe the concentrations of ions in equilibrium with an ionic solid using an equilibrium constant expression.

The Solubility Product

When a slightly soluble ionic compound is added to water, some of it dissolves to form a solution, establishing an equilibrium between the pure solid and a solution of its ions. For the dissolution of calcium phosphate, one of the two main components of kidney stones, the equilibrium can be written as follows, with the solid salt on the left:

$$Ca_3(PO_4)_{2(s)} \rightleftharpoons 3Ca^{2+}_{(aq)} + 2PO^{3-}_{4(aq)} \tag{14.3.2.1}$$

As you will discover in more advanced chemistry courses, basic anions, such as S^{2-}, PO_4^{3-}, and CO_3^{2-}, react with water to produce OH^- and the corresponding protonated anion. Consequently, their calculated molarities, assuming no protonation in aqueous solution, are only approximate.

The equilibrium constant for the dissolution of a sparingly soluble salt is the **solubility product (K_{sp})** of the salt. Because the concentration of a pure solid such as $Ca_3(PO_4)_2$ is a constant, it does not appear explicitly in the equilibrium constant expression. The equilibrium constant expression for the dissolution of calcium phosphate is therefore

$$K = \frac{[\mathrm{Ca^{2+}}]^3[\mathrm{PO_4^{3-}}]^2}{[\mathrm{Ca_3(PO_4)_2}]} \tag{14.3.2.2}$$

$$[\mathrm{Ca_3(PO_4)_2}]K = K_{sp} = [\mathrm{Ca^{2+}}]^3[\mathrm{PO_4^{3-}}]^2 \tag{14.3.2.3}$$

At 25°C and pH 7.00, Ksp for calcium phosphate is 2.07×10^{-33}, indicating that the concentrations of Ca^{2+} and PO_4^{3-} ions in solution that are in equilibrium with solid calcium phosphate are very low. The values of K_{sp} for some common salts are listed in Table 14.3.2.1, which shows that the magnitude of K_{sp} varies dramatically for different compounds. Although K_{sp} is not a function of pH in Equations 14.3.2.2 and 14.3.2.3, changes in pH can affect the solubility of a compound as discussed later.

> *As with K, the concentration of a pure solid does not appear explicitly in K_{sp}.*

Table 14.3.2.1: Solubility Products for Selected Ionic Substances at 25°C

Solid	Color	Ksp	Solid	Color	Ksp
Acetates			**Iodides**		
$Ca(O_2CCH_3)_2·3H_2O$	white	4×10^{-3}	Hg_2I_2*	yellow	5.2×10^{-29}
Bromides			PbI_2	yellow	9.8×10^{-9}
AgBr	off-white	5.35×10^{-13}	**Oxalates**		
Hg_2Br_2*	yellow	6.40×10^{-23}	$Ag_2C_2O_4$	white	5.40×10^{-12}
Carbonates			$MgC_2O_4·2H_2O$	white	4.83×10^{-6}
$CaCO_3$	white	3.36×10^{-9}	PbC_2O_4	white	4.8×10^{-10}
$PbCO_3$	white	7.40×10^{-14}	**Phosphates**		

*These contain the Hg_2^{2+} ion.

Solid	Color	Ksp	Solid	Color	Ksp
Chlorides			Ag_3PO_4	white	8.89×10^{-17}
AgCl	white	1.77×10^{-10}	$Sr_3(PO_4)_2$	white	4.0×10^{-28}
Hg_2Cl_2*	white	1.43×10^{-18}	$FePO_4 \cdot 2H_2O$	pink	9.91×10^{-16}
$PbCl_2$	white	1.70×10^{-5}	**Sulfates**		
Chromates			Ag_2SO_4	white	1.20×10^{-5}
$CaCrO_4$	yellow	7.1×10^{-4}	$BaSO_4$	white	1.08×10^{-10}
$PbCrO_4$	yellow	2.8×10^{-13}	$PbSO_4$	white	2.53×10^{-8}
Fluorides			**Sulfides**		
BaF_2	white	1.84×10^{-7}	Ag_2S	black	6.3×10^{-50}
PbF_2	white	3.3×10^{-8}	CdS	yellow	8.0×10^{-27}
Hydroxides			PbS	black	8.0×10^{-28}
$Ca(OH)_2$	white	5.02×10^{-6}	ZnS	white	1.6×10^{-24}
$Cu(OH)_2$	pale blue	1×10^{-14}			
$Mn(OH)_2$	light pink	1.9×10^{-13}			
$Cr(OH)_3$	gray-green	6.3×10^{-31}			
$Fe(OH)_3$	rust red	2.79×10^{-39}			

*These contain the Hg_2^{2+} ion.

Solubility products are determined experimentally by directly measuring either the concentration of one of the component ions or the solubility of the compound in a given amount of water. However, whereas solubility is usually expressed in terms of mass of solute per 100 mL of solvent, K_{sp}, like K, is defined in terms of the molar concentrations of the component ions.



A color photograph of a kidney stone, 8 mm in length. Kidney stones form from sparingly soluble calcium salts and are largely composed of $Ca(O_2CCO_2) \cdot H_2O$ and $Ca_3(PO_4)_2$. from Wikipedia.

Example 14.3.2.1: Kidney Stones

Calcium oxalate monohydrate [$Ca(O_2CCO_2) \cdot H_2O$, also written as $CaC_2O_4 \cdot H_2O$] is a sparingly soluble salt that is the other major component of kidney stones [along with $Ca_3(PO_4)_2$]. Its solubility in water at 25°C is 7.36×10^{-4} g/100 mL. Calculate its K_{sp}.

Given: solubility in g/100 mL

Asked for: K_{sp}

Strategy:

A. Write the balanced dissolution equilibrium and the corresponding solubility product expression.
B. Convert the solubility of the salt to moles per liter. From the balanced dissolution equilibrium, determine the equilibrium concentrations of the dissolved solute ions. Substitute these values into the solubility product expression to calculate K_{sp}.

Solution

A We need to write the solubility product expression in terms of the concentrations of the component ions. For calcium oxalate monohydrate, the balanced dissolution equilibrium and the solubility product expression (abbreviating oxalate as ox^{2-}) are as follows:

$$\mathrm{Ca(O_2CCO_2)\cdot H_2O(s) \rightleftharpoons Ca^{2+}(aq) + {^-O_2CCO_2^-}(aq) + H_2O(l)} \quad K_{sp} = [\mathrm{Ca^{2+}}][\mathrm{ox^{2-}}]$$

Neither solid calcium oxalate monohydrate nor water appears in the solubility product expression because their concentrations are essentially constant.

B Next we need to determine [Ca^{2+}] and [ox^{2-}] at equilibrium. We can use the mass of calcium oxalate monohydrate that dissolves in 100 mL of water to calculate the number of moles that dissolve in 100 mL of water. From this we can determine the number of moles that dissolve in 1.00 L of water. For dilute solutions, the density of the solution is nearly the same as that of water, so dissolving the salt in 1.00 L of water gives essentially 1.00 L of solution. Because each 1 mol of dissolved calcium oxalate monohydrate dissociates to produce 1 mol of calcium ions and 1 mol of oxalate ions, we can obtain the equilibrium concentrations that must be inserted into the solubility product expression. The number of moles of calcium oxalate monohydrate that dissolve in 100 mL of water is as follows:

$$\frac{7.36 \times 10^{-4}\ \mathrm{g}}{146.1\ \mathrm{g/mol}} = 5.04 \times 10^{-6}\ \mathrm{mol\ Ca(O_2CCO_2)\cdot H_2O}$$

The number of moles of calcium oxalate monohydrate that dissolve in 1.00 L of the saturated solution is as follows:

$$\left(\frac{5.04 \times 10^{-6}\ \mathrm{mol\ Ca(O_2CCO_2\cdot)H_2O}}{100\ \mathrm{mL}}\right)\left(\frac{1000\ \mathrm{mL}}{1.00\ \mathrm{L}}\right) = 5.04 \times 10^{-5}\ \mathrm{mol/L} = 5.04 \times 10^{-5}\ \mathrm{M}$$

Because of the stoichiometry of the reaction, the concentration of Ca^{2+} and ox^{2-} ions are both 5.04 × 10^{-5} M. Inserting these values into the solubility product expression,

$$K_{sp} = [Ca^{2+}][ox^{2-}] = (5.04 \times 10^{-5})(5.04 \times 10^{-5}) = 2.54 \times 10^{-9}$$

In our calculation, we have ignored the reaction of the weakly basic anion with water, which tends to make the actual solubility of many salts greater than the calculated value.

? Exercise 14.3.2.1

One crystalline form of calcium carbonate ($CaCO_3$) is the mineral sold as “calcite” in mineral and gem shops. The solubility of calcite in water is 0.67 mg/100 mL. Calculate its K_{sp}.

Answer 4.5 × 10^{-9}

> *The reaction of weakly basic anions with H_2O tends to make the actual solubility of many salts higher than predicted.*



A crystal of calcite ($CaCO_3$), illustrating the phenomenon of double refraction. When a transparent crystal of calcite is placed over a page, we see two images of the letters. Image used with permisison from Wikipedia

Calcite, a structural material for many organisms, is found in the teeth of sea urchins. The urchins create depressions in limestone that they can settle in by grinding the rock with their teeth. Limestone, however, also consists of calcite, so how can the urchins grind the rock without also grinding their teeth? Researchers have discovered that the teeth are shaped like needles and plates and contain magnesium. The concentration of magnesium increases toward the tip, which contributes to the hardness. Moreover, each tooth is composed of two blocks of the polycrystalline calcite matrix that are interleaved near the tip. This creates a corrugated surface that presumably increases grinding efficiency. Toolmakers are particularly interested in this approach to grinding.

Tabulated values of K_{sp} can also be used to estimate the solubility of a salt with a procedure that is essentially the reverse of the one used in Example 14.3.2.1. In this case, we treat the problem as a typical equilibrium problem and set up a table of initial concentrations, changes in concentration, and final concentrations (ICE Tables), remembering that the concentration of the pure solid is essentially constant.

Example 14.3.2.2

We saw that the K_{sp} for $Ca_3(PO_4)_2$ is 2.07×10^{-33} at 25°C. Calculate the aqueous solubility of $Ca_3(PO_4)_2$ in terms of the following:

a. the molarity of ions produced in solution
b. the mass of salt that dissolves in 100 mL of water at 25°C

Given: K_{sp}

Asked for: molar concentration and mass of salt that dissolves in 100 mL of water

Strategy:

A. Write the balanced equilibrium equation for the dissolution reaction and construct a table showing the concentrations of the species produced in solution. Insert the appropriate values into the solubility product expression and calculate the molar solubility at 25°C.
B. Calculate the mass of solute in 100 mL of solution from the molar solubility of the salt. Assume that the volume of the solution is the same as the volume of the solvent.

Solution:

A. **A** The dissolution equilibrium for $Ca_3(PO_4)_2$ (Equation 14.3.2.2) is shown in the following ICE table. Because we are starting with distilled water, the initial concentration of both calcium and phosphate ions is zero. For every 1 mol of $Ca_3(PO_4)_2$ that dissolves, 3 mol of Ca^{2+} and 2 mol of PO_4^{3-} ions are produced in solution. If we let x equal the solubility of $Ca_3(PO_4)_2$ in moles per liter, then the change in $[Ca^{2+}]$ will be $+3x$, and the change in $[PO_4^{3-}]$ will be $+2x$. We can insert these values into the table.

$$\mathbf{Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)}$$

	$Ca_3(PO_4)_2$	$[Ca^{2+}]$	\ce{[PO4^{3-}]}
initial	pure solid	0	0
change	—	$+3x$	$+2x$
final	pure solid	$3x$	$2x$

Although the amount of solid $Ca_3(PO_4)_2$ changes as some of it dissolves, its molar concentration does not change. We now insert the expressions for the equilibrium concentrations of the ions into the solubility product expression (Equation 17.2):

$$\begin{aligned} K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 &= (3x)^3(2x)^2 \\ 2.07 \times 10^{-33} &= 108x^5 \\ 1.92 \times 10^{-35} &= x^5 \\ 1.14 \times 10^{-7}\ \text{M} &= x \end{aligned}$$

This is the molar solubility of calcium phosphate at 25°C. However, the molarity of the ions is $2x$ and $3x$, which means that $[PO_4^{3-}] = 2.28 \times 10^{-7}$ and $[Ca^{2+}] = 3.42 \times 10^{-7}$.

b. **B** To find the mass of solute in 100 mL of solution, we assume that the density of this dilute solution is the same as the density of water because of the low solubility of the salt, so that 100 mL of water gives 100 mL of solution. We can then determine the amount of salt that dissolves in 100 mL of water:

$$\left(\frac{1.14\times10^{-7}\text{ mol}}{1\text{ L}}\right)100\text{ mL}\left(\frac{1\text{ L}}{1000\text{ mL}}\right)\left(\frac{310.18\text{ g Ca}_3(\text{PO}_4)_2}{1\text{ mol}}\right)=3.54\times10^{-6}\text{ g Ca}_3(\text{PO}_4)_2$$

? Exercise 14.3.2.2

The solubility product of silver carbonate (Ag_2CO_3) is 8.46×10^{-12} at 25°C. Calculate the following:

a. the molarity of a saturated solution
b. the mass of silver carbonate that will dissolve in 100 mL of water at this temperature

Answer a

1.28×10^{-4} M

Answer a

3.54 mg

Relating Solubilities to Solubility Constants

The *solubility* (by which we usually mean the *molar solubility*) of a solid is expressed as the concentration of the "dissolved solid" in a *saturated solution.* In the case of a simple 1:1 solid such as AgCl, this would just be the concentration of Ag^+ or Cl^- in the saturated solution. But for a more complicated stoichiometry such as as silver chromate, the solubility would be only one-half of the Ag^+ concentration.

For example, let us denote the solubility of Ag_2CrO_4 as S mol L^{-1}. Then for a saturated solution, we have

- $[Ag^+] = 2S$
- $[CrO_4^{2-}] = S$

Substituting this into Eq 5b above,

$$(2S)^2(S) = 4S^3 = 2.76\times10^{-12} \tag{14.3.2.4}$$

$$S = (dfracK_{sp}4)^{1/3} = (6.9\times10^{-13})^{1/3} = 0.88\times10^{-4} \tag{14.3.2.5}$$

thus the solubility is $8.8 \times 10^{-5}\ M$.

Note that the relation between the solubility and the solubility product constant depends on the stoichiometry of the dissolution reaction. For this reason it is meaningless to compare the solubilities of two salts having the formulas A_2B and AB_2, say, on the basis of their K_s values.

> It is *meaningless* to compare the solubilities of two salts having different formulas on the basis of their K_s values.

✓ Example 14.3.2.2

The solubility of CaF_2 (molar mass 78.1) at 18°C is reported to be 1.6 mg per 100 mL of water. Calculate the value of K_s under these conditions.

Solution

moles of solute in 100 mL; S = 0.0016 g / 78.1 g/mol = 2.05×10^{-5} mol

$$S = \frac{2.05\times10^{-5}mol}{0.100\ L}$$
$$= 2.05\times10^{-4}M$$

$$\begin{aligned} K_{sp} &= [Ca^{2+}][F^-]^2 \\ &= (S)(2S)^2 \\ &= 4 \times (2.05 \times 10^{-4})^3 \\ &= 3.44 \times 10^{-11} \end{aligned}$$

Example 14.3.2.3

Estimate the solubility of $La(IO_3)_3$ and calculate the concentration of iodate in equilibrium with solid lanthanum iodate, for which $K_s = 6.2 \times 10^{-12}$.

Solution

The equation for the dissolution is

$$La(IO_3)_3 \rightleftharpoons La^{3+} + 3\,IO_3^-$$

If the solubility is *S*, then the equilibrium concentrations of the ions will be

$[La^{3+}] = S$ and $[IO_3^-] = 3S$. Then $K_s = [La^{3+}][IO_3^-]^3 = S(3S)^3 = 27S^4$

$27S^4 = 6.2 \times 10^{-12}$, $S = ((6.2 \div 27) \times 10^{-12})^{¼} = 6.92 \times 10^{-4}$ *M*

$[IO_3^-] = 3S = 2.08 \times 10^{-5}$ (*M*)

Example 14.3.2.4: Cadmium

Cadmium is a highly toxic environmental pollutant that enters wastewaters associated with zinc smelting (Cd and Zn commonly occur together in ZnS ores) and in some electroplating processes. One way of controlling cadmium in effluent streams is to add sodium hydroxide, which precipitates insoluble $Cd(OH)_2$ (K_s = 2.5E–14). If 1000 L of a certain wastewater contains Cd^{2+} at a concentration of 1.6E–5 *M*, what concentration of Cd^{2+} would remain after addition of 10 L of 4 *M* NaOH solution?

Solution

As with most real-world problems, this is best approached as a series of smaller problems, making simplifying approximations as appropriate.

Volume of treated water: 1000 L + 10 L = 1010 L

Concentration of OH^- on addition to 1000 L of pure water:

(4 *M*) × (10 L)/(1010 L) = 0.040 *M*

Initial concentration of Cd^{2+} in 1010 L of water:

$$(1.6 \times 10^{-5}\ M)\left(\frac{100}{101}\right) \approx 1.6 \times 10^{-5}\ M \qquad (14.3.2.6)$$

The easiest way to tackle this is to start by assuming that a stoichiometric quantity of $Cd(OH)_2$ is formed — that is, *all* of the Cd^{2+} gets precipitated.

Concentrations	$[Cd^{2+}]$, *M*	$[OH^-]$, *M*
initial	1.6E–5	0.04
change	–1.6E–5	–3.2E–5
final:	0	0.04 – 3.2E–5 ≈ .04

Now "turn on the equilibrium" — find the concentration of Cd^{2+} that can exist in a 0.04*M* OH^- solution:

Concentrations	$[Cd^{2+}]$, *M*	$[OH^-]$, *M*

Concentrations	$[Cd^{2+}]$, $\underline{M}$	$[OH^-]$, $\underline{M}$
initial	o	0.04
change	$+x$	$+2x$
at equilibrium	x	$.04 + 2x \approx .04$

Substitute these values into the solubility product expression:

$$Cd(OH)_2(s) = [Cd^{2+}]\,[OH^-]^2 = 2.5E{-}14$$

$$[Cd^{2+}] = (2.5E{-}14) / (16E{-}4) = 1.6E{-}13\ \underline{M}$$

Note that the effluent will now be very alkaline:

$$pH = 14 + log 0.04 = 12.6 \qquad (14.3.2.7)$$

so in order to meet environmental standards an equivalent quantity of strong acid must be added to neutralize the water before it is released.

Summary

The solubility product (K_{sp}) is used to calculate equilibrium concentrations of the ions in solution, whereas the ion product (Q) describes concentrations that are not necessarily at equilibrium. The equilibrium constant for a dissolution reaction, called the solubility product (K_{sp}), is a measure of the solubility of a compound. Whereas solubility is usually expressed in terms of mass of solute per 100 mL of solvent, K_{sp} is defined in terms of the molar concentrations of the component ions.

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14.3.3: Precipitation and the Solubility Product

Learning Objectives

- Define K_{sp}, the solubility product.
- Explain solid/solution equilibria using K_{sp} and Q_{sp}.
- Calculate molarity of saturated solution from K_{sp}.
- Calculate K_{sp} from molarity of saturated solution.

Precipitation reactions occur when cations and anions in aqueous solution combine to form an insoluble ionic solid called a **precipitate**. Whether or not such a reaction occurs can be determined by using the **solubility rules** for common ionic solids. Because not all aqueous reactions form precipitates, one must consult the solubility rules before determining the state of the products and writing a **net ionic equation.** The ability to predict these reactions allows scientists to determine which ions are present in a solution, and allows industries to form chemicals by extracting components from these reactions.

Properties of Precipitates

Precipitates are insoluble ionic solid products of a reaction, formed when certain cations and anions combine in an aqueous solution. The determining factors of the formation of a precipitate can vary. Some reactions depend on temperature, such as solutions used for buffers, whereas others are dependent only on solution concentration. The solids produced in precipitate reactions are crystalline solids, and can be suspended throughout the liquid or fall to the bottom of the solution. The remaining fluid is called **supernatant liquid** (or just the supernate). The two components of the mixture (precipitate and supernate) can be separated by various methods, such as filtration, centrifuging, or decanting.

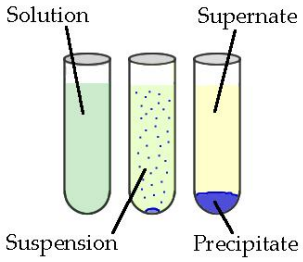


Figure 14.3.3.1: Above is a diagram of the formation of a precipitate in solution. (Public Domain; ZabMilenko)

The use of solubility rules require an understanding of the way that ions react. Most precipitation reactions are single replacement reactions or double replacement reactions. A double replacement reaction occurs when two ionic reactants dissociate and bond with the respective anion or cation from the other reactant. The ions replace each other based on their charges as either a cation or an anion. This can be thought of as a double displacement reaction where the partners "switching; that is, the two reactants each "lose" their partner and form a bond with a different partner:

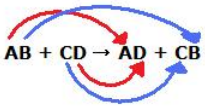


Figure 14.3.3.2: A double replacement reaction

A double replacement reaction is specifically classified as a **precipitation reaction** when the chemical equation in question occurs in aqueous solution and one of the of the products formed is insoluble. An example of a precipitation reaction is given below:

$$\mathrm{CdSO_4(aq) + K_2S(aq) \rightarrow CdS(s) + K_2SO_4(aq)} \tag{14.3.3.1}$$

Both reactants are aqueous and one product is solid. Because the reactants are ionic and aqueous, they dissociate and are therefore **soluble**. However, there are six solubility guidelines used to predict which molecules are insoluble in water. These molecules form a solid precipitate in solution.

Solubility Rules

Whether or not a reaction forms a precipitate is dictated by the solubility rules. These rules provide guidelines that tell which ions form solids and which remain in their ionic form in aqueous solution. The rules are to be followed from the top down, meaning that if something is insoluble (or soluble) due to rule 1, it has precedence over a higher-numbered rule.

1. Salts formed with group 1 cations and NH_4^+ cations are **soluble**. There are some exceptions for certain Li^+ salts.
2. Acetates ($C_2H_3O_2^-$), nitrates (NO_3^-), and perchlorates (ClO_4^-) are **soluble.**
3. Bromides, chlorides, and iodides are **soluble.**
4. Sulfates (SO_4^{2-}) are **soluble** with the exception of sulfates formed with Ca^{2+}, Sr^{2+}, and Ba^{2+}.
5. Salts containing silver, lead, and mercury (I) are **insoluble.**
6. Carbonates (CO_3^{2-}), phosphates (PO_4^{3-}), sulfides, oxides, and hydroxides (OH^-) are **insoluble**. Sulfides formed with group 2 cations and hydroxides formed with calcium, strontium, and barium are exceptions.

If the rules state that an ion is soluble, then it remains in its aqueous ion form. If an ion is insoluble based on the solubility rules, then it forms a solid with an ion from the other reactant. If all the ions in a reaction are shown to be soluble, then no precipitation reaction occurs.

Net Ionic Equations

To understand the definition of a **net ionic equation**, recall the equation for the double replacement reaction. Because this particular reaction is a precipitation reaction, states of matter can be assigned to each variable pair:

$$AB(aq) + CD(aq) \rightarrow AD(aq) + CB(s) \tag{14.3.3.2}$$

The first step to writing a net ionic equation is to separate the soluble (aqueous) reactants and products into their respective cations and anions. Precipitates do not dissociate in water, so the solid should not be separated. The resulting equation looks like that below:

$$A^+(aq) + B^-(aq) + C^+(aq) + D^-(aq) \rightarrow A^+(aq) + D^-(aq) + CB(s) \tag{14.3.3.3}$$

In the equation above, $\mathbf{A^+}$ and $\mathbf{D^-}$ ions are present on both sides of the equation. These are called **spectator ions** because they remain unchanged throughout the reaction. Since they go through the equation unchanged, they can be eliminated to show the **net ionic equation**:

$$B^-(aq) + C^+(aq) \rightarrow + CB(s) \tag{14.3.3.4}$$

The net ionic equation only shows the precipitation reaction. A net ionic equation must be balanced on both sides not only in terms of atoms of elements, but also in terms of electric charge. Precipitation reactions are usually represented solely by net ionic equations. If all products are aqueous, a net ionic equation cannot be written because all ions are canceled out as spectator ions. Therefore, **no precipitation reaction occurs**

Equilibrium and non-Equilibrium Conditions

The **ion product (*Q*)** of a salt is the product of the concentrations of the ions in solution raised to the same powers as in the solubility product expression. It is analogous to the reaction quotient (*Q*) discussed for gaseous equilibria. Whereas K_{sp} describes equilibrium concentrations, the ion product describes concentrations that are not necessarily equilibrium concentrations. An ion product can in principle have *any* positive value, depending on the concentrations of the ions involved. Only in the special case when its value is identical with K_s does it become the solubility product. A solution in which this is the case is said to be *saturated*. Thus when

$$[Ag^+]^2\ [CrO_4^{2-}] = 2.76 \times 10^{-12} \tag{14.3.3.5}$$

at the temperature and pressure at which this value K_{sp} of applies, we say that the "solution is saturated in silver chromate".

The ion product Q is analogous to the reaction quotient Q for gaseous equilibria.

As summarized in Figure 14.3.3.3, there are three possible conditions for an aqueous solution of an ionic solid:

- $Q < K_{sp}$. The solution is unsaturated, and more of the ionic solid, if available, will dissolve.
- $Q = K_{sp}$. The solution is saturated and at equilibrium.
- $Q > K_{sp}$. The solution is supersaturated, and ionic solid will precipitate.

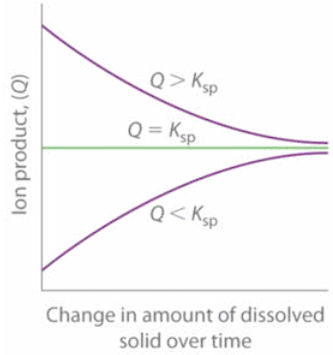


Figure 14.3.3.3: The Relationship between Q and K_{sp}. If Q is less than K_{sp}, the solution is unsaturated and more solid will dissolve until the system reaches equilibrium ($Q = K_{sp}$). If Q is greater than K_{sp}, the solution is supersaturated and solid will precipitate until $Q = K_{sp}$. If $Q = K_{sp}$, the rate of dissolution is equal to the rate of precipitation; the solution is saturated, and no net change in the amount of dissolved solid will occur. (CC BY-SA-NC; Anonymous)

The process of calculating the value of the ion product and comparing it with the magnitude of the solubility product is a straightforward way to determine whether a solution is unsaturated, saturated, or supersaturated. More important, the ion product tells chemists whether a precipitate will form when solutions of two soluble salts are mixed.

Example 14.3.3.3: barium milkshakes

Barium sulfate is used in medical imaging of the gastrointestinal tract. Its solubility product is 1.08×10^{-10} at 25°C, so it is ideally suited for this purpose because of its low solubility when a "barium milkshake" is consumed by a patient. The pathway of the sparingly soluble salt can be easily monitored by x-rays. Will barium sulfate precipitate if 10.0 mL of 0.0020 M Na_2SO_4 is added to 100 mL of 3.2×10^{-4} M $BaCl_2$? Recall that $NaCl$ is highly soluble in water.

Given: K_{sp} and volumes and concentrations of reactants

Asked for: whether precipitate will form

Strategy:

A. Write the balanced equilibrium equation for the precipitation reaction and the expression for K_{sp}.
B. Determine the concentrations of all ions in solution when the solutions are mixed and use them to calculate the ion product (Q).
C. Compare the values of Q and K_{sp} to decide whether a precipitate will form.

Solution

A The only slightly soluble salt that can be formed when these two solutions are mixed is $BaSO_4$ because $NaCl$ is highly soluble. The equation for the precipitation of $BaSO_4$ is as follows:

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

The solubility product expression is as follows:

$$K_{sp} = [Ba^{2+}][SO_4^{2-}] = 1.08 \times 10^{-10}$$

B To solve this problem, we must first calculate the ion product:

$$Q = [Ba^{2+}][SO_4^{2-}]$$

using the concentrations of the ions that are present after the solutions are mixed and before any reaction occurs. The concentration of Ba^{2+} when the solutions are mixed is the total number of moles of Ba^{2+} in the original 100 mL of $BaCl_2$ solution divided by the final volume (100 mL + 10.0 mL = 110 mL):

$$\text{moles } Ba^{2+} = 100 \text{ mL}\left(\frac{1 \text{ L}}{1000 \text{ mL}}\right)\left(\frac{3.2 \times 10^{-4} \text{ mol}}{1 \text{ L}}\right) = 3.2 \times 10^{-5} \text{ mol } Ba^{2+}$$

$$[Ba^{2+}] = \left(\frac{3.2 \times 10^{-5} \text{ mol } Ba^{2+}}{110 \text{ mL}}\right)\left(\frac{1000 \text{ mL}}{1 \text{ L}}\right) = 2.9 \times 10^{-4} \text{ M } Ba^{2+}$$

Similarly, the concentration of SO_4^{2-} after mixing is the total number of moles of SO_4^{2-} in the original 10.0 mL of Na_2SO_4 solution divided by the final volume (110 mL):

$$\text{moles } SO_4^{2-} = 10.0 \text{ mL}\left(\frac{1 \text{ L}}{1000 \text{ mL}}\right)\left(\frac{0.0020 \text{ mol}}{1 \text{ L}}\right) = 2.0 \times 10^{-5} \text{ mol } SO_4^{2-}$$

$$[SO_4^{2-}] = \left(\frac{2.0 \times 10^{-5} \text{ mol } SO_4^{2-}}{110 \text{ mL}}\right)\left(\frac{1000 \text{ mL}}{1 \text{ L}}\right) = 1.8 \times 10^{-4} \text{ M } SO_4^{2-}$$

We can now calculate \(Q\):

$$Q = [Ba^{2+}][SO_4^{2-}] = (2.9 \times 10^{-4})(1.8 \times 10^{-4}) = 5.2 \times 10^{-8}$$

C We now compare Q with the K_{sp}. If $Q > K_{sp}$, then $BaSO_4$ will precipitate, but if $Q < K_{sp}$, it will not. Because $Q > K_{sp}$, we predict that $BaSO_4$ will precipitate when the two solutions are mixed. In fact, $BaSO_4$ will continue to precipitate until the system reaches equilibrium, which occurs when

$$[Ba^{2+}][SO_4^{2-}] = K_{sp} = 1.08 \times 10^{-10}.$$

? Exercise 14.3.3.3

The solubility product of calcium fluoride (CaF_2) is 3.45×10^{-11}. If 2.0 mL of a 0.10 M solution of NaF is added to 128 mL of a 2.0×10^{-5} M solution of $Ca(NO_3)_2$, will CaF_2 precipitate?

Answer

Yes, since $Q_{sp} = 4.7 \times 10^{-11} > K_{sp}$.

A solution must be saturated to be in equilibrium with the solid. This is a *necessary* condition for solubility equilibrium, but it is not by itself *sufficient*. True chemical equilibrium can only occur when all components are simultaneously present. A solubility system can be in equilibrium only when some of the solid is in contact with a saturated solution of its ions. Failure to appreciate this is a very common cause of errors in solving solubility problems.

Undersaturated and supersaturated solutions

If the ion product is smaller than the solubility product, the system is not in equilibrium and no solid can be present. Such a solution is said to be *undersaturated*. A *supersaturated* solution is one in which the ion product exceeds the solubility product. A supersaturated solution is not at equilibrium, and no solid can ordinarily be present in such a solution. If some of the solid is added, the excess ions precipitate out and until solubility equilibrium is achieved.

How to know the saturation status of a solution? Just comparing the ion product Q_s with the solubility product K_{sp}. as shown in Table 14.3.3.1

Table 14.3.3.1: relationship among Q_{sp}, K_{sp} and saturation

Q_{sp}/K_{sp}	Status
> 1	Product concentration too high for equilibrium; net reaction proceeds to **left**.
= 1	System is at equilibrium; **no net change** will occur.
< 1	Product concentration too low for equilibrium; net reaction proceeds to **right**.

For example, for the system

$$\mathrm{Ag_2CrO_4(s) \rightleftharpoons 2\,Ag^+ + CrO_4^{2-}} \tag{14.3.3.6}$$

a solution in which $Q_s < K_s$ (i.e., $K_s/Q_s > 1$) is undersaturated (blue shading) and the no solid will be present. The combinations of $[Ag^+]$ and $[CrO_4^{2-}]$ that correspond to a saturated solution (and thus to equilibrium) are limited to those described by the curved line. The pink area to the right of this curve represents a supersaturated solution.

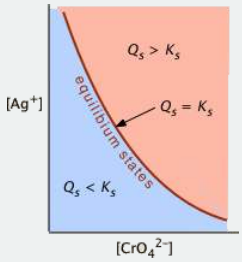


Figure 14.3.3.4: Equilibrium vs. non-equilibrium states for $\mathrm{Ag_2CrO_4(s)}$. (CC BY; Stephen Lower).

For some substances, formation of a solid or crystallization does not occur automatically whenever a solution is saturated. These substances have a tendency to form oversaturated solutions. For example, syrup and honey are oversaturated sugar solutions, containing other substances such as citric acids. For oversatureated solutions, Q_{sp} is greater than K_{sp}. When a seed crystal is provided or formed, a precipitate will form immediately due to equilibrium of requiring Q_{sp} to approach K_{sp}. For example Sodium acetate trihydrate, $\mathrm{NaCH_3COO \cdot 3\,H_2O}$, when heated to 370 K will become a liquid and stays as a liquid when cooled to room temperature or even below 273 K (Video 14.3.3.1). As soon as a seed crystal is present, crystallization occurs rapidly. In such a process, heat is released since this is an exothermic process $\Delta H < 0$.



Video* 14.3.3.1*: *"hot ice" (sodium acetate) crystallized from a non-equilibrium supersaturated ($Q_{sp} > K_{sp}$) solution*

Example 14.3.3.1

A sample of groundwater that has percolated through a layer of gypsum ($\mathrm{CaSO_4}$) with $K_{sp} = 4.9 \times 10^{-5} = 10^{-4.3}$) is found to have be 8.4×10^{-5} M in Ca^{2+} and 7.2×10^{-5} M in SO_4^{2-}. What is the equilibrium state of this solution with respect to gypsum?

Solution

The ion product

$$Q_s = (8.4 \times 10^{-5})(7.2 \times 10^{-5}) = 6.0 \times 10^{-4}$$

exceeds K_{sp}, so the ratio $K_{sp}\ /Q_{sp} > 1$ and the solution is *supersaturated* in $\mathrm{CaSO_4}$.

Relating Solubilities to Solubility Constants

The *solubility* (by which we usually mean the *molar solubility*) of a solid is expressed as the concentration of the "dissolved solid" in a *saturated solution.* In the case of a simple 1:1 solid such as AgCl, this would just be the concentration of Ag^+ or $Cl^–$ in the saturated solution. But for a more complicated stoichiometry such as as silver chromate, the solubility would be only one-half of the Ag^+ concentration.

For example, let us denote the solubility of Ag_2CrO_4 as *S* mol $L^{–1}$. Then for a saturated solution, we have

- $[Ag^+] = 2S$
- $[CrO_4^{2-}] = S$

Substituting this into Eq 5b above,

$$(2S)^2(S) = 4S^3 = 2.76 \times 10^{-12} \tag{14.3.3.7}$$

$$S = \left(\frac{K_{sp}}{4}\right)^{1/3} = (6.9 \times 10^{-13})^{1/3} = 0.88 \times 10^{-4} \tag{14.3.3.8}$$

thus the solubility is $8.8 \times 10^{-5}\ M$.

Note that the relation between the solubility and the solubility product constant depends on the stoichiometry of the dissolution reaction. For this reason it is meaningless to compare the solubilities of two salts having the formulas A_2B and AB_2, say, on the basis of their K_s values.

> It is *meaningless* to compare the solubilities of two salts having different formulas on the basis of their K_s values.

Example 14.3.3.2

The solubility of CaF_2 (molar mass 78.1) at 18°C is reported to be 1.6 mg per 100 mL of water. Calculate the value of K_s under these conditions.

Solution

moles of solute in 100 mL; *S* = 0.0016 g / 78.1 g/mol = 2.05×10^{-5} mol

$$S = \frac{2.05 \times 10^{-5} mol}{0.100\ L} = 2.05 \times 10^{-4} M \tag{14.3.3.9}$$

$$K_{sp} = [Ca^{2+}][F^-]^2 = (S)(2S)^2 = 4 \times (2.05 \times 10^{-4})^3 = 3.44 \times 10^{-11} \tag{14.3.3.10}$$

Example 14.3.3.3

Estimate the solubility of $La(IO_3)_3$ and calculate the concentration of iodate in equilibrium with solid lanthanum iodate, for which $K_s = 6.2 \times 10^{-12}$.

Solution

The equation for the dissolution is

$$La(IO_3)_3 \rightleftharpoons La^{3+} + 3IO_3^- \tag{14.3.3.11}$$

If the solubility is *S*, then the equilibrium concentrations of the ions will be

$[La^{3+}] = S$ and $[IO_3^-] = 3S$. Then $K_s = [La^{3+}][IO_3^-]^3 = S(3S)^3 = 27S^4$

$27S^4 = 6.2 \times 10^{-12}$, $S = ((6.2 \div 27) \times 10^{-12})^{¼} = 6.92 \times 10^{-4}$ $\underline{M}$

$[IO_3^-] = 3S = 2.08 \times 10^{-5}$ ($\underline{M}$)

Example 14.3.3.4: Cadmium

Cadmium is a highly toxic environmental pollutant that enters wastewaters associated with zinc smelting (Cd and Zn commonly occur together in ZnS ores) and in some electroplating processes. One way of controlling cadmium in effluent streams is to add sodium hydroxide, which precipitates insoluble $Cd(OH)_2$ (K_s = 2.5E–14). If 1000 L of a certain wastewater contains Cd^{2+} at a concentration of 1.6E–5 *M*, what concentration of Cd^{2+} would remain after addition of 10 L of 4 *M* NaOH solution?

Solution

As with most real-world problems, this is best approached as a series of smaller problems, making simplifying approximations as appropriate.

Volume of treated water: 1000 L + 10 L = 1010 L

Concentration of OH^- on addition to 1000 L of pure water:

$$(4\ M) \times (10\ L)/(1010\ L) = 0.040\ M$$

Initial concentration of Cd^{2+} in 1010 L of water:

$$(1.6 \times 10^{-5}\ M)\left(\frac{100}{101}\right) \approx 1.6 \times 10^{-5}\ M \tag{14.3.3.12}$$

The easiest way to tackle this is to start by assuming that a stoichiometric quantity of $Cd(OH)_2$ is formed — that is, *all* of the Cd^{2+} gets precipitated.

Concentrations	$[Cd^{2+}]$, M	$[OH^-]$, M
initial	1.6E–5	0.04
change	–1.6E–5	–3.2E–5
final:	0	0.04 – 3.2E–5 ≈ .04

Now "turn on the equilibrium" — find the concentration of Cd^{2+} that can exist in a 0.04*M* OH^- solution:

Concentrations	$[Cd^{2+}]$, M	$[OH^-]$, M
initial	o	0.04
change	+*x*	+2*x*
at equilibrium	*x*	.04 + 2*x* ≈ .04

Substitute these values into the solubility product expression:

$$Cd(OH)_2(s) = [Cd^{2+}]\,[OH^-]^2 = 2.5E{-}14$$

$$[Cd^{2+}] = (2.5E{-}14) / (16E{-}4) = 1.6E{-}13\ M$$

Note that the effluent will now be very alkaline:

$$pH = 14 + \log 0.04 = 12.6 \tag{14.3.3.13}$$

so in order to meet environmental standards an equivalent quantity of strong acid must be added to neutralize the water before it is released.

The Common Ion Effect

It has long been known that the solubility of a sparingly soluble ionic substance is markedly decreased in a solution of another ionic compound when the two substances have an ion in common. This is just what would be expected on the basis of the Le Chatelier Principle; whenever the process

$$CaF_{2(s)} \rightleftharpoons Ca^{2+} + 2F^- \tag{14.3.3.14}$$

is in equilibrium, addition of more fluoride ion (in the form of highly soluble NaF) will shift the composition to the left, reducing the concentration of Ca^{2+}, and thus effectively reducing the solubility of the solid. We can express this quantitatively by noting that the *solubility product expression*

$$[Ca^{2+}][F^-]^2 = 1.7 \times 10^{-10} \tag{14.3.3.15}$$

must always hold, even if some of the ionic species involved come from sources other than CaF_2*(s)*. For example, if some quantity *x* of fluoride ion is added to a solution initially in equilibrium with solid CaF_2, we have

- $[Ca^{2+}] = S$
- $[F^-] = 2S + x$

so that

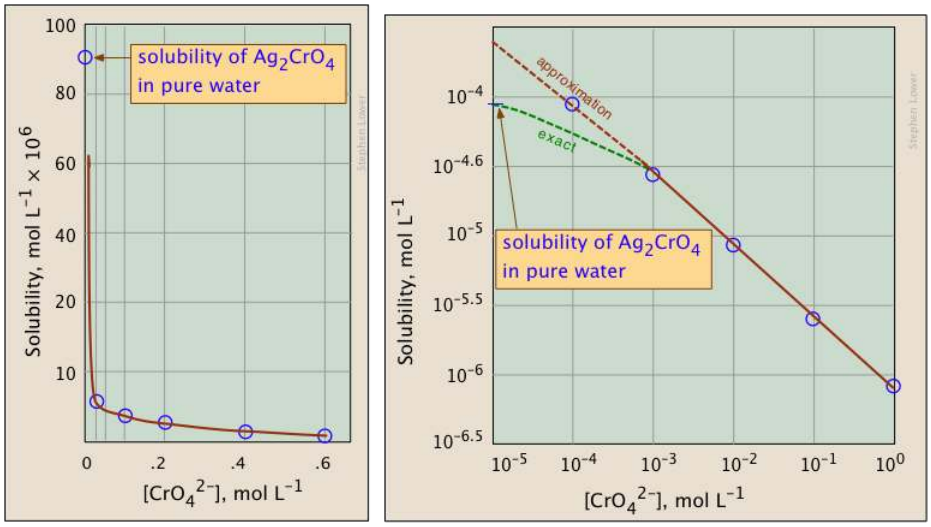
$$K_{sp} = [Ca^{2+}][F^-]^2 = S(2S + x)^2. \tag{14.3.3.16}$$

University-level students should be able to derive these relations for ion-derived solids of any stoichiometry. In most practical cases *x* will be large compared to *S* so that the 2*S* term can be dropped and the relation becomes

$$K_{sp} \approx S\ x^2 \tag{14.3.3.17}$$

$$S = \frac{K_{sp}}{x^2} \tag{14.3.3.18}$$

The plots shown below illustrate the common ion effect for silver chromate as the chromate ion concentration is increased by addition of a soluble chromate such as Na_2CrO_4.



What's different about the plot on the right? If you look carefully at the scales, you will see that this one is plotted logarithmically (that is, in powers of 10.) Notice how a much wider a range of values can display on a logarithmic plot. The point of showing this pair of plots is to illustrate the great utility of log-concentration plots in equilibrium calculations in which simple approximations (such as that made in Equation 14.3.3.18) can yield straight-lines within the range of values for which the approximation is valid.

✔ Example 14.3.3.5: strontium sulfate

Calculate the solubility of strontium sulfate (K_s = 2.8 × 10^{-7}) in

a. pure water and
b. in a 0.10 mol L^{-1} solution of Na_2SO_4.

Solution:

(a) In pure water, $K_s = [Sr^{2+}][SO_4^{2-}] = S^2$

$$S = \sqrt{K_s} = (2.8 \times 10^{-7})^{½} = 5.3 \times 10^{-4}$$

(b) In 0.10 mol L^{-1} Na_2SO_4, we have

$$K_s = [Sr^{2+}][SO_4^{2-}] = S \times (0.10 + S) = 2.8 \times 10^{-7}$$

Because S is negligible compared to 0.10 M, we make the approximation

$$K_s = [Sr^{2+}][SO_4^{2-}] \approx S \times (0.10\ M) = 2.8 \times 10^{-7}$$

so $S \approx (2.8 \times 10^{-7}) / 0.10M = 2.8 \times 10^{-6}$ $\underline{M}$ — which is roughly 100 times smaller than the result from *(a)*.

Note

The common ion effect usually decreases the solubility of a sparingly soluble salt.

Example 14.3.3.6

Calculate the solubility of calcium phosphate [$Ca_3(PO_4)_2$] in 0.20 M $CaCl_2$.

Given: concentration of $CaCl_2$ solution

Asked for: solubility of $Ca_3(PO_4)_2$ in $CaCl_2$ solution

Strategy:

A. Write the balanced equilibrium equation for the dissolution of $Ca_3(PO_4)_2$. Tabulate the concentrations of all species produced in solution.
B. Substitute the appropriate values into the expression for the solubility product and calculate the solubility of $Ca_3(PO_4)_2$.

Solution

A The balanced equilibrium equation is given in the following table. If we let x equal the solubility of $Ca_3(PO_4)_2$ in moles per liter, then the change in [Ca^{2+}] is once again +3x, and the change in [PO_4^{3-}] is +2x. We can insert these values into the ICE table.

$$Ca_3(PO_4)_{2(s)} \rightleftharpoons 3Ca^{2+}(aq) + 2PO^{3-}_{4(aq)} \tag{14.3.3.19}$$

	$Ca_3(PO_4)_2$	$[Ca_2^+]$	$[PO_{43}-]$
initial	pure solid	0.20	0
change	—	+3x	+2x
final	pure solid	0.20 + 3x	2x

B The K_{sp} expression is as follows:

$$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 = (0.20 + 3x)^3(2x)^2 = 2.07 \times 10^{-33}$$

Because $Ca_3(PO_4)_2$ is a sparingly soluble salt, we can reasonably expect that x << 0.20. Thus (0.20 + 3x) M is approximately 0.20 M, which simplifies the K_{sp} expression as follows:

$$K_{sp} = (0.20)^3(2x)^2 = 2.07 \times 10^{-33} \tag{14.3.3.20}$$

$$x^2 = 6.5 \times 10^{-32} \tag{14.3.3.21}$$

$$x = 2.5 \times 10^{-16}\ \text{M} \tag{14.3.3.22}$$

This value is the solubility of $Ca_3(PO_4)_2$ in 0.20 M $CaCl_2$ at 25°C. It is approximately nine orders of magnitude less than its solubility in pure water, as we would expect based on Le Chatelier's principle. With one exception, this example is identical to Example 14.3.3.2—here the initial [Ca^{2+}] was 0.20 M rather than 0.

Exercise 14.3.3.6

Calculate the solubility of silver carbonate in a 0.25 M solution of sodium carbonate. The solubility of silver carbonate in pure water is 8.45×10^{-12} at 25°C.

Answer

2.9×10^{-6} M (versus 1.3×10^{-4} M in pure water)

Applications and Examples

Precipitation reactions are useful in determining whether a certain element is present in a solution. If a precipitate is formed when a chemical reacts with lead, for example, the presence of lead in water sources could be tested by adding the chemical and monitoring for precipitate formation. In addition, precipitation reactions can be used to extract elements, such as magnesium from seawater. Precipitation reactions even occur in the human body between antibodies and antigens; however, the environment in which this occurs is still being studied.

Example 14.3.3.7

Complete the double replacement reaction and then reduce it to the net ionic equation.

$$NaOH(aq) + MgCl_{2\ (aq)} \rightarrow$$

First, *predict the products* of this reaction using knowledge of double replacement reactions (remember the cations and anions "switch partners").

$$2NaOH(aq) + MgCl_{2\ (aq)} \rightarrow 2NaCl + Mg(OH)_2$$

Second, *consult the solubility rules* to determine if the products are soluble. Group 1 cations (Na^+) and chlorides are soluble from rules 1 and 3 respectively, so $NaCl$ will be soluble in water. However, rule 6 states that hydroxides are insoluble, and thus $Mg(OH)_2$ will form a precipitate. The resulting equation is the following:

$$2NaOH(aq) + MgCl_{2\ (aq)} \rightarrow 2NaCl(aq) + Mg(OH)_{2\ (s)}$$

Third, *separate the reactants* into their ionic forms, as they would exist in an aqueous solution. Be sure to balance both the electrical charge and the number of atoms:

$$2Na^+(aq) + 2OH^-(aq) + Mg^{2+}(aq) + 2Cl^-(aq) \rightarrow Mg(OH)_{2\ (s)} + 2Na^+(aq) + 2Cl^-(aq)$$

Lastly, *eliminate the spectator ions* (the ions that occur on both sides of the equation unchanged). In this case, they are the sodium and chlorine ions. The final *net ionic equation* is:

$$Mg^{2+}(aq) + 2OH^-(aq) \rightarrow Mg(OH)_{2(s)}$$

Example 14.3.3.8

Complete the double replacement reaction and then reduce it to the net ionic equation.

$$CoCl_{2\ (aq)} + Na_2SO_{4\ (aq)} \rightarrow$$

Solution

The predicted products of this reaction are $CoSO_4$ and $NaCl$. From the solubility rules, $CoSO_4$ is soluble because rule 4 states that sulfates (SO_4^{2-}) are soluble. Similarly, we find that $NaCl$ is soluble based on rules 1 and 3. After balancing, the resulting equation is as follows:

$$CoCl_{2\ (aq)} + Na_2SO_{4\ (aq)} \rightarrow CoSO_{4\ (aq)} + 2NaCl(aq)$$

Separate the species into their ionic forms, as they would exist in an aqueous solution. Balance the charge and the atoms. Cancel out all spectator ions (those that appear as ions on both sides of the equation.):

$$\cancel{Co}^{2-}(aq) + \cancel{2Cl}^{-}(aq) + \cancel{2Na}^{+}(aq) + \cancel{SO_4}^{2-}(aq) \rightarrow \cancel{Co}^{2-}(aq) + \cancel{SO_4}^{2-}(aq) + \cancel{2Na}^{+}(aq) + \cancel{2Cl}^{-}(aq)$$

No precipitation reaction

This particular example is important because all of the reactants and the products are aqueous, meaning they cancel out of the net ionic equation. There is no solid precipitate formed; therefore, no precipitation reaction occurs.

Example 14.3.3.9

Write the net ionic equation for the potentially double displacement reactions. Make sure to include the states of matter and balance the equations.

a. $Fe(NO_3)_{3\ (aq)} + NaOH(aq) \rightarrow$
b. $Al_2(SO_4)_{3\ (aq)} + BaCl_{2\ (aq)} \rightarrow$
c. $HI(aq) + Zn(NO_3)_{2\ (aq)} \rightarrow$
d. $CaCl_{2\ (aq)} + Na_3PO_{4\ (aq)} \rightarrow$
e. $Pb(NO_3)_{2\ (aq)} + K_2SO_{4\ (aq)} \rightarrow$

Solutions

a. Regardless of physical state, the products of this reaction are $Fe(OH)_3$ and $NaNO_3$. The solubility rules predict that $NaNO_3$ is soluble because all nitrates are soluble (rule 2). However, $Fe(OH)_3$ is insoluble, because hydroxides are insoluble (rule 6) and Fe is not one of the cations which results in an exception. After dissociation, the ionic equation is as follows:

$$Fe^{3+}(aq) + NO^{-}_{3\ (aq)} + Na^{+}(aq) + 3OH^{-}(aq) \rightarrow Fe(OH)_{3\ (s)} + Na^{+}(aq) + NO^{-}_{3\ (aq)}$$

Canceling out spectator ions leaves the net ionic equation:

$$Fe^{3+}(aq) + OH^{-}(aq) \rightarrow Fe(OH)_{\ 3(s)}$$

b. From the double replacement reaction, the products are $AlCl_3$ and $BaSO_4$. $AlCl_3$ is soluble because it contains a chloride (rule 3); however, $BaSO_4$ is insoluble: it contains a sulfate, but the Ba^{2+} ion causes it to be insoluble because it is one of the cations that causes an exception to rule 4. The ionic equation is (after balancing):

$$2Al^{3+}(aq) + 6Cl^{-}(aq) + 3Ba^{2+}(aq) + 3SO^{2-}_{4\ (aq)} \rightarrow 2Al^{3+}(aq) + 6Cl^{-}(aq) + 3BaSO_{4\ (s)}$$

Canceling out spectator ions leaves the following net ionic equation:

$$Ba^{2+}(aq) + SO^{2-}_{4\ (aq)} \rightarrow BaSO_{4\ (s)}$$

c. From the double replacement reaction, the products HNO_3 and ZnI_2 are formed. Looking at the solubility rules, HNO_3 is soluble because it contains nitrate (rule 2), and ZnI_2 is soluble because iodides are soluble (rule 3). This means that both the products are aqueous (i.e. dissociate in water), and thus no precipitation reaction occurs.

d. The products of this double replacement reaction are $Ca_3(PO_4)_2$ and $NaCl$. Rule 1 states that $NaCl$ is soluble, and according to solubility rule 6, $Ca_3(PO_4)_2$ is insoluble. The ionic equation is:

$$Ca^{2+}(aq) + Cl^{-}(aq) + Na^{+}(aq) + PO^{3-}_{4\ (aq)} \rightarrow Ca_3(PO_4)_{2\ (s)} + Na^{+}(aq) + Cl^{-}(aq)$$

After canceling out spectator ions, the net ionic equation is given below:

$$Ca^{2+}(aq) + PO^{3-}_{4\ (aq)} \rightarrow Ca_3(PO_4)_{2\ (s)}$$

e. The first product of this reaction, $PbSO_4$, is soluble according to rule 4 because it is a sulfate. The second product, KNO_3, is also soluble because it contains nitrate (rule 2). Therefore, no precipitation reaction occurs.

References

1. Campbell, Dan, Linus Pauling, and Davis Pressman. "The Nature of the Forces Between Antigen and Antibody and of the Precipitation Reaction." *Physiological Reviews 23.3* (1943): 203-219. Online.

2. Harwood, William, F Herring, Jeffry Madura, and Ralph Petrucci. *General Chemistry*. 9th ed. Upper Saddle River: Pearson Pretence Hall, 2007. Print.
3. Freeouf, J.L, Grischkowsky, D., McInturff, D.T., Warren, A.C., & Woodall, J.M. (1990). Arsenic precipitates and the semi-insulating properties of gaas buffer layers grown by low-temperature molecular beam epitaxy. *Applied Physics Letters*, 57(13)
4. Petrucci, et al. General Chemistry: Principles & Modern Applications. 9th ed. Upper Saddle River, New Jersey 2007.

Summary

In contrast to K_{sp}, the ion product (Q_{sp}) describes concentrations that are not necessarily equilibrium concentrations. Comparing Q and K_{sp} enables us to determine whether a precipitate will form when solutions of two soluble salts are mixed. Adding a common cation or common anion to a solution of a sparingly soluble salt shifts the solubility equilibrium in the direction predicted by Le Chatelier's principle. The solubility of the salt is almost always decreased by the presence of a common ion.

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14.3.4: The Effects of pH on Solubility

Learning Objectives

- To understand why the solubility of many compounds depends on pH.

The solubility of many compounds depends strongly on the pH of the solution. For example, the anion in many sparingly soluble salts is the conjugate base of a weak acid that may become protonated in solution. In addition, the solubility of simple binary compounds such as oxides and sulfides, both strong bases, is often dependent on pH. In this section, we discuss the relationship between the solubility of these classes of compounds and pH.

The Effect of Acid–Base Equilibria the Solubility of Salts

We begin our discussion by examining the effect of pH on the solubility of a representative salt, $\mathrm{M^+A^-}$, where $\mathrm{A^-}$ is the conjugate base of the weak acid HA. When the salt dissolves in water, the following reaction occurs:

$$\mathrm{MA(s) \rightleftharpoons M^+(aq) + A^-(aq)}$$

with

$$K_{sp} = [\mathrm{M^+}][\mathrm{A^-}]$$

The anion can also react with water in a hydrolysis reaction:

$$\mathrm{A^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + HA(aq)} \tag{14.3.4.1}$$

Because of the reaction described in Equation 14.3.4.1, the predicted solubility of a sparingly soluble salt that has a basic anion such as S^{2-}, PO_4^{3-}, or CO_3^{2-} is increased. If instead a strong acid is added to the solution, the added H^+ will react essentially completely with A^- to form HA. This reaction decreases $[A^-]$, which decreases the magnitude of the ion product

$$Q = [\mathrm{M^+}][\mathrm{A^-}] \tag{14.3.4.2}$$

According to Le Chatelier's principle, more MA will dissolve until $Q = K_{sp}$. Hence an acidic pH dramatically increases the solubility of virtually all sparingly soluble salts whose anion is the conjugate base of a weak acid. In contrast, pH has little to no effect on the solubility of salts whose anion is the conjugate base of a stronger weak acid or a strong acid, respectively (e.g., chlorides, bromides, iodides, and sulfates). For example, the hydroxide salt $Mg(OH)_2$ is relatively insoluble in water:

$$Mg(OH)_{2(s)} \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq) \tag{14.3.4.3}$$

with

$$K_{sp} = 5.61 \times 10^{-12} \tag{14.3.4.4}$$

When acid is added to a saturated solution that contains excess solid $Mg(OH)_2$, the following reaction occurs, removing OH^- from solution:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l) \tag{14.3.4.5}$$

The overall equation for the reaction of $Mg(OH)_2$ with acid is thus

$$Mg(OH)_{2(s)} + 2H^+(aq) \rightleftharpoons Mg^{2+}(aq) + 2H_2O(l) \tag{14.3.4.6}$$

As more acid is added to a suspension of $Mg(OH)_2$, the equilibrium shown in Equation 14.3.4.6 is driven to the right, so more $Mg(OH)_2$ dissolves.

Such pH-dependent solubility is not restricted to salts that contain anions derived from water. For example, CaF_2 is a sparingly soluble salt:

$$CaF_{2(s)} \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq) \tag{14.3.4.7}$$

with

$$K_{sp} = 3.45 \times 10^{-11} \tag{14.3.4.8}$$

When strong acid is added to a saturated solution of CaF_2, the following reaction occurs:

$$H^+(aq) + F^-(aq) \rightleftharpoons HF(aq) \tag{14.3.4.9}$$

Because the forward reaction decreases the fluoride ion concentration, more CaF_2 dissolves to relieve the stress on the system. The net reaction of CaF_2 with strong acid is thus

$$CaF_{2(s)} + 2H^+(aq) \rightarrow Ca^{2+}(aq) + 2HF(aq) \tag{14.3.4.10}$$

Example 14.3.4.1shows how to calculate the solubility effect of adding a strong acid to a solution of a sparingly soluble salt.

> *Sparingly soluble salts derived from weak acids tend to be more soluble in an acidic solution.*

Example 14.3.4.1

Lead oxalate (PbC_2O_4), lead iodide (PbI_2), and lead sulfate ($PbSO_4$) are all rather insoluble, with K_{sp} values of 4.8×10^{-10}, 9.8×10^{-9}, and 2.53×10^{-8}, respectively. What effect does adding a strong acid, such as perchloric acid, have on their relative solubilities?

Given: K_{sp} values for three compounds

Asked for: relative solubilities in acid solution

Strategy:

Write the balanced chemical equation for the dissolution of each salt. Because the strongest conjugate base will be most affected by the addition of strong acid, determine the relative solubilities from the relative basicity of the anions.

Solution

The solubility Equilibria for the three salts are as follows:

$$PbC_2O_{4(s)} \rightleftharpoons Pb^{2+}(aq) + C_2O^{2-}_{4(aq)}$$

$$PbI_{2(s)} \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$$

$$PbSO_{4(s)} \rightleftharpoons Pb^{2+}(aq) + SO^{2-}_{4(aq)}$$

The addition of a strong acid will have the greatest effect on the solubility of a salt that contains the conjugate base of a weak acid as the anion. Because HI is a strong acid, we predict that adding a strong acid to a saturated solution of PbI_2 will not greatly affect its solubility; the acid will simply dissociate to form H^+(aq) and the corresponding anion. In contrast, oxalate is the fully deprotonated form of oxalic acid (HO_2CCO_2H), which is a weak diprotic acid (pK_{a1} = 1.23 and pK_{a2} = 4.19). Consequently, the oxalate ion has a significant affinity for one proton and a lower affinity for a second proton. Adding a strong acid to a saturated solution of lead oxalate will result in the following reactions:

$$C_2O^{2-}_{4(aq)} + H^+(aq) \rightarrow HO_2CCO^-_{2(aq)}$$

$$HO_2CCO^-_{2(aq)} + H^+(aq) \rightarrow HO_2CCO_2H(aq)$$

These reactions will decrease $[C_2O_4^{2-}]$, causing more lead oxalate to dissolve to relieve the stress on the system. The pK_a of HSO_4^- (1.99) is similar in magnitude to the pK_{a1} of oxalic acid, so adding a strong acid to a saturated solution of $PbSO_4$ will result in the following reaction:

$$SO^{2-}_{4(aq)} + H^+(aq) \rightleftharpoons HSO^-_{4(aq)}$$

Because HSO_4^- has a pKa of 1.99, this reaction will lie largely to the left as written. Consequently, we predict that the effect of added strong acid on the solubility of $PbSO_4$ will be significantly less than for PbC_2O_4.

Exercise 14.3.4.1

Which of the following insoluble salts—AgCl, Ag_2CO_3, Ag_3PO_4, and/or AgBr—will be substantially more soluble in 1.0 M HNO_3 than in pure water?

Answer

Ag_2CO_3 and Ag_3PO_4



Solubility Products and pH: https://youtu.be/XJ0s5SATZgQ

Caves and their associated pinnacles and spires of stone provide one of the most impressive examples of pH-dependent solubility Equilbria(part (a) in Figure 14.3.4.1). Perhaps the most familiar caves are formed from limestone, such as Carlsbad Caverns in New Mexico, Mammoth Cave in Kentucky, and Luray Caverns in Virginia. The primary reactions that are responsible for the formation of limestone caves are as follows:

$$\mathrm{CO_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + HCO_3^-(aq)} \tag{14.3.4.11}$$

$$\mathrm{HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)} \tag{14.3.4.12}$$

$$\mathrm{Ca^{2+}(aq) + CO_3^{2-}(aq) \rightleftharpoons CaCO_3(s)} \tag{14.3.4.13}$$

Limestone deposits that form caves consist primarily of $CaCO_3$ from the remains of living creatures such as clams and corals, which used it for making structures such as shells. When a saturated solution of $CaCO_3$ in CO_2-rich water rises toward Earth's surface or is otherwise heated, CO_2 gas is released as the water warms. $CaCO_3$ then precipitates from the solution according to the following equation (part (b) in Figure 14.3.4.1):

$$Ca^{2+}(aq) + 2HCO_{3(aq)}^- \rightleftharpoons CaCO_{3(s)} + CO_{2(g)} + H_2O(l) \tag{14.3.4.14}$$

The forward direction is the same reaction that produces the solid called scale in teapots, coffee makers, water heaters, boilers, and other places where hard water is repeatedly heated.



Figure 14.3.4.1: The Chemistry of Cave Formation. (a) This cave in Campanet, Mallorca, Spain, and its associated formations are examples of pH-dependent solubility equilibriums. (b) A cave forms when groundwater containing atmospheric CO_2, forming an acidic solution, dissolves limestone ($CaCO_3$) in a process that may take tens of thousands of years. As groundwater seeps into a cave, water evaporates from the solution of $CaCO_3$ in CO_2-rich water, producing a supersaturated solution and a shift in equilibrium that causes precipitation of the $CaCO_3$. The deposited limestone eventually forms stalactites and stalagmites.

When groundwater-containing atmospheric CO_2 (Equations 14.3.4.11and 14.3.4.12) finds its way into microscopic cracks in the limestone deposits, $CaCO_3$ dissolves in the acidic solution in the reverse direction of Equation 14.3.4.14 The cracks gradually enlarge from 10–50 µm to 5–10 mm, a process that can take as long as 10,000 yr. Eventually, after about another 10,000 yr, a cave forms. Groundwater from the surface seeps into the cave and clings to the ceiling, where the water evaporates and causes the equilibrium in Equation 14.3.4.14to shift to the right. A circular layer of solid $CaCO_3$ is deposited, which eventually produces a long, hollow spire of limestone called a stalactite that grows down from the ceiling. Below, where the droplets land when they fall from the ceiling, a similar process causes another spire, called a stalagmite, to grow up. The same processes that carve out hollows below ground are also at work above ground, in some cases producing fantastically convoluted landscapes like that of Yunnan Province in China (Figure 14.3.4.2).



Figure 14.3.4.2: Solubility Equilbriain the Formation of Karst Landscapes. Landscapes such as the steep limestone pinnacles of the Stone Forest in Yunnan Province, China, are formed from the same process that produces caves and their associated formations.

Acidic, Basic, and Amphoteric Oxides and Hydroxides

One of the earliest classifications of substances was based on their solubility in acidic versus basic solution, which led to the classification of oxides and hydroxides as being either basic or acidic. **Basic oxides** and hydroxides either react with water to produce a basic solution or dissolve readily in aqueous acid. **Acidic oxides** or hydroxides either react with water to produce an acidic solution or are soluble in aqueous base. There is a clear correlation between the acidic or the basic character of an oxide and the position of the element combined with oxygen in the periodic table. Oxides of metallic elements are generally basic oxides, and oxides of nonmetallic elements are acidic oxides. Compare, for example, the reactions of a typical metal oxide, cesium oxide, and a typical nonmetal oxide, sulfur trioxide, with water:

$$Cs_2O(s) + H_2O(l) \rightarrow 2Cs^+(aq) + 2OH^-(aq) \tag{14.3.4.15}$$

$$SO_{3(g)} + H_2O(l) \rightarrow H_2SO_{4(aq)} \tag{14.3.4.16}$$

Cesium oxide reacts with water to produce a basic solution of cesium hydroxide, whereas sulfur trioxide reacts with water to produce a solution of sulfuric acid—very different behaviors indeed

> *Metal oxides generally react with water to produce basic solutions, whereas nonmetal oxides produce acidic solutions.*

The difference in reactivity is due to the difference in bonding in the two kinds of oxides. Because of the low electronegativity of the metals at the far left in the periodic table, their oxides are best viewed as containing discrete M^{n+} cations and O^{2-} anions. At the other end of the spectrum are nonmetal oxides; due to their higher electronegativities, nonmetals form oxides with covalent bonds to oxygen. Because of the high electronegativity of oxygen, however, the covalent bond between oxygen and the other atom, E, is usually polarized: $E^{\delta+}$–$O^{\delta-}$. The atom E in these oxides acts as a Lewis acid that reacts with the oxygen atom of water to produce an oxoacid. Oxides of metals in high oxidation states also tend to be acidic oxides for the same reason: they contain covalent bonds to oxygen. An example of an acidic metal oxide is MoO_3, which is insoluble in both water and acid but dissolves in strong base to give solutions of the molybdate ion (MoO_4^{2-}):

$$MoO_{3(s)} + 2OH^-(aq) \rightarrow MoO^{2-}_{4(aq)} + H_2O(l) \tag{14.3.4.17}$$

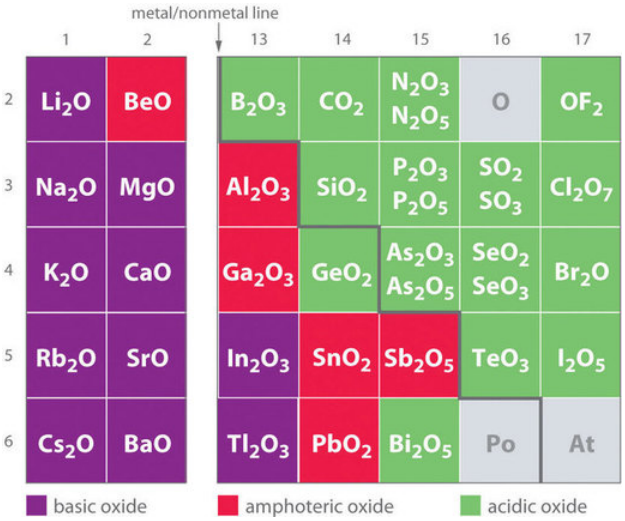


Figure 14.3.4.3: Classification of the Oxides of the Main Group Elements According to Their Acidic or Basic Character. There is a gradual transition from basic oxides to acidic oxides from the lower left to the upper right in the periodic table. Oxides of metallic elements are generally basic oxides, which either react with water to form a basic solution or dissolve in aqueous acid. In contrast, oxides of nonmetallic elements are acidic oxides, which either react with water to form an acidic solution or are soluble in aqueous base. Oxides of intermediate character, called amphoteric oxides, are located along a diagonal line between the two extremes. Amphoteric oxides either dissolve in acid to produce water or dissolve in base to produce a soluble complex ion. (Radioactive elements are not classified.)

As shown in Figure 14.3.4.3, there is a gradual transition from basic metal oxides to acidic nonmetal oxides as we go from the lower left to the upper right in the periodic table, with a broad diagonal band of oxides of intermediate character separating the two extremes. Many of the oxides of the elements in this diagonal region of the periodic table are soluble in both acidic and basic solutions; consequently, they are called **amphoteric oxides** (from the Greek ampho, meaning “both,” as in amphiprotic).

Amphoteric oxides either dissolve in acid to produce water or dissolve in base to produce a soluble complex. As shown in Video 14.3.4.1, for example, mixing the amphoteric oxide $Cr(OH)_3$ (also written as Cr_2O_3•$3H_2O$) with water gives a muddy, purple-brown suspension. Adding acid causes the $Cr(OH)_3$ to dissolve to give a bright violet solution of $Cr^{3+}(aq)$, which contains the $[Cr(H_2O)_6]^{3+}$ ion, whereas adding strong base gives a green solution of the $[Cr(OH)_4]^-$ ion. The chemical equations for the reactions are as follows:

$$\underset{\text{violet}}{Cr(OH)_3(s) + 3H^+(aq) \rightarrow Cr^{3+}(aq)} + 3H_2O(l) \tag{14.3.4.18}$$

$$Cr(OH)_3(s) + OH^-(aq) \rightarrow \underset{\text{green}}{[Cr(OH)_4]^-(aq)} \tag{14.3.4.19}$$



Video* 14.3.4.1*: *Chromium(III) Hydroxide [$Cr(OH)_3$ or Cr_2O_3•$3H_2O$] is an Example of an Amphoteric Oxide. All three beakers originally contained a suspension of brownish purple $Cr(OH)_3(s)$ (center). When concentrated acid (6 M H_2SO_4) was added to the beaker on the left, $Cr(OH)_3$ dissolved to produce violet $[Cr(H_2O)_6]^{3+}$ ions and water. The addition of concentrated base (6 M NaOH) to the beaker on the right caused $Cr(OH)_3$ to dissolve, producing green $[Cr(OH)_4]^-$ions. For a more complete description, see https://www.youtube.com/watch?v=IQNcLH6OZK0*

Example 14.3.4.2

Aluminum hydroxide, written as either $Al(OH)_3$ or Al_2O_3•$3H_2O$, is amphoteric. Write chemical equations to describe the dissolution of aluminum hydroxide in (a) acid and (b) base.

Given: amphoteric compound

Asked for: dissolution reactions in acid and base

Strategy:

Using Equations 14.3.4.18and 14.3.4.19as a guide, write the dissolution reactions in acid and base solutions.

Solution

a. An acid donates protons to hydroxide to give water and the hydrated metal ion, so aluminum hydroxide, which contains three OH^- ions per Al, needs three H^+ ions:

$$Al(OH)_{3(s)} + 3H^+(aq) \rightarrow Al^{3+}(aq) + 3H_2O(l)$$

In aqueous solution, Al^{3+} forms the complex ion $[Al(H_2O)_6]^{3+}$.

b. In basic solution, OH^- is added to the compound to produce a soluble and stable poly(hydroxo) complex:

$$Al(OH)_{3(s)} + OH^-(aq) \rightarrow [Al(OH)_4]^-(aq)$$

Exercise 14.3.4.2

Copper(II) hydroxide, written as either $Cu(OH)_2$ or $CuO•H_2O$, is *amphoteric*. Write chemical equations that describe the dissolution of cupric hydroxide both in an acid and in a base.

Answer

$$Cu(OH)_{2(s)} + 2H^+(aq) \rightarrow Cu^{2+}(aq) + 2H_2O(l)$$

$$Cu(OH)_{2(s)} + 2OH^-(aq) \rightarrow [Cu(OH)_4]^2_{-(aq)}$$

Selective Precipitation Using pH

Many dissolved metal ions can be separated by the selective precipitation of the cations from solution under specific conditions. In this technique, pH is often used to control the concentration of the anion in solution, which controls which cations precipitate.

> *The concentration of anions in solution can often be controlled by adjusting the pH, thereby allowing the selective precipitation of cations.*

Suppose, for example, we have a solution that contains 1.0 mM Zn^{2+} and 1.0 mM Cd^{2+} and want to separate the two metals by selective precipitation as the insoluble sulfide salts, ZnS and CdS. The relevant solubility equilbria can be written as follows:

$$ZnS(s) \rightleftharpoons Zn^{2+}(aq) + S^{2-}(aq) \tag{14.3.4.20}$$

with

$$K_{sp} = 1.6 \times 10^{-24} \tag{14.3.4.21}$$

and

$$CdS(s) \rightleftharpoons Cd^{2+}(aq) + S^{2-}(aq) \tag{14.3.4.22}$$

with

$$K_{sp} = 8.0 \times 10^{-27} \tag{14.3.4.23}$$

Because the S^{2-} ion is quite basic and reacts extensively with water to give HS^- and OH^-, the solubility equilbria are more accurately written as $MS(s) \rightleftharpoons M^{2+}(aq) + HS^-(aq) + OH^-$ rather than $MS(s) \rightleftharpoons M^{2+}(aq) + S^{2-}(aq)$. Here we use the simpler form involving S^{2-}, which is justified because we take the reaction of S^{2-} with water into account later in the solution, arriving at the same answer using either equilibrium equation.

The sulfide concentrations needed to cause ZnS and CdS to precipitate are as follows:

$$K_{sp} = [Zn^{2+}][S^{2-}] \tag{14.3.4.24}$$

$$1.6 \times 10^{-24} = (0.0010\ M)[S^{2-}] \tag{14.3.4.25}$$

$$1.6 \times 10^{-21}\ M = [S^{2-}] \tag{14.3.4.26}$$

and

$$K_{sp} = [Cd^{2+}][S^{2-}] \tag{14.3.4.27}$$

$$8.0 \times 10^{-27} = (0.0010\ M)[S^{2-}] \tag{14.3.4.28}$$

$$8.0 \times 10^{-24}\ M = [S^{2-}] \tag{14.3.4.29}$$

Thus sulfide concentrations between 1.6×10^{-21} M and 8.0×10^{-24} M will precipitate CdS from solution but not ZnS. How do we obtain such low concentrations of sulfide? A saturated aqueous solution of H_2S contains 0.10 M H_2S at 20°C. The $pK_{a1}$for H_2S is 6.97, and pK_{a2} corresponding to the formation of $[S^{2-}]$ is 12.90. The equations for these reactions are as follows:

$$H_2S(aq) \rightleftharpoons H^+(aq) + HS^-(aq) \tag{14.3.4.30}$$

with

$$pK_{a1} = 6.97 \text{ and hence } K_{a1} = 1.1 \times 10^{-7} \tag{14.3.4.31}$$

$$HS^-(aq) \rightleftharpoons H^+(aq) + S^{2-}(aq) \tag{14.3.4.32}$$

with

$$pK_{a2} = 12.90 \text{ and hence } K_{a2} = 1.3 \times 10^{-13} \tag{14.3.4.33}$$

We can show that the concentration of S^{2-} is 1.3×10^{-13} by comparing K_{a1} and K_{a2} and recognizing that the contribution to $[H^+]$ from the dissociation of HS^- is negligible compared with $[H^+]$ from the dissociation of H_2S. Thus substituting 0.10 M in the equation for K_{a1} for the concentration of H_2S, which is essentially constant regardless of the pH, gives the following:

$$K_{a1} = 1.1 \times 10^{-7} = \frac{[H^+][HS^-]}{[H_2S]} = \frac{x^2}{0.10\ M} \tag{14.3.4.34}$$

$$x = 1.1 \times 10^{-4}\ M = [H^+] = [HS^-]$$

Substituting this value for $[H^+]$ and $[HS^-]$ into the equation for K_{a2},

$$K_{a2} = 1.3 \times 10^{-13} = \frac{[H^+][S^{2-}]}{[HS^-]} = \frac{(1.1 \times 10^{-4}\ M)x}{1.1 \times 10^{-4}\ M} = x = [S^{2-}] \tag{14.3.4.35}$$

Although $[S^{2-}]$ in an H_2S solution is very low (1.3×10^{-13} M), bubbling H_2S through the solution until it is saturated would precipitate both metal ions because the concentration of S^{2-} would then be much greater than 1.6×10^{-21} M. Thus we must adjust $[S^{2-}]$ to stay within the desired range. The most direct way to do this is to adjust $[H^+]$ by adding acid to the H_2S solution (recall Le Chatelier's principle), thereby driving the equilibrium in Equation 14.3.4.33to the left. The overall equation for the dissociation of H_2S is as follows:

$$H_2S(aq) \rightleftharpoons 2H^+(aq) + S^{2-}(aq) \tag{14.3.4.36}$$

Now we can use the equilibrium constant K for the overall reaction, which is the product of K_{a1} and K_{a2}, and the concentration of H_2S in a saturated solution to calculate the H^+ concentration needed to produce $[S^{2-}]$ of 1.6×10^{-21} M:

$$K = K_{a1}K_{a2} = (1.1 \times 10^{-7})(1.3 \times 10^{-13}) = 1.4 \times 10^{-20} = \frac{[H^+]^2[S^{2-}]}{[H_2S]} \tag{14.3.4.37}$$

$$[H^+]^2 = \frac{K[H_2S]}{[S^{2-}]} = \frac{(1.4 \times 10^{-20})(0.10\ M)}{1.6 \times 10^{-21}\ M} = 0.88 \tag{14.3.4.38}$$

$$[H^+] = 0.94 \tag{14.3.4.39}$$

Thus adding a strong acid such as HCl to make the solution 0.94 M in H^+ will prevent the more soluble ZnS from precipitating while ensuring that the less soluble CdS will precipitate when the solution is saturated with H_2S.

Example 14.3.4.3

A solution contains 0.010 M Ca^{2+} and 0.010 M La^{3+}. What concentration of HCl is needed to precipitate $La_2(C_2O_4)_3 \cdot 9H_2O$ but not $Ca(C_2O_4) \cdot H_2O$ if the concentration of oxalic acid is 1.0 M? K_{sp} values are 2.32×10^{-9} for $Ca(C_2O_4)$ and 2.5×10^{-27} for $La_2(C_2O_4)_3$; $pK_{a1} = 1.25$ and $pK_{a2} = 3.81$ for oxalic acid.

Given: concentrations of cations, K_{sp} values, and concentration and pK_a values for oxalic acid

Asked for: concentration of HCl needed for selective precipitation of $La_2(C_2O_4)_3$

Strategy:

A. Write each solubility product expression and calculate the oxalate concentration needed for precipitation to occur. Determine the concentration range needed for selective precipitation of $La_2(C_2O_4)_3 \cdot 9H_2O$.

B. Add the equations for the first and second dissociations of oxalic acid to get an overall equation for the dissociation of oxalic acid to oxalate. Substitute the $[ox^{2-}]$ needed to precipitate $La_2(C_2O_4)_3 \cdot 9H_2O$ into the overall equation for the dissociation of oxalic acid to calculate the required $[H^+]$.

Solution

A Because the salts have different stoichiometries, we cannot directly compare the magnitudes of the solubility products. Instead, we must use the equilibrium constant expression for each solubility product to calculate the concentration of oxalate needed for precipitation to occur. Using ox^{2-} for oxalate, we write the solubility product expression for calcium oxalate as follows:

$$K_{sp} = [Ca^{2+}][ox^{2-}] = (0.010)[ox^{2-}] = 2.32 \times 10^{-9}$$

$$[ox^{2-}] = 2.32 \times 10^{-7}\ M$$

The expression for lanthanum oxalate is as follows:

$$K_{sp} = [La^{3+}]^2[ox^{2-}]^3 = (0.010)^2[ox^{2-}]^3 = 2.5 \times 10^{-27}$$

$$[ox^{2-}] = 2.9 \times 10^{-8}\ M$$

Thus lanthanum oxalate is less soluble and will selectively precipitate when the oxalate concentration is between $2.9 \times 10^{-8} M$ and $2.32 \times 10^{-7} M$.

B To prevent Ca^{2+} from precipitating as calcium oxalate, we must add enough H^+ to give a maximum oxalate concentration of 2.32×10^{-7} M. We can calculate the required $[H^+]$ by using the overall equation for the dissociation of oxalic acid to oxalate:

$$HO_2CCO_2H(aq) \rightleftharpoons 2H^+(aq) + C_2O_{4(aq)}^{2-} \tag{14.3.4.40}$$

$$K = K_{a1}K_{a2} = (10^{-1.25})(10^{-3.81}) = 10^{-5.06} = 8.7\times10^{-6}$$

Substituting the desired oxalate concentration into the equilibrium constant expression,

$$8.7 \times 10^{-6} = \frac{[\mathrm{H^+}]^2[\mathrm{ox^{2-}}]}{[\mathrm{HO_2CCO_2H}]} = \frac{[\mathrm{H^+}]^2(2.32 \times 10^{-7})}{1.0} \tag{14.3.4.41}$$

$$[\mathrm{H^+}] = 6.1\ \mathrm{M} \tag{14.3.4.42}$$

Thus adding enough HCl to give $[H^+]$ = 6.1 M will cause only $La_2(C_2O_4)_3 \cdot 9H_2O$ to precipitate from the solution.

Exercise 14.3.4.3

A solution contains 0.015 M Fe^{2+} and 0.015 M Pb^{2+}. What concentration of acid is needed to ensure that Pb^{2+} precipitates as PbS in a saturated solution of H_2S, but Fe^{2+} does not precipitate as FeS? K_{sp} values are 6.3×10^{-18} for FeS and 8.0×10^{-28} for PbS.

Answer

0.018 M H^+

Summary

The anion in sparingly soluble salts is often the conjugate base of a weak acid that may become protonated in solution, so the solubility of simple oxides and sulfides, both strong bases, often depends on pH. The anion in many sparingly soluble salts is the conjugate base of a weak acid. At low pH, protonation of the anion can dramatically increase the solubility of the salt. Oxides can be classified as acidic oxides or basic oxides. Acidic oxides either react with water to give an acidic solution or dissolve in strong base; most acidic oxides are nonmetal oxides or oxides of metals in high oxidation states. Basic oxides either react with water to give a basic solution or dissolve in strong acid; most basic oxides are oxides of metallic elements. Oxides or hydroxides that are soluble in both acidic and basic solutions are called amphoteric oxides. Most elements whose oxides exhibit amphoteric behavior are located along the diagonal line separating metals and nonmetals in the periodic table. In solutions that contain mixtures of dissolved metal ions, the pH can be used to control the anion concentration needed to selectively precipitate the desired cation.

Contributors and Attributions

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14.3.5: Complex Ions and Solubility

Learning Objectives

- To be introduced to complex ions, including ligands.

Previously, you learned that metal ions in aqueous solution are hydrated—that is, surrounded by a shell of usually four or six water molecules. A hydrated ion is one kind of a **complex ion** (or, simply, complex), a species formed between a central metal ion and one or more surrounding **ligands**, molecules or ions that contain at least one lone pair of electrons, such as the $[Al(H_2O)_6]^{3+}$ ion.

A complex ion forms from a metal ion and a ligand because of a Lewis acid–base interaction. The positively charged metal ion acts as a Lewis acid, and the ligand, with one or more lone pairs of electrons, acts as a Lewis base. Small, highly charged metal ions, such as Cu^{2+} or Ru^{3+}, have the greatest tendency to act as Lewis acids, and consequently, they have the greatest tendency to form complex ions.

As an example of the formation of complex ions, consider the addition of ammonia to an aqueous solution of the hydrated Cu^{2+} ion $\{[Cu(H_2O)_6]^{2+}\}$. Because it is a stronger base than H_2O, ammonia replaces the water molecules in the hydrated ion to form the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ion. Formation of the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex is accompanied by a dramatic color change, as shown in Figure 14.3.5.1. The solution changes from the light blue of $[Cu(H_2O)_6]^{2+}$ to the blue-violet characteristic of the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ion.



Figure 14.3.5.1: The Formation of Complex Ions. An aqueous solution of $CuSO_4$ consists of hydrated Cu^{2+} ions in the form of pale blue $[Cu(H_2O)_6]^{2+}$ (left). The addition of aqueous ammonia to the solution results in the formation of the intensely blue-violet $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ions, usually written as $[Cu(NH_3)_4]^{2+}$ ion (right) because ammonia, a stronger base than H_2O, replaces water molecules from the hydrated Cu^{2+} ion. For a more complete description, see www.youtube.com/watch?v=IQNcLH6OZK0.

The Formation Constant

The replacement of water molecules from $[Cu(H_2O)_6]^{2+}$ by ammonia occurs in sequential steps. Omitting the water molecules bound to Cu^{2+} for simplicity, we can write the equilibrium reactions as follows:

$$Cu^{2+}(aq) + NH_{3(aq)} \rightleftharpoons [Cu(NH_3)]^{2+}_{(aq)} \quad K_1 \tag{14.3.5.1}$$

$$[Cu(NH_3)]^{2+}_{(aq)} + NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_2]^{2+}_{(aq)} \quad K_2 \tag{14.3.5.2}$$

$$[Cu(NH_3)_2]^{2+}_{(aq)} + NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_3]^{2+}_{(aq)} \quad K_3 \tag{14.3.5.3}$$

$$[Cu(NH_3)_3]^{2+}_{(aq)} + NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_4]^{2+}_{(aq)} \quad K_4 \tag{14.3.5.4}$$

The sum of the stepwise reactions is the overall equation for the formation of the complex ion: The hydrated Cu^{2+} ion contains six H_2O ligands, but the complex ion that is produced contains only four NH_3 ligands, not six.

$$Cu^{2+}_{(aq)} + 4NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_4]^{2+}_{(aq)} \tag{14.3.5.5}$$

The equilibrium constant for the formation of the complex ion from the hydrated ion is called the **formation constant (K_f)**. The equilibrium constant expression for K_f has the same general form as any other equilibrium constant expression. In this case, the expression is as follows:

$$K_f = \frac{\left[[Cu(NH_3)_4]^{2+}\right]}{[Cu^{2+}][NH_3]^4} = 2.1 \times 10^{13} = K_1K_2K_3K_4 \tag{14.3.5.6}$$

> *The formation constant (K_f) has the same general form as any other equilibrium constant expression.*

Water, a pure liquid, does not appear explicitly in the equilibrium constant expression, and the hydrated $Cu^{2+}(aq)$ ion is represented as Cu^{2+} for simplicity. As for any equilibrium, the larger the value of the equilibrium constant (in this case, K_f), the more stable the product. With $K_f = 2.1 \times 10^{13}$, the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex ion is very stable. The formation constants for some common complex ions are listed in Table 14.3.5.1.

Table 14.3.5.1: Common Complex Ions

	Complex Ion	Equilibrium Equation	K_f
Ammonia Complexes	$[Ag(NH_3)_2]^+$	$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$	1.1×10^7
	$[Cu(NH_3)_4]^{2+}$	$Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$	2.1×10^{13}
	$[Ni(NH_3)_6]^{2+}$	$Ni^{2+} + 6NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+}$	5.5×10^8
Cyanide Complexes	$[Ag(CN)_2]^-$	$Ag^+ + 2CN^- \rightleftharpoons [Ag(CN)_2]^-$	1.1×10^{18}
	$[Ni(CN)_4]^{2-}$	$Ni^{2+} + 4CN^- \rightleftharpoons [Ni(CN)_4]^{2-}$	2.2×10^{31}
	$[Fe(CN)_6]^{3-}$	$Fe^{3+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{3-}$	1×10^{42}
Hydroxide Complexes	$[Zn(OH)_4]^{2-}$	$Zn^{2+} + 4OH^- \rightleftharpoons [Zn(OH)_4]^{2-}$	4.6×10^{17}
	$[Cr(OH)_4]^-$	$Cr^{3+} + 4OH^- \rightleftharpoons [Cr(OH)_4]^-$	8.0×10^{29}
Halide Complexes	$[HgCl_4]^{2-}$	$Hg^{2+} + 4Cl^- \rightleftharpoons [HgCl_4]^{2-}$	1.2×10^{15}
	$[CdI_4]^{2-}$	$Cd^{2+} + 4I \rightleftharpoons [CdI_4]^{2-}$	2.6×10^5
	$[AlF_6]^{3-}$	$Al^{3+} + 6F^- \rightleftharpoons [AlF_6]^{3-}$	6.9×10^{19}
Other Complexes	$[Ag(S_2O_3)_2]^{3-}$	$Ag^+ + 2S_2O_3^{2-} \rightleftharpoons [Ag(S_2O_3)_2]^{3-}$	2.9×10^{13}
	$[Fe(C_2O_4)_3]^{3-}$	$Fe^{3+} + 3C_2O_4^{2-} \rightleftharpoons [Fe(C_2O_4)_3]^{3-}$	2.0×10^{20}

*Reported values are overall formation constants. Source: Data from Lange's Handbook of Chemistry, 15th ed. (1999).

Example 14.3.5.1

If 12.5 g of $Cu(NO_3)_2 \bullet 6\,H_2O$ is added to 500 mL of 1.00 M aqueous ammonia, what is the equilibrium concentration of $Cu^{2+}(aq)$?

Given: mass of Cu^{2+} salt and volume and concentration of ammonia solution

Asked for: equilibrium concentration of $Cu^{2+}(aq)$

Strategy:

A. Calculate the initial concentration of Cu^{2+} due to the addition of copper(II) nitrate hexahydrate. Use the stoichiometry of the reaction shown in Equation 14.3.5.5to construct a table showing the initial concentrations, the changes in concentrations, and the final concentrations of all species in solution.

B. Substitute the final concentrations into the expression for the formation constant (Equation 14.3.5.6) to calculate the equilibrium concentration of $Cu^{2+}(aq)$.

Solution

Adding an ionic compound that contains Cu^{2+} to an aqueous ammonia solution will result in the formation of $[Cu(NH_3)_4]^{2+}(aq)$, as shown in Equation 14.3.5.5. We assume that the volume change caused by adding solid copper(II) nitrate to aqueous ammonia is negligible.

A The initial concentration of Cu^{2+} from the amount of added copper nitrate prior to any reaction is as follows:

$$12.5\ \cancel{g}\ Cu(NO_3)_2 \cdot 6H_2O \left(\frac{1\ mol}{295.65\ \cancel{g}}\right)\left(\frac{1}{500\ \cancel{mL}}\right)\left(\frac{1000\ \cancel{mL}}{1\ L}\right) = 0.0846\ M \qquad (14.3.5.7)$$

Because the stoichiometry of the reaction is four NH_3 to one Cu^{2+}, the amount of NH_3 required to react completely with the Cu^{2+} is 4(0.0846) = 0.338 M. The concentration of ammonia after complete reaction is 1.00 M − 0.338 M = 0.66 M. These results are summarized in the first two lines of the following table. Because the equilibrium constant for the reaction is large (2.1×10^{13}), the equilibrium will lie far to the right. Thus we will assume that the formation of $[Cu(NH_3)_4]^{2+}$ in the first step is complete and allow some of it to dissociate into Cu^{2+} and NH_3 until equilibrium has been reached. If we define *x* as the amount of Cu^{2+} produced by the dissociation reaction, then the stoichiometry of the reaction tells us that the change in the concentration of $[Cu(NH_3)_4]^{2+}$ is −*x*, and the change in the concentration of ammonia is +4*x*, as indicated in the table. The final concentrations of all species (in the bottom row of the table) are the sums of the concentrations after complete reaction and the changes in concentrations.

$$Cu^{2+} + 4\,NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$$

	$[Cu^{2+}]$	$[NH_3]$	$[[Cu(NH_3)_4]^{2+}]$
initial	0.0846	1.00	0
after complete reaction	0	0.66	0.0846
change	+*x*	+4*x*	−*x*
final	*x*	0.66 + 4*x*	0.0846 − *x*

B Substituting the final concentrations into the expression for the formation constant (Equation 14.3.5.6) and assuming that *x* << 0.0846, which allows us to remove *x* from the sum and difference,

$$K_f = \frac{[[Cu(NH_3)_4]^{2+}]}{[Cu^{2+}][NH_3]^4} = \frac{0.0846 - x}{x(0.66 + 4x)^4} \approx \frac{0.0846}{x(0.66)^4} = 2.1 \times 10^{13}$$

$$x = 2.1 \times 10^{-14}$$

The value of *x* indicates that our assumption was justified. The equilibrium concentration of $Cu^{2+}(aq)$ in a 1.00 M ammonia solution is therefore 2.1×10^{-14} M.

? Exercise 14.3.5.1

The ferrocyanide ion $\{[Fe(CN)_6]^{4-}\}$ is very stable, with a K_f of 1×10^{35}. Calculate the concentration of cyanide ion in equilibrium with a 0.65 M solution of $K_4[Fe(CN)_6]$.

Answer

2×10^{-6} M

The Effect of the Formation of Complex Ions on Solubility

What happens to the solubility of a sparingly soluble salt if a ligand that forms a stable complex ion is added to the solution? One such example occurs in conventional black-and-white photography. Recall that black-and-white photographic film contains light-sensitive microcrystals of AgBr, or mixtures of AgBr and other silver halides. AgBr is a sparingly soluble salt, with a K_{sp} of 5.35×10^{-13} at 25°C. When the shutter of the camera opens, the light from the object being photographed strikes some of the crystals on the film and initiates a photochemical reaction that converts AgBr to black Ag metal. Well-formed, stable negative images appear in tones of gray, corresponding to the number of grains of AgBr converted, with the areas exposed to the most light being darkest. To fix the image and prevent more AgBr crystals from being converted to Ag metal during processing of the film, the unreacted AgBr on the film is removed using a complexation reaction to dissolve the sparingly soluble salt.

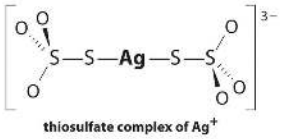
The reaction for the dissolution of silver bromide is as follows:

$$AgBr_{(s)} \rightleftharpoons Ag^+_{(aq)} + Br^-_{(aq)} \qquad (14.3.5.8)$$

with

$$K_{sp} = 5.35 \times 10^{-13} \text{ at } 25^\circ\text{C} \tag{14.3.5.9}$$

The equilibrium lies far to the left, and the equilibrium concentrations of Ag^+ and Br^- ions are very low (7.31×10^{-7} M). As a result, removing unreacted AgBr from even a single roll of film using pure water would require tens of thousands of liters of water and a great deal of time. Le Chatelier's principle tells us, however, that we can drive the reaction to the right by removing one of the products, which will cause more AgBr to dissolve. Bromide ion is difficult to remove chemically, but silver ion forms a variety of stable two-coordinate complexes with neutral ligands, such as ammonia, or with anionic ligands, such as cyanide or thiosulfate ($S_2O_3^{2-}$). In photographic processing, excess AgBr is dissolved using a concentrated solution of sodium thiosulfate.



thiosulfate complex of Ag^+

The reaction of Ag^+ with thiosulfate is as follows:

$$Ag^+_{(aq)} + 2S_2O^{2-}_{3(aq)} \rightleftharpoons [Ag(S_2O_3)_2]^{3-}_{(aq)} \tag{14.3.5.10}$$

with

$$K_f = 2.9 \times 10^{13} \tag{14.3.5.11}$$

The magnitude of the equilibrium constant indicates that almost all Ag^+ ions in solution will be immediately complexed by thiosulfate to form $[Ag(S_2O_3)_2]^{3-}$. We can see the effect of thiosulfate on the solubility of AgBr by writing the appropriate reactions and adding them together:

$$\mathrm{AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)} \quad K_{\mathrm{sp}} = 5.35 \times 10^{-13} \tag{14.3.5.12}$$

$$\mathrm{Ag^+(aq) + 2S_2O_3^{2-}(aq) \rightleftharpoons [Ag(S_2O_3)_2]^{3-}(aq)} \quad K_{\mathrm{f}} = 2.9 \times 10^{13} \tag{14.3.5.13}$$

$$\mathrm{AgBr(s) + 2S_2O_3^{2-}(aq) \rightleftharpoons [Ag(S_2O_3)_2]^{3-}(aq) + Br^-(aq)} \quad K = K_{\mathrm{sp}}K_{\mathrm{f}} = 15 \tag{14.3.5.14}$$

Comparing K with K_{sp} shows that the formation of the complex ion increases the solubility of AgBr by approximately 3×10^{13}. The dramatic increase in solubility combined with the low cost and the low toxicity explains why sodium thiosulfate is almost universally used for developing black-and-white film. If desired, the silver can be recovered from the thiosulfate solution using any of several methods and recycled.

> *If a complex ion has a large K_f, the formation of a complex ion can dramatically increase the solubility of sparingly soluble salts.*

Example 14.3.5.2

Due to the common ion effect, we might expect a salt such as AgCl to be much less soluble in a concentrated solution of KCl than in water. Such an assumption would be incorrect, however, because it ignores the fact that silver ion tends to form a two-coordinate complex with chloride ions ($AgCl_2^-$). Calculate the solubility of AgCl in each situation:

a. in pure water
b. in 1.0 M KCl solution, ignoring the formation of any complex ions
c. the same solution as in part (b) except taking the formation of complex ions into account, assuming that $AgCl_2^-$ is the only Ag^+ complex that forms in significant concentrations

At 25°C, $K_{sp} = 1.77 \times 10^{-10}$ for AgCl and $K_f = 1.1 \times 10^5$ for $AgCl_2^-$.

Given: K_{sp} of AgCl, K_f of $AgCl_2^-$, and KCl concentration

Asked for: solubility of AgCl in water and in KCl solution with and without the formation of complex ions

Strategy:

A. Write the solubility product expression for AgCl and calculate the concentration of Ag^+ and Cl^- in water.
B. Calculate the concentration of Ag^+ in the KCl solution.

C. Write balanced chemical equations for the dissolution of AgCl and for the formation of the $AgCl_2^-$ complex. Add the two equations and calculate the equilibrium constant for the overall equilibrium.
D. Write the equilibrium constant expression for the overall reaction. Solve for the concentration of the complex ion.

Solution

a. **A** If we let *x* equal the solubility of AgCl, then at equilibrium [Ag+] = [Cl^-] = *x* M. Substituting this value into the solubility product expression,

$$K_{sp} = [Ag^+][Cl^-] = (x)(x) = x^2 = 1.77\times10^{-10}$$

$$x = 1.33\times10^{-5}$$

Thus the solubility of AgCl in pure water at 25°C is 1.33×10^{-5} M.

b. **B** If *x* equals the solubility of AgCl in the KCl solution, then at equilibrium [Ag^+] = *x* M and [Cl^-] = (1.0 + *x*) M. Substituting these values into the solubility product expression and assuming that $x << 1.0$,

$$K_{sp} = [Ag^+][Cl^-] = (x)(1.0 + x) \approx x(1.0) = 1.77\times10^{-10} = x$$

If the common ion effect were the only important factor, we would predict that AgCl is approximately five orders of magnitude less soluble in a 1.0 M KCl solution than in water.

c. **C** To account for the effects of the formation of complex ions, we must first write the equilibrium equations for both the dissolution and the formation of complex ions. Adding the equations corresponding to K_{sp} and K_f gives us an equation that describes the dissolution of AgCl in a KCl solution. The equilibrium constant for the reaction is therefore the product of K_{sp} and K_f:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \quad K_{sp} = 1.77 \times 10^{-10} \tag{14.3.5.15}$$

$$Ag^+(aq) + 2Cl^- \rightleftharpoons [AgCl_2]^- \quad K_f = 1.1 \times 10^5 \tag{14.3.5.16}$$

$$AgCl(s) + Cl^- \rightleftharpoons [AgCl_2]^- \quad K = K_{sp}K_f = 1.9 \times 10^{-5} \tag{14.3.5.17}$$

D If we let *x* equal the solubility of AgCl in the KCl solution, then at equilibrium [$AgCl_2^-$] = *x* and [Cl^-] = 1.0 − *x*. Substituting these quantities into the equilibrium constant expression for the net reaction and assuming that $x << 1.0$,

$$K = \frac{[AgCl_2^-]}{[Cl^-]} = \frac{x}{1.0 - x} \approx 1.9 \times 10^{-5} = x$$

That is, AgCl dissolves in 1.0 M KCl to produce a 1.9×10^{-5} M solution of the $AgCl_2^-$ complex ion. Thus we predict that AgCl has approximately the same solubility in a 1.0 M KCl solution as it does in pure water, which is 10^5 times greater than that predicted based on the common ion effect. (In fact, the measured solubility of AgCl in 1.0 M KCl is almost a factor of 10 greater than that in pure water, largely due to the formation of other chloride-containing complexes.)

? Exercise 14.3.5.2

Calculate the solubility of mercury(II) iodide (HgI_2) in each situation:

a. pure water
b. a 3.0 M solution of NaI, assuming $[HgI_4]^{2-}$ is the only Hg-containing species present in significant amounts

$K_{sp} = 2.9 \times 10^{-29}$ for HgI_2 and $K_f = 6.8 \times 10^{29}$ for $[HgI_4]^{2-}$.

Answer a

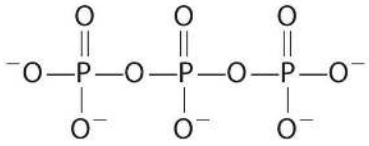
1.9×10^{-10} M

Answer a

1.4 M

Complexing agents, molecules or ions that increase the solubility of metal salts by forming soluble metal complexes, are common components of laundry detergents. Long-chain carboxylic acids, the major components of soaps, form insoluble salts with Ca^{2+} and Mg^{2+}, which are present in high concentrations in “hard” water. The precipitation of these salts produces a bathtub ring and gives a gray tinge to clothing. Adding a complexing agent such as pyrophosphate ($O_3POPO_3^{4-}$, or $P_2O_7^{4-}$) or triphosphate ($P_3O_{10}^{5-}$) to

detergents prevents the magnesium and calcium salts from precipitating because the equilibrium constant for complex-ion formation is large:



triphosphate

$$Ca^{2+}(aq) + O_3POPO_4^{4-}(aq) \rightleftharpoons [Ca(O_3POPO_3)]^{2-}(aq) \tag{14.3.5.18}$$

with

$$K_f = 4 \times 10^4 \tag{14.3.5.19}$$

However, phosphates can cause environmental damage by promoting eutrophication, the growth of excessive amounts of algae in a body of water, which can eventually lead to large decreases in levels of dissolved oxygen that kill fish and other aquatic organisms. Consequently, many states in the United States have banned the use of phosphate-containing detergents, and France has banned their use beginning in 2007. “Phosphate-free” detergents contain different kinds of complexing agents, such as derivatives of acetic acid or other carboxylic acids. The development of phosphate substitutes is an area of intense research.

Commercial water softeners also use a complexing agent to treat hard water by passing the water over ion-exchange resins, which are complex sodium salts. When water flows over the resin, sodium ion is dissolved, and insoluble salts precipitate onto the resin surface. Water treated in this way has a saltier taste due to the presence of Na^+, but it contains fewer dissolved minerals.

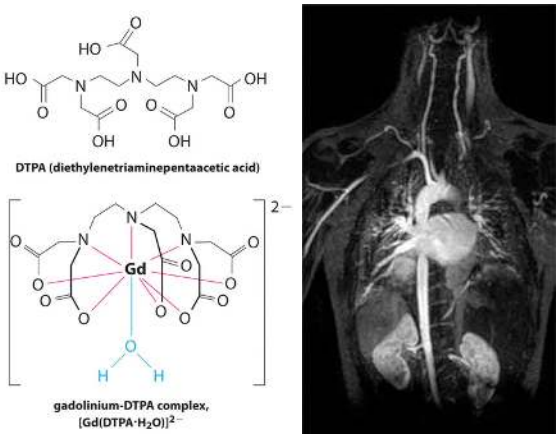


Figure 14.3.5.2 An MRI Image of the Heart, Arteries, and Veins. When a patient is injected with a paramagnetic metal cation in the form of a stable complex known as an MRI contrast agent, the magnetic properties of water in cells are altered. Because the different environments in different types of cells respond differently, a physician can obtain detailed images of soft tissues.

Another application of complexing agents is found in medicine. Unlike x-rays, magnetic resonance imaging (MRI) can give relatively good images of soft tissues such as internal organs. MRI is based on the magnetic properties of the ^1H nucleus of hydrogen atoms in water, which is a major component of soft tissues. Because the properties of water do not depend very much on whether it is inside a cell or in the blood, it is hard to get detailed images of these tissues that have good contrast. To solve this problem, scientists have developed a class of metal complexes known as “MRI contrast agents.” Injecting an MRI contrast agent into a patient selectively affects the magnetic properties of water in cells of normal tissues, in tumors, or in blood vessels and allows doctors to “see” each of these separately (Figure 14.3.5.2). One of the most important metal ions for this application is Gd^{3+}, which with seven unpaired electrons is highly paramagnetic. Because $Gd^{3+}(aq)$ is quite toxic, it must be administered as a very stable complex that does not dissociate in the body and can be excreted intact by the kidneys. The complexing agents used for gadolinium are ligands such as $DTPA^{5-}$ (diethylene triamine pentaacetic acid), whose fully protonated form is shown here.

Summary

The formation of complex ions can substantially increase the solubility of sparingly soluble salts if the complex ion has a large K_f. A complex ion is a species formed between a central metal ion and one or more surrounding ligands, molecules or ions that contain at least one lone pair of electrons. Small, highly charged metal ions have the greatest tendency to act as Lewis acids and form complex ions. The equilibrium constant for the formation of the complex ion is the formation constant (K_f). The formation of a complex ion by adding a complexing agent increases the solubility of a compound.

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14.3.6: A Deeper Look- Selective Precipitation of Ions

Learning Objectives

- To know how to separate metal ions by selective precipitation.
- To understand how several common metal cations can be identified in a solution using selective precipitation.

The composition of relatively complex mixtures of metal ions can be determined using **qualitative analysis**, a procedure for discovering the identity of metal ions present in the mixture (rather than quantitative information about their amounts). The procedure used to separate and identify more than 20 common metal cations from a single solution consists of selectively precipitating only a few kinds of metal ions at a time under given sets of conditions. Consecutive precipitation steps become progressively less selective until almost all of the metal ions are precipitated, as illustrated in Figure 14.3.6.1.

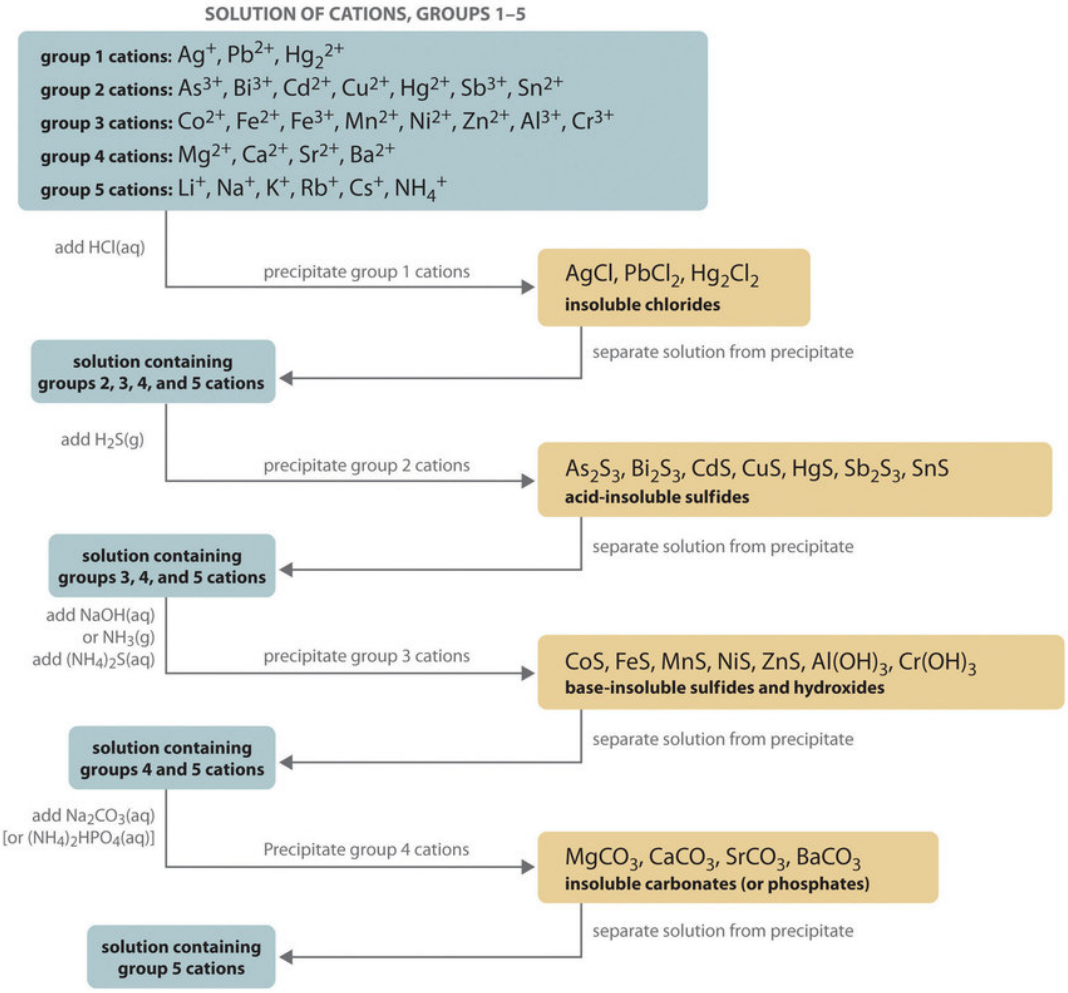


Figure 14.3.6.1: Steps in a Typical Qualitative Analysis Scheme for a Solution That Contains Several Metal Ions

Group 1: Insoluble Chlorides

Most metal chloride salts are soluble in water; only Ag^+, Pb^{2+}, and Hg_2^{2+} form chlorides that precipitate from water. Thus the first step in a qualitative analysis is to add about 6 M HCl, thereby causing AgCl, $PbCl_2$, and/or Hg_2Cl_2 to precipitate. If no precipitate forms, then these cations are not present in significant amounts. The precipitate can be collected by filtration or centrifugation.

Group 2: Acid-Insoluble Sulfides

Next, the acidic solution is saturated with H_2S gas. Only those metal ions that form very insoluble sulfides, such as As^{3+}, Bi^{3+}, Cd^{2+}, Cu^{2+}, Hg^{2+}, Sb^{3+}, and Sn^{2+}, precipitate as their sulfide salts under these acidic conditions. All others, such as Fe^{2+} and Zn^{2+}, remain in solution. Once again, the precipitates are collected by filtration or centrifugation.

Group 3: Base-Insoluble Sulfides (and Hydroxides)

Ammonia or $NaOH$ is now added to the solution until it is basic, and then $(NH_4)_2S$ is added. This treatment removes any remaining cations that form insoluble hydroxides or sulfides. The divalent metal ions Co^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, and Zn^{2+} precipitate as their sulfides, and the trivalent metal ions Al^{3+} and Cr^{3+} precipitate as their hydroxides: $Al(OH)_3$ and $Cr(OH)_3$. If the mixture contains Fe^{3+}, sulfide reduces the cation to Fe^{2+}, which precipitates as FeS.

Group 4: Insoluble Carbonates or Phosphates

The next metal ions to be removed from solution are those that form insoluble carbonates and phosphates. When Na_2CO_3 is added to the basic solution that remains after the precipitated metal ions are removed, insoluble carbonates precipitate and are collected. Alternatively, adding $(NH_4)_2HPO_4$ causes the same metal ions to precipitate as insoluble phosphates.

Group 5: Alkali Metals

At this point, we have removed all the metal ions that form water-insoluble chlorides, sulfides, carbonates, or phosphates. The only common ions that might remain are any alkali metals (Li^+, Na^+, K^+, Rb^+, and Cs^+) and ammonium (NH_4^+). We now take a second sample from the original solution and add a small amount of $NaOH$ to neutralize the ammonium ion and produce NH_3. (We cannot use the same sample we used for the first four groups because we added ammonium to that sample in earlier steps.) Any ammonia produced can be detected by either its odor or a litmus paper test. A flame test on another original sample is used to detect sodium, which produces a characteristic bright yellow color. The other alkali metal ions also give characteristic colors in flame tests, which allows them to be identified if only one is present.

Metal ions that precipitate together are separated by various additional techniques, such as forming complex ions, changing the pH of the solution, or increasing the temperature to redissolve some of the solids. For example, the precipitated metal chlorides of group 1 cations, containing Ag^+, Pb^{2+}, and Hg_2^{2+}, are all quite insoluble in water. Because $PbCl_2$ is much more soluble in hot water than are the other two chloride salts, however, adding water to the precipitate and heating the resulting slurry will dissolve any $PbCl_2$ present. Isolating the solution and adding a small amount of Na_2CrO_4 solution to it will produce a bright yellow precipitate of $PbCrO_4$ if Pb^{2+} were in the original sample (Figure 14.3.6.2).



Figure 14.3.6.2: When a small amount of Na_2CrO_4 solution is added to a sample containing Pb^{2+} ions in water, a bright yellow precipitate of $PbCrO_4$ forms. (CC BY-SA 3.0 Unported; PRHaney via Wikipedia).

As another example, treating the precipitates from group 1 cations with aqueous ammonia will dissolve any $AgCl$ because Ag^+ forms a stable complex with ammonia: $[Ag(NH_3)_2]^+$. In addition, Hg_2Cl_2 disproportionates in ammonia.

$$2\,Hg_2^{2+} \rightarrow Hg + Hg^{2+}$$

to form a black solid that is a mixture of finely divided metallic mercury and an insoluble mercury(II) compound, which is separated from solution:

$$Hg_2Cl_2(s) + 2\,NH_3(aq) \rightarrow Hg(l) + Hg(NH_2)Cl(s) + NH_4^+(aq) + Cl^-(aq)$$

Any silver ion in the solution is then detected by adding HCl, which reverses the reaction and gives a precipitate of white $AgCl$ that slowly darkens when exposed to light:

$$[\mathrm{Ag(NH_3)_2}]^+(\mathrm{aq}) + 2\,\mathrm{H}^+(\mathrm{aq}) + \mathrm{Cl}^-(\mathrm{aq}) \rightarrow \mathrm{AgCl(s)} + 2\,\mathrm{NH_4^+(aq)}$$

Similar but slightly more complex reactions are also used to separate and identify the individual components of the other groups.

Summary

In qualitative analysis, the identity, not the amount, of metal ions present in a mixture is determined. The technique consists of selectively precipitating only a few kinds of metal ions at a time under given sets of conditions. Consecutive precipitation steps become progressively less selective until almost all the metal ions are precipitated. Other additional steps are needed to separate metal ions that precipitate together.

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14.3.E: Solubility and Precipitation (Exercises)

These are homework exercises to accompany the Textmap created for "Principles of Modern Chemistry" by Oxtoby et al. Complementary General Chemistry question banks can be found for other Textmaps and can be accessed here.

Q5

State the balanced equation representing the dissolution of potassium chromate and write its solubility product expression.

Answer

$$\mathrm{K_2CrO_4 \rightleftharpoons 2K^+ + CrO_4^{2-}}$$

$$\mathrm{K_{sp} = [K^+]^2[CrO_4^{2-}]}$$

Q11

Consider Mercury(I) bromide. Estimate the concentration of Hg_2^{2+} and Br^- given the K_{sp} as 5.6 x 10^{-23}.

Answer

$$\mathrm{Hg_2Br_2(s) \rightleftharpoons Hg_2^{2+}(aq) + 2\,Br^-(aq)} \tag{14.3.E.1}$$

$$K_{sp} = 5.6 \cdot 10^{-23} = [Hg_2^{2+}][Br^-]^2 = x(2x)^2 \tag{14.3.E.2}$$

$$\mathrm{x = 2.41 \times 10^{-8} = [Hg_2^{2+}]}$$

$$\mathrm{[Br^-] = 4.82 \times 10^{-8}}$$

Q13

The solubility product constant of Calcium chlorate ($Ca(ClO_3)_2$) of water is 7.1 × 10^{-7} at 25°C. How many grams of $Ca(ClO_3)_2$ were dissolved in 750 mL?

Answer

First, write out the solubility product constant expression for $\mathrm{Ca(ClO_3)_2}$

$$\mathrm{Ca(ClO_3)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,ClO_3^-(aq)}$$

$$\mathrm{K_{sp} = [Ca^{2+}][ClO_3^-]^2}$$

ICE Table	$Ca(ClO_3)_2$	Ca^{2+}	ClO_3^-
Initial	-	0	0
Change	-	+x	+2x
Equilibrium	-	x	2x

$Ca(ClO_3)_2$ does not matter because it is a solid

$$\mathrm{K_{sp} = [x] \cdot [2x]^2}$$

$$\mathrm{7.1 \times 10^{-7} = 4x^3}$$

$$\mathrm{x = 0.0056\ M}$$

The number of moles of Ca^{2-} is the same as the number of moles of $Ca(ClO_3)_2$ because matter cannot be created or destroyed.

$$\mathrm{\frac{0.0056\ moles}{L} \times 0.750\ L = 0.0042\ moles\ Ca(ClO_3)_2}$$

Finally, the mass can be calculated by multiplying the number of moles with the molar mass:

$$0.0042 \text{ moles} \text{Ca}(\text{ClO}_3)_2 \times (\frac{206.98 \text{ g}}{1 \text{ mole}}) = 0.872 \text{ g}$$

Q15

At 25°C, water dissolves 0.8108g of $PbCl_2$ per liter, calculate the K_{sp} of $PbCl_2$ at 25°C.

Answer

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$

$$K_{sp} = [Pb^{2+}] \cdot [Cl^-]^2$$

$$n(PbCl_2) = \frac{0.8108g}{278.1g/mol} = 2.9155 \times 10^{-3} mol = n(Pb^{2+}) = 0.5n(Cl^-)$$

$$K_{sp} = \frac{2.9155 \times 10^{-3} mol}{1L} \cdot (\frac{5.831 \times 10^{-3} mol}{1L})^2 = 9.91 \times 10^{-8}$$

Q17

0.986635g of BaCO_3 is dissolved in 1.00dm^3 water at 80°C. the solution was then cooled down to 25°C. Given that the Ksp of BaCO_3 in water is 2.58x10^{-9} at 25°C, determine with an explanation whether or not a precipitate will form at 25°C.

Answer

x moles of BaCO_3 dissolves into x moles of Ba^{2+} and x moles CO_3^{2-} due to equal stoichiometric coefficients (since solution is 1.00L, the moles also equal to molarities). Calculate the moles of BaCO_3, then square the result to find Qsp, then compare Qsp to Ksp at 25^{0}C.

$$\text{moles of } \text{BaCO}_3 = 0.986635 \text{ g} \times (137.327 \frac{\text{g}}{\text{mol}} + 12 \frac{\text{g}}{\text{mol}} + 3 \times 16 \frac{\text{g}}{\text{mol}}) = 5.0 \times 10^{-3} \text{ mol}$$

$$\text{Q}_{\text{sp}} = (5.0 \times 10^{-3} \text{ M})^2 = 2.5 \times 10^{-5}$$

$$2.5 \times 10^{-5} > 2.58 \times 10^{-9}$$

$$\text{Q}_{\text{sp}} > \text{K}_{\text{sp}}$$

Therefore, precipitate forms.

Q19

Suppose that you take a solution of 500.0-mL of 0.001234 M FeF_2 and mix it well with a 500.0-mL solution of 0.003142 M KOH at 25ºC. Given that $\text{K}_{\text{sp}} = 4.87 \times 10^{-17}$ is for $Fe(OH)_2$, determine whether or not a precipitate will be formed from the mixture.

Answer

Before starting any calculations it is important to write down the equation for precipitation of the Fe(OH)_2.

$$\text{Fe(OH)}_2(s) \rightleftharpoons \text{Fe}^{2+}(aq) + 2\,\text{OH}^-(aq)$$

State the solubility product expression and set it equal to the solubility product constant:

$$K_{sp} = [Fe^2+][OH-]^2 = 4.87 \times 10^{-17}$$

Now that the essential basic steps are out of the way, find the new concentrations of both Fe^{2+} Fe^{2+} and OH^- by first finding the number of moles in the original unmixed solutions and then dividing that number by the total new volume in liters.

$$\text{moles Fe}^{2+} = 500 \cancel{mL} \left(\frac{1 \cancel{L}}{1000 \cancel{mL}} \right) \left(\frac{0.001234 \text{ mol}}{1 \cancel{L}} \right) = 6.17 \times 10^{-4} \text{ mol Fe}^{2+}$$

$$[Fe^{2+}] = \left(\frac{6.17 \times 10^{-4} \text{ mol } Fe^{2+}}{1000 \cancel{mL}}\right)\left(\frac{1000 \cancel{mL}}{1 \text{ L}}\right) = 6.17 \times 10^{-4} \text{ M } Fe^{2+}$$

$$\text{moles OH-} = 500 \cancel{mL}\left(\frac{1 \cancel{L}}{1000 \cancel{mL}}\right)\left(\frac{0.003142 \text{ mol}}{1 \cancel{L}}\right) = 1.57 \times 10^{-3} \text{ mol OH-}$$

$$[OH-] = \left(\frac{1.57 \times 10^{-3} \text{ mol OH-}}{1000 \cancel{mL}}\right)\left(\frac{1000 \cancel{mL}}{1 \text{ L}}\right) = 1.57 \times 10^{-3} \text{ M OH-}$$

Now that the new concentrations have been found they can be substituted in the Q_{sp} equation and solved for.

$$Q_{sp} = [6.17 \times 10^{-4}][1.57 \times 10^{-3}]^2 = 1.52 \times 10^{-9}$$

As shown above the $Q_{sp} > K_{sp}$, therefore a precipitate does in fact form.

Q23

The solubility product constant of Ag_2CO_3 is 8.1×10^{-12} at 25°C. Calculate $[Ag^+]$ and $[CO_3^{2-}]$ in the solution at equilibrium when 6 mL of 0.1M Na_2CO_3 are mixed with 3 mL of 0.5M $AgNO_3$.

Answer

$$2AgNO_{3(aq)} + Na_2CO_{3(aq)} \rightleftharpoons Ag_2CO_{3(s)} + 2NaNO_{3(aq)} \tag{14.3.E.3}$$

$$mole_{AgNO_3} = mole_{Ag^+} = (0.003\ L)(0.5\ M) = 1.5 \times 10^{-3}\ mol \tag{14.3.E.4}$$

$$mole_{Na_2CO_3} = mole_{CO_3^{2-}} = (0.006\ L)(0.1\ M) = 6 \times 10^{-4}\ mol \tag{14.3.E.5}$$

$$Total\ Volume = 3\ mL + 6\ mL = 9\ mL = 0.009\ L \tag{14.3.E.6}$$

$$M_{CO_3^{2-}} = \frac{6 \times 10^{-4} mol}{0.009\ L} = 0.0667\ M \tag{14.3.E.7}$$

$$M_{Ag^+} = \frac{1.5 \times 10^{-3}\ mol}{0.009\ L} = 0.1667\ M \tag{14.3.E.8}$$

$$2Ag^+ + CO_3^{2-} \rightarrow Ag_2CO_{3(s)} \tag{14.3.E.9}$$

	$2\,Ag^+$	CO_3^{2-}	Ag_2CO_3
Initial	0.1667M	0.0667M	X
Change	-2x	-x	X
Equilibrium	0.1667-2x	0.0667-x	X

$$K_{sp} = 8.1 \times 10^{-12} = [CO_3^-][Ag^+]^2 \tag{14.3.E.10}$$

$$8.1 \times 10^{-12} = [0.0667 - x][0.1667 - 2x]^2 \tag{14.3.E.11}$$

$$x = 0.06669999M \tag{14.3.E.12}$$

$$[Ag^+] = 0.1667 - 2x = 0.03336M \tag{14.3.E.13}$$

$$[CO_3^{2-}] = 0.0667 - x = 7.30 \times 10^{-9} \tag{14.3.E.14}$$

Q25

Your nemesis has prepared a perfectly saturated solution of CaF_2. To sabotage their work, you add 10 M NaF to their solution. How many grams of CaF_2 fall out of solution if they had prepared 500 mL.

CaF_2 : $K_{sp} = 4.0 \times 10^{-11}$

Answer

First, calculate the molar solubility of CaF_2 from it's K_{sp} with the expression:

$$K_{sp} = (s)(2s)^2 = 4s^3$$

$$4.0 \times 10^{-11} = 4s^3$$

$$s = 2.15 \times 10^{-4}$$

Then, create an ICE table for the addition of F^- as NaF:

Products	F^-	Ca^{2+}
Initial	s+10	s
Change	-2x	-x
Equilibrium	(s+10) -2x	s-x

Now, it's reasonable to assume that 10>>x and s, so our expression simplifies to:

$$K_{sp} = 10^2(s-x)$$

Solving for x yields the moles/L which fall out, so multiplying x by 0.5 L (500 mL) yields the correct answer.

$$K_{sp} = 4.0 \times 10^{-11} = 10^2(s-x)$$

$$x = 0.000215\ M$$

$$0.5\ L(0.000215\ M)(78.07\ \frac{g}{mol}) = 0.00839\ g$$

Q27

Given copper(II) hydroxide, $Cu(OH)_2$. The concentration of Cu^{2+} and OH^- at equilibrium in 25°C water is 1.765 x 10^{-7}M and 3.530 x 10^{-7}M respectively.

a. Find the K_{sp}.
b. Find the molar solubility of $Cu(OH)_2$ in 0.100M NaOH.

Answer

$$Cu(OH)_{2(s)} \rightleftharpoons Cu^{2+}_{(aq)} + 2OH^-_{(aq)} \tag{14.3.E.15}$$

1)

Since the solubilities given are already at equilibrium, K_{sp} is found as such:

$$K_{sp} = [Cu^{2+}][OH^-]^2 = (1.765 \times 10^{-7}M)(3.530 \times 10^{-7}M)^2 = 2.2 \times 10^{-20} \tag{14.3.E.16}$$

2)

ICE Table	$Cu(OH)_{2(s)}$	$Cu^{2+}_{(aq)}$	$OH^-_{(aq)}$
Initial	-	0	0.100
Change	-	+Z	+2Z
Equilibrium	-	Z	0.100+2Z

Apply the ice table result to the K_{sp} found in 1), we get

$$K_{sp} = 2.2 \times 10^{-20} = [Cu^{2+}][OH^-]^2 = (z)(0.100+2z)^2 \tag{14.3.E.17}$$

Z can be found either by plugging in quadratic formula or finding intersection in a graphing calculator.

$$K_{sp} = 2.2 \times 10^{-20} = (z)(0.100 + 2z)^2 \tag{14.3.E.18}$$

$$\text{z} = 2.2 \times 10^{-18}\ \text{M}$$

Q28

Barium Carbonate ($BaCO_3$) has a solubility product of K_{sp} = 8.1 x 10^{-9} at 25°C for the equilibrium

$$BaCO_3 \rightleftharpoons Ba^{2+} + CO_3^{2-}$$

a. Calculate the molar solubility of Barium Carbonate in the water at 25°C.
b. Calculate the molar solubility of Barium Carbonate in 0.1M $PbCO_3$.

Answer

a) The expression for solubility product is

$$[Ba^{2+}][{CO_3}^{2-}] = K_{sp} \tag{14.3.E.19}$$

Let

$$[Ba^{2+}] = S \tag{14.3.E.20}$$

$$S^2 = K_p = 8.1 \times 10^{-9} \tag{14.3.E.21}$$

Hence, S = 9 x 10^{-5}

Molar Solubility of Barium Carbonate = 9 x 10^{-5} M

b) due to the common ion effect, $PbCO_3$ reduces the molar solubility of Barium Carbonate.

$$BaCO_3 \rightleftharpoons Ba^{2+} \quad + \quad CO_3^{2-} \tag{14.3.E.22}$$

	Ba^{2+}	CO_3^{2-}
Initial	0	0.1
Change	+S	+S
Final	+S	0.1+S

$$[Ba^{2+}][{CO_3}^{2-}] = K_{sp} \tag{14.3.E.23}$$

$$S(0.1 + S) = K_{sp} \tag{14.3.E.24}$$

$$S + 0.1 \approx 0.1 \tag{14.3.E.25}$$

⇒

$$S(0.1) = K_{sp} \tag{14.3.E.26}$$

⇒

$$S = \frac{8.1 \times 10^{-9}}{0.1} = 8.1 \times 10^{-8} \tag{14.3.E.27}$$

⇒

$$S = 8.1 \times 10^{-8} << 0.1 \tag{14.3.E.28}$$

Hence, Molar Solubility = 8.1 x 10^{-8} M

Q33

Determine how will the solubility of the following compounds change (increase, decrease, or unchanged) if the neutral solution is made to be more acidic. Explain your answer in one sentence.

a. NO_3^-
b. NH_3
c. CO_3^{2-}

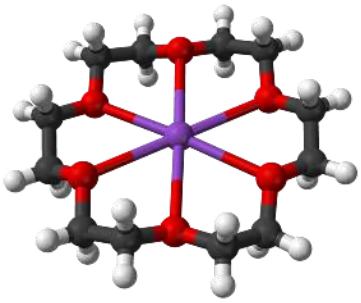
Answer

As the acidity of a solution increases, the solubility of salts consist of conjugate bases of weak acids will increases.

a. NO_3^- is the conjugate base of a strong acid so the solubility will not change
b. NH_3 is the conjugate base of a weak acid so the solubility will increase
c. CO_3^{2-} is also a conjugate base of a weak acid so the solubility will increase

Q37

18-crown-6, or $C_{12}H_{24}O_6$, is an organic compound that can bind to group 1 metal ions by wrapping around them when in aqueous solutions. Due to its particular size, it can fit the K^+ ion better than any other.



Ball-and-stick model of the 18-crown-6 potassium complex in crystalline (18-crown-6)potassium chlorochromate, [K($C_{12}H_{24}O_6$)] [$CrClO_3$]. X-ray diffraction data from S. A. Kotlyar, R. I. Zubatyuk, O. V. Shishkin, G. N. Chuprin, A. V. Kiriyak and G. L. Kamalov (February 2005). "(18-Crown-6)potassium chlorochromate". Acta. Cryst. ***E61*** *(2): m293-m295. DOI:10.1107/S1600536805000085. (Public domain; Ben Mills).*

This physical property can be seen in the equilibrium constants for 18-crown-6 and various alkali metals:

$$Na^+_{(aq)} + C_{12}H_{24}O_{6\ (aq)} \rightarrow Na{-}crown^+_{(aq)}$$

K = 6.6

$$K^+_{(aq)} + C_{12}H_{24}O_{6\ (aq)} \rightarrow K{-}crown^+_{(aq)}$$

K = 111.6

$$Rb^+_{(aq)} + C_{12}H_{24}O_{6\ (aq)} \rightarrow Rb{-}crown^+_{(aq)}$$

K = 36

If an aqueous solution is made that is 0.006 M in both 18-crown-6 and Rb^+, what is the concentration of unbound Rb^+ at equilibrium? If the same solution is made, but with K^+ instead of Rb^+ ions, what is the concentration of unbound K+ ions at equilibrium?

Answer

First, construct an ICE table.

$$Rb^+_{aq} + C_{12}H_{24}O_{6\ (aq)} \rightleftharpoons Rb{-}crown^+_{aq}$$

	Rb^+	$C_{12}H_{24}O_6$	Rb-crown+
I	0.006	0.006	0
C	-x	-x	+x

	Rb^+	$C_{12}H_{24}O_6$	Rb-crown+
E	0.006-x	0.006-x	x

Then, use the K value of the reaction to solve for x. Use x to solve for the concentration of the desired ion.

$$K = \frac{[Rb-crown+]}{[Rb+][C_{12}H_{24}O_6]}$$

$$36 = \frac{[x]}{[0.006-x][0.006-x]}$$

$$x = 9.2954 \times 10^{-4}$$

$$[Rb^+] = 0.0507M$$

Repeat this process for the other reaction.

$$\mathrm{K^+_{aq} + C_{12}H_{24}O_{6\ (aq)} \rightleftharpoons K{-}crown^+_{aq}}$$

	K^+	$C_{12}H_{24}O_6$	**K-crown+**
I	0.006	0.006	0
C	-x	-x	+x
E	0.006-x	0.006-x	x

$$K = \frac{[K-crown^+]}{[K^+][C_{12}H_{24}O_6]}$$

$$111.6 = \frac{[x]}{[0.006-x][0.006-x]}$$

$$x = 0.0019$$

$$[K^+] = 0.0041M$$

Q39

Is it easier to dissolve CuBr into 1M of NaBr solution than to dissolve it into pure water? Does the answer change if when the concentration of NaBr is 0.5M?

Answer

1. When CuBr is added into NaBr solution, the common ion effect occurs. Common ion effect explains that the solvent is responsible for the decrease in the solubility of the precipitate when the soluble compound contains one of the ions of the precipitate that is added to the solution in equilibrium. According to Le Chatelier's principle, some of the ions in excess should be removed from the solution. So it is harder to dissolve CuBr into NaBr solution than dissolve it into pure water.

2. If the concentration is changed to 0.5M, it is still harder to dissolve CuBr in NaBr solution, but less difficult.

Q41

Identify the salt $\mathrm{NH_4F}$ as either acidic, basic, or neutral. Then explain the mechanism behind why the salt is acidic, basic, or neutral using chemical equations and their $\mathrm{K_a}$ or $\mathrm{K_b}$ values provided here and here.

Answer

- For a salt to have an acidic character, it must be able to accept $\mathrm{OH^-}$ ions when it dissociates in an aqueous solution and leave an excess of $\mathrm{H^+}$ in the solution to have an acidic effect.
- For a salt to have a basic character, it must be able to either accept an $\mathrm{H^+}$ when it dissociates in an aqueous solution and leave an excess of $\mathrm{OH^-}$ in the solution to have an basic effect.

NH_4F can be classified as either acidic or basic depending upon which species is present in a greater concentration (H^+ or OH^-) in the solution when NH_4F is added.

$$NH^+_{4\,(aq)} + F^-_{(aq)} + H_2O_{(l)} \rightleftharpoons NH_{3\,(aq)} + HF_{(aq)} + H_3O^+_{(aq)} + OH^-_{(aq)}$$

$$Ka = 5 \cdot 6 \times 10^{-10} \text{ for } NH^+_{4\,(aq)} + H_2O_{(1)} \rightleftharpoons NH_{3\,(aq)} + H_3O^+_{(aq)}$$

$$Kb = 1 \cdot 6 \times 10^{-11} \text{ for } F^-_{(aq)} + H_2O_{(1)} \rightleftharpoons HF_{(aq)} + OH^-_{(aq)}$$

Since $K_a > K_b$, NH_4^+ has a greater affect on the solution and therefore the salt is acidic.

** See key for problem 15.23 on how to calculate K_b or K_a given K_a or K_b

Q43

For the complex ion, $Fe(H_2O)^{3+}_{6(aq)}$, the acid ionization constant for 298K is 7.7×10^{-3}. What is the pH of a 50 mL solution that contains 0.02 mols of $Fe(NO_3)_2$?

Answer

Complex ion problems are solved identically to other equilibrium problems.

First, write the balanced equation:

$$[Fe(H_2O)_6]^{3+}_{(aq)} + H_2O_{(aq)} \rightleftharpoons [Fe(H_2O)_5OH]^{2+}_{(aq)} + H_3O^+_{(aq)}$$

Then, create and solve an ICE table.

$[Fe(H_2O)_6]^{3+}$	H_2O	H_3O^{3+}	$[Fe(H_2O)_5OH]^{2+}$
0.40	-	0	0
-x	-	+x	+x
0.40-x	-	x	x

From the ICE table:

$$K_a = \frac{[H_3O^{3+}][Fe(H_2O)_5OH^{2+}]}{[Fe(H_2O)^{3+}_6]}$$

$$7.7 \times 10^{-3} = K_a = \frac{[x]\,[x]}{[0.4 - x]}$$

By rearranging the equation:

$$x^2 + 0.0077x - 0.00308 = 0$$

and using the quadratic,

$$\frac{-0.0077 \pm \sqrt{0.0077^2 - 4\,(1)\,(-0.00308)}}{2}$$

$$x = 0.05178$$

$$pH = -\log[H_3O^+] = 1.286$$

Q45

Calculate the concentration of H_3O^+ in a 0.3 M solution of oxalic acid ($pK_{a1} = 1.25; pK_{a2} = 3.81$).

Answer

$K_a = 10^{-1.25} = 0.0562$

Balanced equation:

$$C_2H_2O_4 + H_2O \rightleftharpoons C_2HO_4^- + H_3O^+$$

	$C_2H_2O_4$	$C_2HO_4^-$	H_3O^+
I	0.3	0	0
C	-x	+x	+x
E	0.3-x	x	x

At equilibrium:

$$\frac{(x)^2}{(0.3-x)} = K_{a1}$$

$$x = 0.1048$$

Balanced equation:

$$C_2HO_4^- + H_2O \rightleftharpoons C_2O_4^{2-} + H_3O^+$$

	$C_2HO_4^-$	$C_2O_4^{2-}$	H_3O^+
I	0.1048	0	0.1048
C	-x	+x	+x
E	0.1048-x	x	x+0.1048

At equilibrium:

$$K_{a2} = 10^{-3.81}$$

$$\frac{x(x+0.1048)}{(0.1048-x)} = K_{a2}$$

$$x = 0.000154$$

$$[H_3O^+] = 0.1048 + 0.000154 \text{ M} = 0.105 \text{ M}$$

Q49

An aqueous solution at 25 °C is 0.10 M in both Ba^{2+} and Ca^{2+} ions. One wants to separate the two ions by taking advantage of the different solubility of $BaCO_3$ and $CaCO_3$.

$BaCO_3$ $K_{sp} = 2.58 \times 10^{-9}$ M

$CaCO_3$ $K_{sp} = 3.36 \times 10^{-9}$ M

What is the highest possible CO_3^{2-} concentration that allows only one salt to present at equilibrium? Which ion is present in the solid, Ba^{2+} or Ca^{2+}?

Answer

$$BaCO_{3(s)} \leftrightharpoons Ba^{2+}_{(aq)} + CO^{2-}_{3(aq)}$$

$$[CO_3^{2-}] < \frac{K_{sp}}{[Ba^{2+}]} = \frac{2.58 \times 10^{-9}}{0.1 \text{ M}} = 2.58 \times 10^{-8} \text{ M (Using the formula for } K_{sp})$$

$$CaCO_{3(s)} \rightleftharpoons Ca^{2+}_{(aq)} + CO^{2-}_{3(aq)}$$

$$[\mathrm{CO_3^{2-}}] < \frac{\mathrm{K_{sp}}}{[\mathrm{Ca^{2+}}]} = \frac{3.36 \times 10^{-9}}{0.1\ \mathrm{M}} = 3.36 \times 10^{-8}\ \mathrm{M}$$

Therefore, the highest possible CO_3^{2-} concentration that allows only one salt to present at equilibrium is 2.58×10^{-8} M. Ba^{2+} is present in the solid.

Q51

A solution was created by dissolving 1.31 kg of $Ba(NO_3)_2$ into 1 L of 0.50 M $Ca(NO_3)_2$. Determine which molecule is more soluble. Then determine the concentration of SO_4 ion is needed to precipitate all of one molecule but leave the other molecule completely unreacted, use Table E3.

Answer

First we must determine the mass action equation for dissolving the salts:

$$\mathrm{K_{sp}} = [\mathrm{Ba^+}][\mathrm{SO_4^-}] = 1.08 \times 10^{-10}$$

$$\mathrm{K_{sp}} = [\mathrm{Ca^+}][\mathrm{SO_4^-}] = 4.93 \times 10^{-5}$$

We will use $CaSO_4$ as the salt because it is the most soluble.

For Ca^+ to to remain in solution, its reaction quotient must remain smaller than then its K_{sp}:

$$\mathrm{Q} = [\mathrm{Ca^+}][\mathrm{SO_4^-}] < 4.93 \times 10^{-5}$$

Now we just need to impute the concentration of Ca^+ and solve for the concentration of SO_4 ion:

$$[0.5\ \mathrm{M}][\mathrm{SO_4^-}] < 4.93 \times 10^{-5}$$

$$[\mathrm{SO_4^-}] < 9.86 \times 10^{-5}\ \mathrm{M}$$

So as long as the concentration of SO_4 ion is smaller than 9.86 x 10^{-5} M, no $CaSO_4$ will precipitate

Q55

Let's say you have a solution that is saturated with HF at a concentration of $[HF] = 0.20M$.

a. If you want some element X whose concentration is equal to 0.20 M to exist entirely in this solution, what will be the highest pH possible for this mixture? ($K_a\ of\ HF\ is\ 6.6 \times 10^{-4}$ and $K\ of\ XF(s) = 2.5 \times 10^{-16}$) . Hint: the reaction is given as $XF(s) + H_2O(l) \leftrightharpoons X(aq) + F^-(aq) + OH^-(aq)$
b. What would be the concentration of some element G in equilibrium with solid GF in this solution at the pH value found in part a) given that $K\ of\ GF(s) = 4.9 \times 10^{-22}$) .

Answer

Part a)

Since you have the equation $XF(s) + H_2O(l) \leftrightharpoons X(aq) + F^-(aq) + OH^-(aq)$, the equilibrium constant K will be equal to

$$K = [X]\ [F^-]\ [OH^-] = 2.5 \times 10^{-16}$$

We now replace these variables above with known derived equations

$$K = [X]\left(\frac{[K_a][HF]}{[H_3O^+]}\right)\left(\frac{[K_w]}{[H_3O^+]}\right) = 2.5 \times 10^{-16}$$

Plug in known values and solve for $[H_3O^+]$

$$[H_3O^+] = \sqrt{\frac{(0.20)\ (6.6 \times 10^{-4})\ (0.20)\ (1.0 \times 10^{-14})}{2.5 \times 10^{-16}}}$$

$$[H_3O^+] = 0.0325\ M$$

Now we solve for pH and see that

$$pH = -log(0.0325) = 1.50$$

Part b)

For part b), we solve the question in a very similar manner as used in part a) with the only differences being a few different variables we plug in. Now, we are solving for our concentration of some element G using the value of H_3O^+ we found above.

Given the reaction $GF(s) + H_2O(l) \leftrightharpoons G(aq) + F^-(aq) + OH^-(aq)$, the equilibirum constant K will be equal to

$$K = [G]\ [F^-]\ [OH^-] = 4.90 \times 10^{-22}$$

We now replace these variables above with known derived equations and this time, solve for $[G]$ using the $[H_3O^+]$ value found above

$$K = [G]\ (\frac{[K_a][HF]}{[H_3O^+]})\ (\frac{[K_w]}{[H_3O^+]}) = 4.9 \times 10^{-22}$$

$$[G] = 3.92 \times 10^{-7}\ M$$

Q63

200 mL of 0.5M NaCl and 800 mL of 0.10M $AgNO_3$ are mixed together. Calculate the mass of $NaNO_3$ precipitated. Assume:

- that the volumes are additive,
- that AgCl is completely insoluble, and
- any other substances that may form are completely soluble.

Answer

Because NaCl and $AgNO_3$ are strong electrolytes, they dissolve in water by dissociation.
$NaNO_3$ precipitates according to the net ionic equation

$$Na^+_{(aq)} + NO^-_{3(aq)} \rightarrow NaNO_{3(s)}$$

First calculate the moles of each ion present.

$$n_{Na^+} = 0.2L \times 0.5M = 0.1molNa^+$$

$$n_{NO_3^-} = 0.8L \times 0.1M = 0.08molNO_3^-$$

Assuming that $NaNO_3$ is completely insoluble, the reaction continues until the entire 0.08 mol of NO_3^- is consumed, which is the limiting reactant, creating 0.08 mol $NaNO_3$.

$$0.08\ mol\ NaNO_3(84.99\frac{g}{mol}) = 6.80\ g\ NaNO_3$$

Q69

Siobhan has a $1L$ solution with containing $0.050M$ of $CO^{2-}_{3\ (aq)}$ and $0.100M$ of $F^-_{(aq)}$. She titrates the solution with a 0.100 M titrand of Iron Iodide, FeI_2. The K_{sp} expressions are:

$$FeCO_{3\ (s)} \rightleftharpoons CO^{2-}_{3\ (aq)} + Fe^{2+}_{(aq)}\ \ K_{sp} = 3.13 \times 10^{-11}$$

$$FeF_{2\ (s)} \rightleftharpoons 2F^-_{(aq)} + Fe^{2+}_{(aq)}\ \ K_{sp} = 2.36 \times 10^{-6}$$

At what volume of iron iodide will the precipitate $FeCO_{3\ (s)}$ appear? How about $FeF_{2\ (s)}$?

Answer

This problem primarily focuses on expanding on how the solubility constant K_{sp} can predict which solution will titrate first. When Iron Iodide is dripped into the solution, it disassociates into Iron(II) and Iodide Ions.

$$FeI_2 \rightarrow Fe^{2+}_{(aq)} + 2I^-_{aq}$$

This facilitates a "common ion effect", where the ions from the dissolution of the titrand Iron Iodide contribute to shifting the concentration of the other two reactions:

$$FeCO_{3\,(s)} \rightleftharpoons CO^{2-}_{3\,(aq)} + Fe^{2+}_{(aq)}$$

$$FeF_{2\,(s)} \rightleftharpoons 2F^{-}_{(aq)} + Fe^{2+}_{(aq)}$$

As seen here, the introduction of Fe^{2+} ions will mean there is a larger iron ion concentration, which shifts both of the above reactions to the left. This concept that explains this phenomena is colloquially known as Le Chatlier's principle. However, in order to precisely determine at what point precipitate will form, the K_{sp} values need to be taken into consideration. Recall that the K constant is defined in terms of either concentrations or partial pressures. As the species in this problem are only aqueous solutes and not gaseous compounds, the resulting K_{sp} will be defined by concentrations as depicted below:

$$FeCO_{3\,(s)} \rightleftharpoons CO^{2-}_{3\,(aq)} + Fe^{2+}_{(aq)} \quad K_{sp} = \frac{\left[CO^{2-}_{3}\right]\left[Fe^{2+}\right]}{1} = 3.13 \times 10^{-11}$$

$$FeF_{2\,(s)} \rightleftharpoons 2F^{-}_{(aq)} + Fe^{2+}_{(aq)} \quad K_{sp} = \frac{\left[F^{-}\right]^2\left[Fe^{2+}\right]}{1} = 2.36 \times 10^{-6}$$

Notice that each K_{sp} is divided by 1. This is to represent the solid reactants. Also, based on the information above, recognize that, at equilibrium, the product of the concentrations of the two ions should equal to thier K_{sp}, and since the problem provided both $\left[CO^{2+}_{3}\right]$ and $\left[F^{-}\right]$. By substituting these concentrations into the respective K_{sp} formulas, the equations can be algebraically manipulated to provide the $\left[Fe^{2+}\right]$ at equilibrium. This process is seen below for $FeF_{2\,s}$. The process is basically the same to finding $\left[Fe^{2+}\right]$ for $\left[CO^{2+}_{3}\right]$, but there is no need to square root the value since there is no stoichiometric coefficients for that particular equation. In contrast, F^{-} has a stoichiometric coefficient of 2). Since only initial concentrations were given, we can determine at which point $Q_{sp} > K_{sp}$

$$Q_{sp} = \frac{\left[F^{-}\right]^2\left[Fe^{2+}\right]}{1} = 2.36 \times 10^{-6}$$

$$Q_{sp} = (0.05M)^2\left[Fe^{2+}\right] = 2.36 \times 10^{-6}$$

$$\left[Fe^{2+}\right] = \frac{2.36 \times 10^{-6}}{(0.100M^2)} = 2.36 \times 10^{-4}M$$

Therefore, $\left[Fe^{2+}\right]$ for $FeF_2 = 2.36 \times 10^{-4}M$

And $\left[Fe^{2+}\right]$ for $FeCO_3 = 6.26 \times 10^{-10}M$, using the same method.

What this information tells us is the calculated $\left[Fe^{2+}\right]$ is the concentration of Fe^{2+} that one would expect to be in equilibrium at the given concentration of the other ion. Therefore, if $\left[Fe^{2+}\right]$ is higher than this value, then the resulting reaction quotient will be larger than K_{sp}, causing the reaction to shift towards the product and consequently causing the precipitate to form. From the values, it is clear that $FeCO_{3\,(s)}$ will end up precipitating first, and then $FeF_{2\,s}$.

Finding the exact volume that the precipitate for each reaction will form is relatively straightforward. Based on the information overviewed before, after the $\left[Fe^{2+}\right]$ reaches the calculated point, precipitate will form. Therefore, to find the volume of titrant needed, just set up the following equation:

$$molarity_{titrant} \times V_{titrant} = mol_{titrant} = mol_{Fe^{2+}toprecipitate}$$

$$0.100M \times V_{titrant} = \left(6.26 \times 10^{-10}M\right)(1L)$$

$$0.100M \times V_{titrant} = 6.26 \times 10^{-10}mol$$

$$V_{titrant} = \frac{6.26 \times 10^{10}mol}{0.100M}$$

$V_{titrant} = 6.26 \times 10^{-9}L$ for $FeCO_{3\,(s)}$ precipitate to form.

Via the same process, $V_{titrant} = 0.00236L$for $FeF_{2\,(s)}$ to form.

Abstract: Use K_{sp} to determine Q_{sp} concentration $\left[Fe^{2+}\right]$. Divide by molarity of titrant to get desired volume for precipitate to form.

Q73

Complex ion plays an important role in the level of solubility. For example:

$$Hg^{2+}_{(aq)} + 2I^{-}_{(aq)} \rightleftharpoons HgI_{2(s)}$$

This reaction results in the formation of solid HgI_2. However, when solid HgI_2 reacts in the same process:

$$HgI_{2(s)} + I^{-}_{(aq)} \rightleftharpoons HgI^{-}_{3(aq)}$$

The solubility increases greatly and the reaction results in an aqueous product. Explain this phenomenon.

Answer

The first reaction produces a solid precipitate and the second reaction is soluble because complex ions are created in the reaction. HgI^{-}_{3} is a complex ion, which means it has Hg ion in the center that is surrounded by iodine molecules that are able to act as Lewis bases and attract the protons of the Lewis acid in the reaction. These properties are brought out as a result of the reaction and result in an aqueous product.

Q73

Why does the inclusion of NH_3 increase the solubility of $CuCl_2$ in an aqueous solution?

Answer

The solubility of Cu^{2+} increases when NH_3 present because NH_3 forms a complex ion with Cu^{2+}. The corresponding the chemical reaction for is as follows,

$$\mathrm{CuCl_{2(s)} \rightleftharpoons Cu^{2+}_{(aq)} + 2Cl^{-}_{(aq)} + 4NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_4]^{2+}}$$

The formation of the complex ion pulls equilibrium towards the right which allows more $CuCl_2$ to dissolve.

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CHAPTER OVERVIEW

15: Chemical Kinetics

An General Chemistry Libretexts Textmap organized around the textbook

Principles of Modern Chemistry

by Oxtoby, Gillis, and Campion

Template:HideTOC

This chapter will present a quantitative description of when the chemical composition of a system is *not* constant with time. Chemical kinetics is the study of reaction rates, the changes in the concentrations of reactants and products with time. With a discussion of chemical kinetics, the reaction rates or the changes in the concentrations of reactants and products with time are studied. The techniques you are about to learn will enable you to describe the speed of many such changes and predict how the composition of each system will change in response to changing conditions. As you learn about the factors that affect reaction rates, the methods chemists use for reporting and calculating those rates, and the clues that reaction rates provide about events at the molecular level.

15.1: Rates of Chemical Reactions
15.2: Rate Laws
15.3: Reaction Mechanisms
15.4: Effect of Temperature on Reaction Rates
15.5: A Deeper Look- Reaction Dynamics
15.6: Kinetics of Catalysis

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15.1: Rates of Chemical Reactions

Learning Objectives

- To determine the reaction rate of a reaction.

Reaction rates are usually expressed as the concentration of reactant consumed or the concentration of product formed per unit time. The units are thus moles per liter per unit time, written as M/s, M/min, or M/h. To measure reaction rates, chemists initiate the reaction, measure the concentration of the reactant or product at different times as the reaction progresses, perhaps plot the concentration as a function of time on a graph, and then calculate the change in the concentration per unit time.

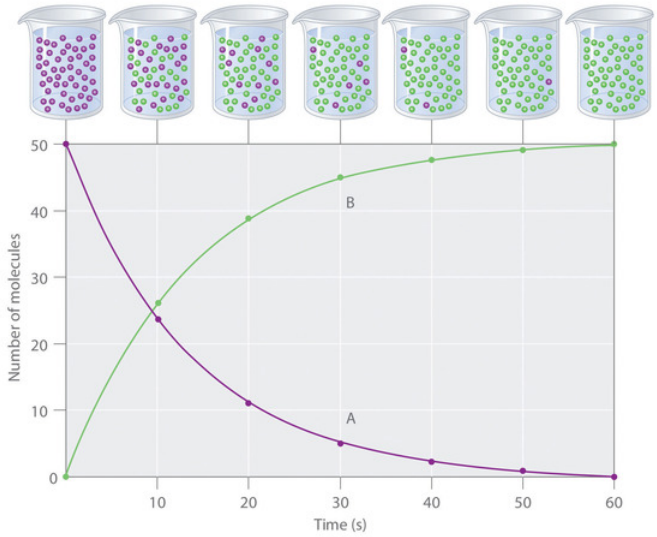


Figure 15.1.1: The Progress of a Simple Reaction (A → B). The mixture initially contains only A molecules (purple). Over time, the number of A molecules decreases and more B molecules (green) are formed (top). The graph shows the change in the number of A and B molecules in the reaction as a function of time over a 1 min period (bottom).

The progress of a simple reaction (A → B) is shown in Figure 15.1.1; the beakers are snapshots of the composition of the solution at 10 s intervals. The number of molecules of reactant (A) and product (B) are plotted as a function of time in the graph. Each point in the graph corresponds to one beaker in Figure 15.1.1. The reaction rate is the change in the concentration of either the reactant or the product over a period of time. The concentration of A decreases with time, while the concentration of B increases with time.

$$\text{rate} = \frac{\Delta[\text{B}]}{\Delta t} = -\frac{\Delta[\text{A}]}{\Delta t} \tag{15.1.1}$$

Square brackets indicate molar concentrations, and the capital Greek delta (Δ) means “change in.” Because chemists follow the convention of expressing all reaction rates as positive numbers, however, a negative sign is inserted in front of Δ[A]/Δt to convert that expression to a positive number. The reaction rate calculated for the reaction A → B using Equation 15.1.1 is different for each interval (this is not true for every reaction, as shown below). A greater change occurs in [A] and [B] during the first 10 s interval, for example, than during the last, meaning that the reaction rate is greatest at first.

> *Reaction rates generally decrease with time as reactant concentrations decrease.*



A Video Discussing Average Reaction Rates. Video Link: Introduction to Chemical Reaction Kinetics(opens in new window) [youtu.be] (opens in new window)

Determining the Reaction Rate of Hydrolysis of Aspirin

We can use Equation 15.1.1 to determine the reaction rate of hydrolysis of aspirin, probably the most commonly used drug in the world (more than 25,000,000 kg are produced annually worldwide). Aspirin (acetylsalicylic acid) reacts with water (such as water in body fluids) to give salicylic acid and acetic acid, as shown in Figure 15.1.2

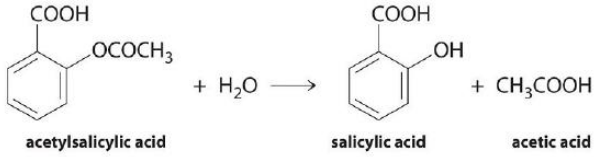


Figure 15.1.2: Hydrolysis of Aspirin reaction.

Because salicylic acid is the actual substance that relieves pain and reduces fever and inflammation, a great deal of research has focused on understanding this reaction and the factors that affect its rate. Data for the hydrolysis of a sample of aspirin are in Table 15.1.1 and are shown in the graph in Figure 15.1.3

Table 15.1.1: Data for Aspirin Hydrolysis in Aqueous Solution at pH 7.0 and 37°C*

Time (h)	[Aspirin] (M)	[Salicylic Acid] (M)
0	5.55×10^{-3}	0
2.0	5.51×10^{-3}	0.040×10^{-3}
5.0	5.45×10^{-3}	0.10×10^{-3}
10	5.35×10^{-3}	0.20×10^{-3}
20	5.15×10^{-3}	0.40×10^{-3}
30	4.96×10^{-3}	0.59×10^{-3}
40	4.78×10^{-3}	0.77×10^{-3}
50	4.61×10^{-3}	0.94×10^{-3}
100	3.83×10^{-3}	1.72×10^{-3}
200	2.64×10^{-3}	2.91×10^{-3}
300	1.82×10^{-3}	3.73×10^{-3}

*The reaction at pH 7.0 is very slow. It is much faster under acidic conditions, such as those found in the stomach.

The data in Table 15.1.1 were obtained by removing samples of the reaction mixture at the indicated times and analyzing them for the concentrations of the reactant (aspirin) and one of the products (salicylic acid).

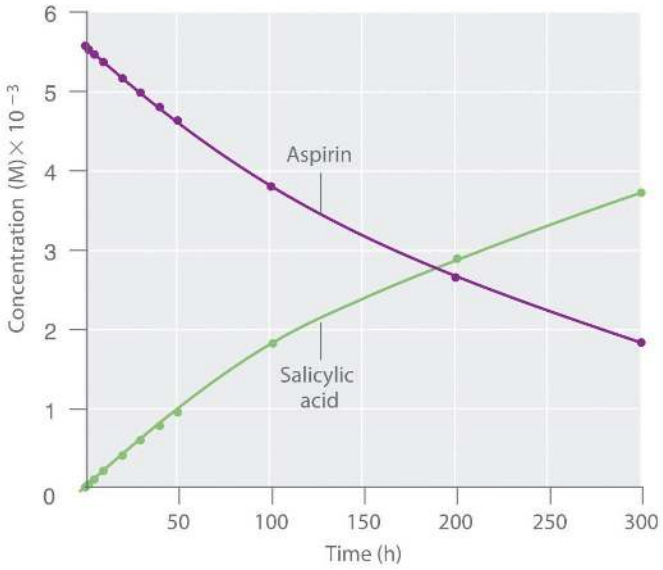


Figure 15.1.3: The Hydrolysis of Aspirin. This graph shows the concentrations of aspirin and salicylic acid as a function of time, based on the hydrolysis data in Table 14.1. The time dependence of the concentration of the other product, acetate, is not shown, but based on the stoichiometry of the reaction, it is identical to the data for salicylic acid.

Graph of concentration against time in hours. The purple line is aspirin. The green line is salicylic acid.

The **average reaction rate** for a given time interval can be calculated from the concentrations of either the reactant or one of the products at the beginning of the interval (time = t_0) and at the end of the interval (t_1). Using salicylic acid, the reaction rate for the interval between t = 0 h and t = 2.0 h (recall that change is always calculated as final minus initial) is calculated as follows:

$$\begin{aligned}\text{rate}_{(t=0-2.0\text{ h})} &= \frac{[\text{salicyclic acid}]_2 - [\text{salicyclic acid}]_0}{2.0\text{ h} - 0\text{ h}} \\ &= \frac{0.040 \times 10^{-3}\text{ M} - 0\text{ M}}{2.0\text{ h}} = 2.0 \times 10^{-5}\text{ M/h}\end{aligned}$$

The reaction rate can also be calculated from the concentrations of aspirin at the beginning and the end of the same interval, remembering to insert a negative sign, because its concentration decreases:

$$\begin{aligned}\text{rate}_{(t=0-2.0\text{ h})} &= -\frac{[\text{aspirin}]_2 - [\text{aspirin}]_0}{2.0\text{ h} - 0\text{ h}} \\ &= -\frac{(5.51 \times 10^{-3}\text{ M}) - (5.55 \times 10^{-3}\text{ M})}{2.0\text{ h}} \\ &= 2 \times 10^{-5}\text{ M/h}\end{aligned}$$

If the reaction rate is calculated during the last interval given in Table 15.1.1 (the interval between 200 h and 300 h after the start of the reaction), the reaction rate is significantly slower than it was during the first interval (t = 0–2.0 h):

$$\begin{aligned}\text{rate}_{(t=200-300\text{h})} &= \frac{[\text{salicyclic acid}]_{300} - [\text{salicyclic acid}]_{200}}{300\text{ h} - 200\text{ h}} \\ &= -\frac{(3.73 \times 10^{-3}\text{ M}) - (2.91 \times 10^{-3}\text{ M})}{100\text{ h}} \\ &= 8.2 \times 10^{-6}\text{ M/h}\end{aligned}$$

Calculating the Reaction Rate of Fermentation of Sucrose

In the preceding example, the stoichiometric coefficients in the balanced chemical equation are the same for all reactants and products; that is, the reactants and products all have the coefficient 1. Consider a reaction in which the coefficients are not all the same, the fermentation of sucrose to ethanol and carbon dioxide:

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \rightarrow 4C_2H_5OH(aq) + 4CO_2(g) \tag{15.1.2}$$

The coefficients indicate that the reaction produces four molecules of ethanol and four molecules of carbon dioxide for every one molecule of sucrose consumed. As before, the reaction rate can be found from the change in the concentration of any reactant or product. In this particular case, however, a chemist would probably use the concentration of either sucrose or ethanol because gases are usually measured as volumes and, as explained in Chapter 10, the volume of CO_2 gas formed depends on the total volume of the solution being studied and the solubility of the gas in the solution, not just the concentration of sucrose. The coefficients in the balanced chemical equation tell us that the reaction rate at which ethanol is formed is always four times faster than the reaction rate at which sucrose is consumed:

$$\frac{\Delta[C_2H_5OH]}{\Delta t} = -\frac{4\Delta[\text{sucrose}]}{\Delta t} \tag{15.1.3}$$

The concentration of the reactant—in this case sucrose—*decreases* with time, so the value of Δ[sucrose] is negative. Consequently, a minus sign is inserted in front of Δ[sucrose] in Equation 15.1.3 so the rate of change of the sucrose concentration is expressed as a positive value. Conversely, the ethanol concentration *increases* with time, so its rate of change is automatically expressed as a positive value.

Often the reaction rate is expressed in terms of the reactant or product with the smallest coefficient in the balanced chemical equation. The smallest coefficient in the sucrose fermentation reaction (Equation 15.1.2) corresponds to sucrose, so the reaction rate is generally defined as follows:

$$\text{rate} = -\frac{\Delta[\text{sucrose}]}{\Delta t} = \frac{1}{4}\left(\frac{\Delta[C_2H_5OH]}{\Delta t}\right) \tag{15.1.4}$$

Example 15.1.1: Decomposition Reaction I

Consider the thermal decomposition of gaseous N_2O_5 to NO_2 and O_2 via the following equation:

$$2N_2O_5(g) \xrightarrow{\Delta} 4NO_2(g) + O_2(g)$$

Write expressions for the reaction rate in terms of the rates of change in the concentrations of the reactant and each product with time.

Given: balanced chemical equation

Asked for: reaction rate expressions

Strategy:

A. Choose the species in the equation that has the smallest coefficient. Then write an expression for the rate of change of that species with time.

B. For the remaining species in the equation, use molar ratios to obtain equivalent expressions for the reaction rate.

Solution

A Because O_2 has the smallest coefficient in the balanced chemical equation for the reaction, define the reaction rate as the rate of change in the concentration of O_2 and write that expression.

B The balanced chemical equation shows that 2 mol of N_2O_5 must decompose for each 1 mol of O_2 produced and that 4 mol of NO_2 are produced for every 1 mol of O_2 produced. The molar ratios of O_2 to N_2O_5 and to NO_2 are thus 1:2 and 1:4, respectively. This means that the rate of change of $[N_2O_5]$ and $[NO_2]$ must be divided by its stoichiometric coefficient to obtain equivalent expressions for the reaction rate. For example, because NO_2 is produced at four times the rate of O_2, the rate of production of NO_2 is divided by 4. The reaction rate expressions are as follows:

$$\text{rate} = \frac{\Delta[O_2]}{\Delta t} = \frac{\Delta[NO_2]}{4\Delta t} = -\frac{\Delta[N_2O_5]}{2\Delta t}$$

Exercise 15.1.1: Contact Process I

The contact process is used in the manufacture of sulfuric acid. A key step in this process is the reaction of SO_2 with O_2 to produce SO_3.

$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$$

Write expressions for the reaction rate in terms of the rate of change of the concentration of each species.

Answer

$$\text{rate} = -\frac{\Delta[\text{O}_2]}{\Delta t} = -\frac{\Delta[\text{SO}_2]}{2\Delta t} = \frac{\Delta[\text{SO}_3]}{2\Delta t}$$

Instantaneous Rates of Reaction

The **instantaneous rate** of a reaction is the reaction rate at any given point in time. As the period of time used to calculate an average rate of a reaction becomes shorter and shorter, the average rate approaches the instantaneous rate. Comparing this to calculus, the instantaneous rate of a reaction at a given time corresponds to the slope of a line tangent to the concentration-versus-time curve at that point—that is, the derivative of concentration with respect to time.

The distinction between the instantaneous and average rates of a reaction is similar to the distinction between the actual speed of a car at any given time on a trip and the average speed of the car for the entire trip. Although the car may travel for an extended period at 65 mph on an interstate highway during a long trip, there may be times when it travels only 25 mph in construction zones or 0 mph if you stop for meals or gas. The average speed on the trip may be only 50 mph, whereas the instantaneous speed on the interstate at a given moment may be 65 mph. Whether the car can be stopped in time to avoid an accident depends on its instantaneous speed, not its average speed. There are important differences between the speed of a car during a trip and the speed of a chemical reaction, however. The speed of a car may vary unpredictably over the length of a trip, and the initial part of a trip is often one of the slowest. In a chemical reaction, the initial interval typically has the fastest rate (though this is not always the case), and the reaction rate generally changes smoothly over time.

> *Chemical kinetics generally focuses on one particular instantaneous rate, which is the initial reaction rate, t = 0. Initial rates are determined by measuring the reaction rate at various times and then extrapolating a plot of rate versus time to t = 0.*



Example 15.1.2: Decomposition Reaction II

Using the reaction shown in Example 15.1.1, calculate the reaction rate from the following data taken at 56°C:

$$2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$$

calculate the reaction rate from the following data taken at 56°C:

Time (s)	$[N_2O_5]$ (M)	$[NO_2]$ (M)	$[O_2]$ (M)
240	0.0388	0.0314	0.00792
600	0.0197	0.0699	0.0175

Given: balanced chemical equation and concentrations at specific times

Asked for: reaction rate

Strategy:

A. Using the equations in Example 15.1.1, subtract the initial concentration of a species from its final concentration and substitute that value into the equation for that species.

B. Substitute the value for the time interval into the equation. Make sure your units are consistent.

Solution

A Calculate the reaction rate in the interval between t_1 = 240 s and t_2 = 600 s. From Example 15.1.1, the reaction rate can be evaluated using any of three expressions:

$$\text{rate} = \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{\Delta[\text{NO}_2]}{4\Delta t} = -\frac{\Delta[\text{N}_2\text{O}_5]}{2\Delta t}$$

Subtracting the initial concentration from the final concentration of N_2O_5 and inserting the corresponding time interval into the rate expression for N_2O_5,

$$\text{rate} = -\frac{\Delta[\text{N}_2\text{O}_5]}{2\Delta t} = -\frac{[\text{N}_2\text{O}_5]_{600} - [\text{N}_2\text{O}_5]_{240}}{2(600\ \text{s} - 240\ \text{s})}$$

B Substituting actual values into the expression,

$$\text{rate} = -\frac{0.0197\ \text{M} - 0.0388\ \text{M}}{2(360\ \text{s})} = 2.65 \times 10^{-5}\ \text{M/s}$$

Similarly, NO_2 can be used to calculate the reaction rate:

$$\text{rate} = \frac{\Delta[\text{NO}_2]}{4\Delta t} = \frac{[\text{NO}_2]_{600} - [\text{NO}_2]_{240}}{4(600\ \text{s} - 240\ \text{s})} = \frac{0.0699\ \text{M} - 0.0314\ \text{M}}{4(360\ \text{s})} = 2.67 \times 10^{-5}\ \text{M/s}$$

Allowing for experimental error, this is the same rate obtained using the data for N_2O_5. The data for O_2 can also be used:

$$\text{rate} = \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{[\text{O}_2]_{600} - [\text{O}_2]_{240}}{600\ \text{s} - 240\ \text{s}} = \frac{0.0175\ \text{M} - 0.00792\ \text{M}}{360\ \text{s}} = 2.66 \times 10^{-5}\ \text{M/s}$$

Again, this is the same value obtained from the N_2O_5 and NO_2 data. Thus, the reaction rate does not depend on which reactant or product is used to measure it.

? Exercise 15.1.2: Contact Process II

Using the data in the following table, calculate the reaction rate of $SO_2(g)$ with $O_2(g)$ to give $SO_3(g)$.

$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$$

calculate the reaction rate of $SO_2(g)$ with $O_2(g)$ to give $SO_3(g)$.

Time (s)	$[SO_2]$ (M)	$[O_2]$ (M)	$[SO_3]$ (M)
300	0.0270	0.0500	0.0072
720	0.0194	0.0462	0.0148

Answer:

9.0×10^{-6} M/s

Summary

In this Module, the quantitative determination of a reaction rate is demonstrated. Reaction rates can be determined over particular time intervals or at a given point in time. A rate law describes the relationship between reactant rates and reactant concentrations. Reaction rates are reported as either the average rate over a period of time or as the instantaneous rate at a single time. Reaction rates can be determined over particular time intervals or at a given point in time.

- General definition of rate for A → B:

$$\text{rate} = \frac{\Delta[\text{B}]}{\Delta t} = -\frac{\Delta[\text{A}]}{\Delta t}$$

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15.2: Rate Laws

Learning Objectives

- To apply rate laws to zeroth, first and second order reactions.

Either the differential rate law or the integrated rate law can be used to determine the reaction order from experimental data. Often, the exponents in the rate law are the positive integers: 1 and 2 or even 0. Thus the reactions are zeroth, first, or second order in each reactant. The common patterns used to identify the reaction order are described in this section, where we focus on characteristic types of differential and integrated rate laws and how to determine the reaction order from experimental data. The learning objective of this Module is to know how to determine the reaction order from experimental data.

Zeroth-Order Reactions

A **zeroth-order reaction** is one whose rate is independent of concentration; its differential rate law is

$$\text{rate} = k.$$

We refer to these reactions as zeroth order because we could also write their rate in a form such that the exponent of the reactant in the rate law is 0:

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{reactant}]^0 = k(1) = k \tag{15.2.1}$$

Because rate is independent of reactant concentration, a graph of the concentration of any reactant as a function of time is a straight line with a slope of $-k$. The value of k is negative because the concentration of the reactant decreases with time. Conversely, a graph of the concentration of any product as a function of time is a straight line with a slope of k, a positive value.

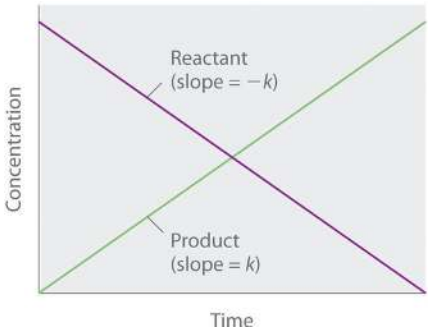


Figure 15.2.1: The graph of a zeroth-order reaction. The change in concentration of reactant and product with time produces a straight line.

Graph of concentration against time. The reactant is in purple and has a slope of minus k. The product is in green and has a slope of positive k.

The integrated rate law for a zeroth-order reaction also produces a straight line and has the general form

$$[A] = [A]_0 - kt \tag{15.2.2}$$

where $[A]_0$ is the initial concentration of reactant A. Equation 15.2.2 has the form of the algebraic equation for a straight line,

$$y = mx + b,$$

with $y = [A]$, $mx = -kt$, and $b = [A]_0$.)

Units

In a zeroth-order reaction, the rate constant must have the same units as the reaction rate, typically moles per liter per second.

Although it may seem counterintuitive for the reaction rate to be independent of the reactant concentration(s), such reactions are rather common. They occur most often when the reaction rate is determined by available surface area. An example is the

decomposition of N_2O on a platinum (Pt) surface to produce N_2 and O_2, which occurs at temperatures ranging from 200°C to 400°C:

$$2N_2O(g) \xrightarrow{Pt} 2N_2(g) + O_2(g) \tag{15.2.3}$$

Without a platinum surface, the reaction requires temperatures greater than 700°C, but between 200°C and 400°C, the only factor that determines how rapidly N_2O decomposes is the amount of Pt surface available (not the amount of Pt). As long as there is enough N_2O to react with the entire Pt surface, doubling or quadrupling the N_2O concentration will have no effect on the reaction rate. At very low concentrations of N_2O, where there are not enough molecules present to occupy the entire available Pt surface, the reaction rate is dependent on the N_2O concentration. The reaction rate is as follows:

$$\text{rate} = -\frac{1}{2}\left(\frac{\Delta[N_2O]}{\Delta t}\right) = \frac{1}{2}\left(\frac{\Delta[N_2]}{\Delta t}\right) = \frac{\Delta[O_2]}{\Delta t} = k[N_2O]^0 = k \tag{15.2.4}$$

Thus the rate at which N_2O is consumed and the rates at which N_2 and O_2 are produced are independent of concentration. As shown in Figure 15.2.2, the change in the concentrations of all species with time is linear. Most important, the exponent (0) corresponding to the N_2O concentration in the experimentally derived rate law is not the same as the reactant's stoichiometric coefficient in the balanced chemical equation (2). For this reaction, as for all others, the rate law must be determined experimentally.

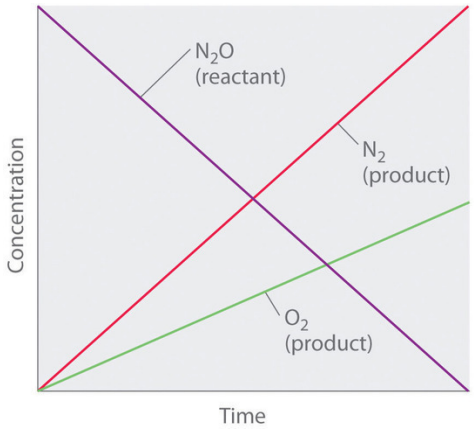


Figure 15.2.2: A Zeroth-Order Reaction. This graph shows the concentrations of reactants and products versus time for the zeroth-order catalyzed decomposition of N_2O to N_2 and O_2 on a Pt surface. The change in the concentrations of all species with time is linear.

Graph of concentration against time. N2O is the reactiant is graphed in purple. O2 is one of the products and is graphed in green. The second product is N2 which is graphed in red

A zeroth-order reaction that takes place in the human liver is the oxidation of ethanol (from alcoholic beverages) to acetaldehyde, catalyzed by the **enzyme** alcohol dehydrogenase. At high ethanol concentrations, this reaction is also a zeroth-order reaction. The overall reaction equation is

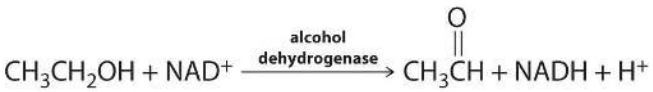


Figure 15.2.2

where \ce{NAD^{+}\} (nicotinamide adenine dinucleotide) and NADH (reduced nicotinamide adenine dinucleotide) are the oxidized and reduced forms, respectively, of a species used by all organisms to transport electrons. When an alcoholic beverage is consumed, the ethanol is rapidly absorbed into the blood. Its concentration then decreases at a constant rate until it reaches zero (Figure 15.2.3*a*). An average 70 kg person typically takes about 2.5 h to oxidize the 15 mL of ethanol contained in a single 12 oz can of beer, a 5 oz glass of wine, or a shot of distilled spirits (such as whiskey or brandy). The actual rate, however, varies a great deal from person to person, depending on body size and the amount of alcohol dehydrogenase in the liver. The reaction rate does not increase if a greater quantity of alcohol is consumed over the same period of time because the reaction rate is determined only by the amount of enzyme present in the liver. Contrary to popular belief, the caffeine in coffee is ineffective at catalyzing the oxidation of ethanol. When the ethanol has been completely oxidized and its concentration drops to essentially zero, the rate of oxidation also drops rapidly (part (b) in Figure 15.2.3).

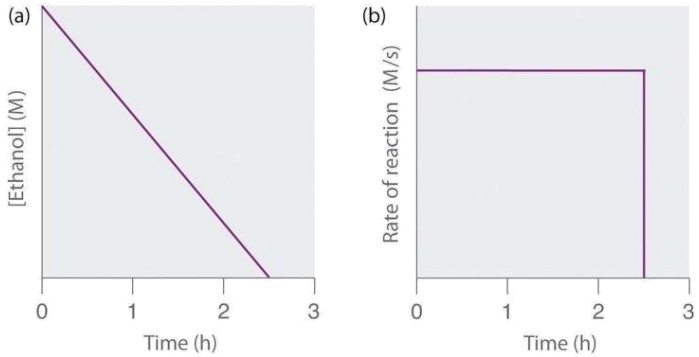


Figure 15.2.3: The Catalyzed Oxidation of Ethanol (a) The concentration of ethanol in human blood decreases linearly with time, which is typical of a zeroth-order reaction. (b) The rate at which ethanol is oxidized is constant until the ethanol concentration reaches essentially zero, at which point the reaction rate drops to zero.

These examples illustrate two important points:

1. In a zeroth-order reaction, the reaction rate does not depend on the reactant concentration.
2. A linear change in concentration with time is a clear indication of a zeroth-order reaction.

First-Order Reactions

In a **first-order reaction**, the reaction rate is directly proportional to the concentration of one of the reactants. First-order reactions often have the general form A → products. The differential rate for a first-order reaction is as follows:

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}] \tag{15.2.5}$$

If the concentration of A is doubled, the reaction rate doubles; if the concentration of A is increased by a factor of 10, the reaction rate increases by a factor of 10, and so forth. Because the units of the reaction rate are always moles per liter per second, the units of a first-order rate constant are reciprocal seconds (s^{-1}).

The integrated rate law for a first-order reaction can be written in two different ways: one using exponents and one using logarithms. The exponential form is as follows:

$$[A] = [A]_0 e^{-kt} \tag{15.2.6}$$

where $[A]_0$ is the initial concentration of reactant A at $t = 0$; k is the rate constant; and e is the base of the natural logarithms, which has the value 2.718 to three decimal places. Recall that an integrated rate law gives the relationship between reactant concentration and time. Equation 15.2.6 predicts that the concentration of A will decrease in a smooth exponential curve over time. By taking the natural logarithm of each side of Equation 15.2.6 and rearranging, we obtain an alternative logarithmic expression of the relationship between the concentration of A and t:

$$\ln[A] = \ln[A]_0 - kt \tag{15.2.7}$$

Because Equation 15.2.7 has the form of the algebraic equation for a straight line,

$$y = mx + b,$$

with $y = \ln[A]$ and $b = \ln[A]_0$, a plot of $\ln[A]$ versus t for a first-order reaction should give a straight line with a slope of $-k$ and an intercept of $\ln[A]_0$. Either the differential rate law (Equation 15.2.5) or the integrated rate law (Equation 15.2.7) can be used to determine whether a particular reaction is first order.

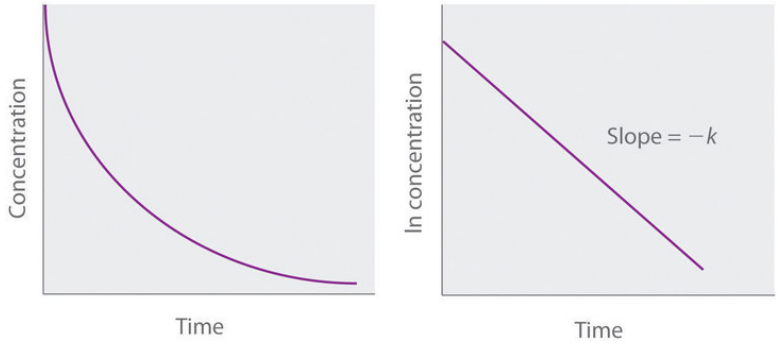


Figure 15.2.4: Graphs of a first-order reaction. The expected shapes of the curves for plots of reactant concentration versus time (top) and the natural logarithm of reactant concentration versus time (bottom) for a first-order reaction.

First-order reactions are very common. One reaction that exhibits apparent first-order kinetics is the hydrolysis of the anticancer drug cisplatin. Cisplatin, the first "inorganic" anticancer drug to be discovered, is unique in its ability to cause complete remission of the relatively rare, but deadly cancers of the reproductive organs in young adults. The structures of cisplatin and its hydrolysis product are as follows:

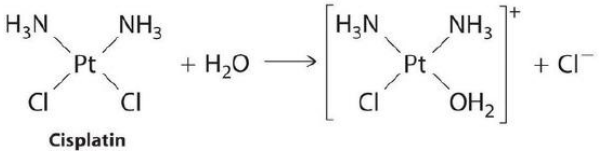


Figure 15.2.5: Cis-platin reaction with water.

Both platinum compounds have four groups arranged in a square plane around a Pt(II) ion. The reaction shown in Figure 15.2.5 is important because cisplatin, the form in which the drug is administered, is not the form in which the drug is active. Instead, at least one chloride ion must be replaced by water to produce a species that reacts with deoxyribonucleic acid (DNA) to prevent cell division and tumor growth. Consequently, the kinetics of the reaction in Figure 15.2.4 have been studied extensively to find ways of maximizing the concentration of the active species.

> *If a plot of reactant concentration versus time is not linear but a plot of the natural logarithm of reactant concentration versus time is linear, then the reaction is first order.*

The rate law and reaction order of the hydrolysis of cisplatin are determined from experimental data, such as those displayed in Table 15.2.1. The table lists initial rate data for four experiments in which the reaction was run at pH 7.0 and 25°C but with different initial concentrations of cisplatin.

Table 15.2.1: Rates of Hydrolysis of Cisplatin as a Function of Concentration at pH 7.0 and 25°C

Experiment	$[\text{Cisplatin}]_0$ (M)	Initial Rate (M/min)
1	0.0060	9.0×10^{-6}
2	0.012	1.8×10^{-5}
3	0.024	3.6×10^{-5}
4	0.030	4.5×10^{-5}

Because the reaction rate increases with increasing cisplatin concentration, we know this cannot be a zeroth-order reaction. Comparing Experiments 1 and 2 in Table 15.2.1 shows that the reaction rate doubles [$(1.8 \times 10^{-5}$ M/min) ÷ $(9.0 \times 10^{-6}$ M/min) = 2.0] when the concentration of cisplatin is doubled (from 0.0060 M to 0.012 M). Similarly, comparing Experiments 1 and 4 shows that the reaction rate increases by a factor of 5 [$(4.5 \times 10^{-5}$ M/min) ÷ $(9.0 \times 10^{-6}$ M/min) = 5.0] when the concentration of cisplatin is increased by a factor of 5 (from 0.0060 M to 0.030 M). Because the reaction rate is directly proportional to the concentration of the reactant, the exponent of the cisplatin concentration in the rate law must be 1, so the rate law is rate = $k[\text{cisplatin}]^1$. Thus the reaction is first order. Knowing this, we can calculate the rate constant using the differential rate law for a first-order reaction and the data in any row of Table 15.2.1. For example, substituting the values for Experiment 3 into Equation 15.2.5,

$$3.6 \times 10^{-5}\ \text{M/min} = k(0.024\ \text{M})$$

$$1.5 \times 10^{-3}\ \text{min}^{-1} = k$$

Knowing the rate constant for the hydrolysis of cisplatin and the rate constants for subsequent reactions that produce species that are highly toxic enables hospital pharmacists to provide patients with solutions that contain only the desired form of the drug.

Example 15.2.1

At high temperatures, ethyl chloride produces HCl and ethylene by the following reaction:

$$CH_3CH_2Cl(g) \xrightarrow{\Delta} HCl(g) + C_2H_4(g)$$

Using the rate data for the reaction at 650°C presented in the following table, calculate the reaction order with respect to the concentration of ethyl chloride and determine the rate constant for the reaction.

data for the reaction at 650°C

Experiment	$[CH_3CH_2Cl]_0$ (M)	Initial Rate (M/s)
1	0.010	1.6×10^{-8}
2	0.015	2.4×10^{-8}
3	0.030	4.8×10^{-8}
4	0.040	6.4×10^{-8}

Given: balanced chemical equation, initial concentrations of reactant, and initial rates of reaction

Asked for: reaction order and rate constant

Strategy:

A. Compare the data from two experiments to determine the effect on the reaction rate of changing the concentration of a species.

B. Compare the observed effect with behaviors characteristic of zeroth- and first-order reactions to determine the reaction order. Write the rate law for the reaction.

C Use measured concentrations and rate data from any of the experiments to find the rate constant.

Solution

The reaction order with respect to ethyl chloride is determined by examining the effect of changes in the ethyl chloride concentration on the reaction rate.

A Comparing Experiments 2 and 3 shows that doubling the concentration doubles the reaction rate, so the reaction rate is proportional to $[CH_3CH_2Cl]$. Similarly, comparing Experiments 1 and 4 shows that quadrupling the concentration quadruples the reaction rate, again indicating that the reaction rate is directly proportional to $[CH_3CH_2Cl]$.

B This behavior is characteristic of a first-order reaction, for which the rate law is rate = $k[CH_3CH_2Cl]$.

C We can calculate the rate constant (k) using any row in the table. Selecting Experiment 1 gives the following:

$$1.60 \times 10^{-8}\ \text{M/s} = k(0.010\ \text{M})$$

$$1.6 \times 10^{-6}\ \text{s}^{-1} = k$$

Exercise 15.2.1

Sulfuryl chloride (SO_2Cl_2) decomposes to SO_2 and Cl_2 by the following reaction:

$$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$$

Data for the reaction at 320°C are listed in the following table. Calculate the reaction order with regard to sulfuryl chloride and determine the rate constant for the reaction.

Data for the reaction at 320°C

Experiment	$[SO_2Cl_2]_0$ (M)	Initial Rate (M/s)
1	0.0050	1.10×10^{-7}
2	0.0075	1.65×10^{-7}
3	0.0100	2.20×10^{-7}
4	0.0125	2.75×10^{-7}

Answer

first order; $k = 2.2 \times 10^{-5}\ s^{-1}$

We can also use the integrated rate law to determine the reaction rate for the hydrolysis of cisplatin. To do this, we examine the change in the concentration of the reactant or the product as a function of time at a single initial cisplatin concentration. Figure 15.2.6*a* shows plots for a solution that originally contained 0.0100 M cisplatin and was maintained at pH 7 and 25°C.

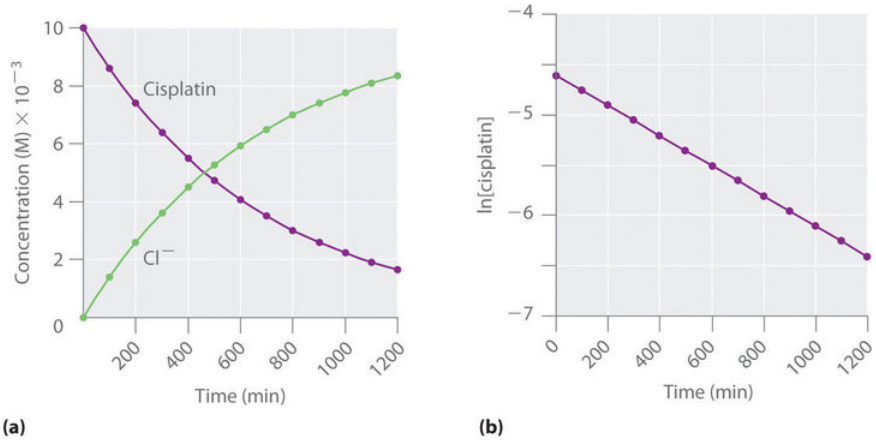


Figure 15.2.6: The Hydrolysis of Cisplatin, a First-Order Reaction. These plots show hydrolysis of cisplatin at pH 7.0 and 25°C as (a) the experimentally determined concentrations of cisplatin and chloride ions versus time and (b) the natural logarithm of the cisplatin concentration versus time. The straight line in (b) is expected for a first-order reaction.

The concentration of cisplatin decreases smoothly with time, and the concentration of chloride ion increases in a similar way. When we plot the natural logarithm of the concentration of cisplatin versus time, we obtain the plot shown in part (b) in Figure 15.2.6. The straight line is consistent with the behavior of a system that obeys a first-order rate law. We can use any two points on the line to calculate the slope of the line, which gives us the rate constant for the reaction. Thus taking the points from part (a) in Figure 15.2.6 for t = 100 min ([cisplatin] = 0.0086 M) and t = 1000 min ([cisplatin] = 0.0022 M),

$$\text{slope} = \frac{\ln[\text{cisplatin}]_{1000} - \ln[\text{cisplatin}]_{100}}{1000\ \text{min} - 100\ \text{min}}$$

$$-k = \frac{\ln 0.0022 - \ln 0.0086}{1000\ \text{min} - 100\ \text{min}} = \frac{-6.12 - (-4.76)}{900\ \text{min}} = -1.51 \times 10^{-3}\ \text{min}^{-1}$$

$$k = 1.5 \times 10^{-3}\ \text{min}^{-1}$$

The slope is negative because we are calculating the rate of disappearance of cisplatin. Also, the rate constant has units of min^{-1} because the times plotted on the horizontal axes in parts (a) and (b) in Figure 15.2.6 are in minutes rather than seconds.

The reaction order and the magnitude of the rate constant we obtain using the integrated rate law are exactly the same as those we calculated earlier using the differential rate law. This must be true if the experiments were carried out under the same conditions.



Video Example Using the First-Order Integrated Rate Law Equation:

Example Using the First-Order Integrated Rate Law Equation(opens in new window) [youtu.be]

Example 15.2.2

If a sample of ethyl chloride with an initial concentration of 0.0200 M is heated at 650°C, what is the concentration of ethyl chloride after 10 h? How many hours at 650°C must elapse for the concentration to decrease to 0.0050 M ($k = 1.6 \times 10^{-6}$ s^{-1}) ?

Given: initial concentration, rate constant, and time interval

Asked for: concentration at specified time and time required to obtain particular concentration

Strategy:

A. Substitute values for the initial concentration ($[A]_0$) and the calculated rate constant for the reaction (k) into the integrated rate law for a first-order reaction. Calculate the concentration ([A]) at the given time t.

B. Given a concentration [A], solve the integrated rate law for time t.

Solution

The exponential form of the integrated rate law for a first-order reaction (Equation 15.2.6) is $[A] = [A]_0 e^{-kt}$.

A Having been given the initial concentration of ethyl chloride ($[A]_0$) and having the rate constant of $k = 1.6 \times 10^{-6}$ s^{-1}, we can use the rate law to calculate the concentration of the reactant at a given time t. Substituting the known values into the integrated rate law,

$$\begin{aligned}[\mathrm{CH_3CH_2Cl}]_{10\ \mathrm{h}} &= [\mathrm{CH_3CH_2Cl}]_0 e^{-kt} \\ &= 0.0200\ \mathrm{M}(e^{-(1.6\times10^{-6}\ \mathrm{s^{-1}})[(10\ \mathrm{h})(60\ \mathrm{min/h})(60\ \mathrm{s/min})]}) \\ &= 0.0189\ \mathrm{M}\end{aligned}$$

We could also have used the logarithmic form of the integrated rate law (Equation 15.2.7):

$$\begin{aligned}\ln[\mathrm{CH_3CH_2Cl}]_{10\,\mathrm{h}} &= \ln[\mathrm{CH_3CH_2Cl}]_0 - kt \\ &= \ln 0.0200 - (1.6 \times 10^{-6}\ \mathrm{s^{-1}})[(10\ \mathrm{h})(60\ \mathrm{min/h})(60\ \mathrm{s/min})] \\ &= -3.912 - 0.0576 = -3.970 \\ [\mathrm{CH_3CH_2Cl}]_{10\,\mathrm{h}} &= e^{-3.970}\ \mathrm{M} \\ &= 0.0189\ \mathrm{M}\end{aligned}$$

B To calculate the amount of time required to reach a given concentration, we must solve the integrated rate law for t. Equation 15.2.7 gives the following:

$$\ln[CH_3CH_2Cl]_t = \ln[CH_3CH_2Cl]_0 - kt$$

$$kt = \ln[CH_3CH_2Cl]_0 - \ln[CH_3CH_2Cl]_t = \ln\frac{[CH_3CH_2Cl]_0}{[CH_3CH_2Cl]_t}$$

$$t = \frac{1}{k}\left(\ln\frac{[CH_3CH_2Cl]_0}{[CH_3CH_2Cl]_t}\right) = \frac{1}{1.6\times10^{-6}\ \text{s}^{-1}}\left(\ln\frac{0.0200\ \text{M}}{0.0050\ \text{M}}\right)$$

$$= \frac{\ln 4.0}{1.6\times10^{-6}\ \text{s}^{-1}} = 8.7\times10^5\ \text{s} = 240\ \text{h} = 2.4\times10^2\ \text{h}$$

? Exercise 15.2.2

In the exercise in Example 15.2.1, you found that the decomposition of sulfuryl chloride (SO_2Cl_2) is first order, and you calculated the rate constant at 320°C.

a. Use the form(s) of the integrated rate law to find the amount of SO_2Cl_2 that remains after 20 h if a sample with an original concentration of 0.123 M is heated at 320°C.
b. How long would it take for 90% of the SO_2Cl_2 to decompose?

Answer a

0.0252 M

Answer b

29 h

Second-Order Reactions

The simplest kind of **second-order reaction** is one whose rate is proportional to the square of the concentration of one reactant. These generally have the form

$$2\ A \rightarrow \text{products}\cdot$$

A second kind of second-order reaction has a reaction rate that is proportional to the product of the concentrations of two reactants. Such reactions generally have the form A + B → products. An example of the former is a dimerization reaction, in which two smaller molecules, each called a monomer, combine to form a larger molecule (a dimer).

The differential rate law for the simplest second-order reaction in which 2A → products is as follows:

$$\text{rate} = -\frac{\Delta[A]}{2\Delta t} = k[A]^2 \tag{15.2.8}$$

Consequently, doubling the concentration of A quadruples the reaction rate. For the units of the reaction rate to be moles per liter per second (M/s), the units of a second-order rate constant must be the inverse ($M^{-1}\cdot s^{-1}$). Because the units of molarity are expressed as mol/L, the unit of the rate constant can also be written as L(mol·s).

For the reaction 2A → products, the following integrated rate law describes the concentration of the reactant at a given time:

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt \tag{15.2.9}$$

Because Equation 15.2.9 has the form of an algebraic equation for a straight line, $y = mx + b$, with $y = 1/[A]$ and $b = 1/[A]_0$, a plot of 1/[A] versus t for a simple second-order reaction is a straight line with a slope of k and an intercept of $1/[A]_0$.

> *Second-order reactions generally have the form 2A → products or A + B → products.*



Video Discussing the Second-Order Integrated Rate Law Equation: Second-Order Integrated Rate Law Equation(opens in new window) [youtu.be]

Simple second-order reactions are common. In addition to dimerization reactions, two other examples are the decomposition of NO_2 to NO and O_2 and the decomposition of HI to I_2 and H_2. Most examples involve simple inorganic molecules, but there are organic examples as well. We can follow the progress of the reaction described in the following paragraph by monitoring the decrease in the intensity of the red color of the reaction mixture.

Many cyclic organic compounds that contain two carbon–carbon double bonds undergo a dimerization reaction to give complex structures. One example is as follows:

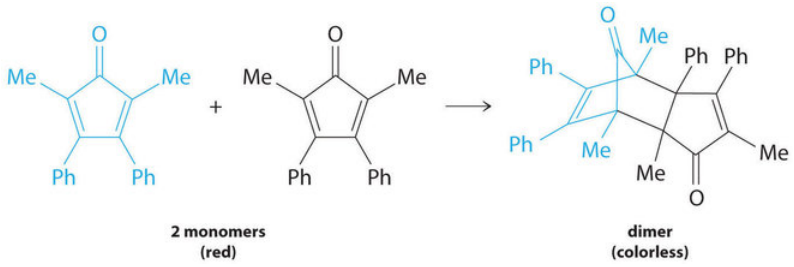


Figure 15.2.7

For simplicity, we will refer to this reactant and product as “monomer” and “dimer,” respectively. The systematic name of the monomer is 2,5-dimethyl-3,4-diphenylcyclopentadienone. The systematic name of the dimer is the name of the monomer followed by “dimer.” Because the monomers are the same, the general equation for this reaction is 2A → product. This reaction represents an important class of organic reactions used in the pharmaceutical industry to prepare complex carbon skeletons for the synthesis of drugs. Like the first-order reactions studied previously, it can be analyzed using either the differential rate law (Equation 15.2.8) or the integrated rate law (Equation 15.2.9).

Table 15.2.2: Rates of Reaction as a Function of Monomer Concentration for an Initial Monomer Concentration of 0.0054 M

Time (min)	[Monomer] (M)	Instantaneous Rate (M/min)
10	0.0044	8.0×10^{-5}
26	0.0034	5.0×10^{-5}
44	0.0027	3.1×10^{-5}
70	0.0020	1.8×10^{-5}
120	0.0014	8.0×10^{-6}

To determine the differential rate law for the reaction, we need data on how the reaction rate varies as a function of monomer concentrations, which are provided in Table 15.2.2 From the data, we see that the reaction rate is not independent of the monomer

concentration, so this is not a zeroth-order reaction. We also see that the reaction rate is not proportional to the monomer concentration, so the reaction is not first order. Comparing the data in the second and fourth rows shows that the reaction rate decreases by a factor of 2.8 when the monomer concentration decreases by a factor of 1.7:

$$\frac{5.0 \times 10^{-5}\ \text{M/min}}{1.8 \times 10^{-5}\ \text{M/min}} = 2.8 \quad \text{and} \quad \frac{3.4 \times 10^{-3}\ \text{M}}{2.0 \times 10^{-3}\ \text{M}} = 1.7$$

Because $(1.7)^2 = 2.9 \approx 2.8$, the reaction rate is approximately proportional to the square of the monomer concentration.

$$\text{rate} \propto [\text{monomer}]^2$$

This means that the reaction is second order in the monomer. Using Equation 15.2.8 and the data from any row in Table 15.2.2, we can calculate the rate constant. Substituting values at time 10 min, for example, gives the following:

$$\text{rate} = k[\text{A}]^2 \tag{15.2.10}$$

$$8.0 \times 10^{-5}\ \text{M/min} = k(4.4 \times 10^{-3}\ \text{M})^2 \tag{15.2.11}$$

$$4.1\ \text{M}^{-1} \cdot \text{min}^{-1} = k \tag{15.2.12}$$

We can also determine the reaction order using the integrated rate law. To do so, we use the decrease in the concentration of the monomer as a function of time for a single reaction, plotted in Figure 15.2.8*a*. The measurements show that the concentration of the monomer (initially 5.4 × 10^{-3} M) decreases with increasing time. This graph also shows that the reaction rate decreases smoothly with increasing time. According to the integrated rate law for a second-order reaction, a plot of 1/[monomer] versus *t* should be a straight line, as shown in Figure 15.2.8*b* Any pair of points on the line can be used to calculate the slope, which is the second-order rate constant. In this example, *k* = 4.1 M^{-1}·min^{-1}, which is consistent with the result obtained using the differential rate equation. Although in this example the stoichiometric coefficient is the same as the reaction order, this is not always the case. The reaction order must always be determined experimentally.

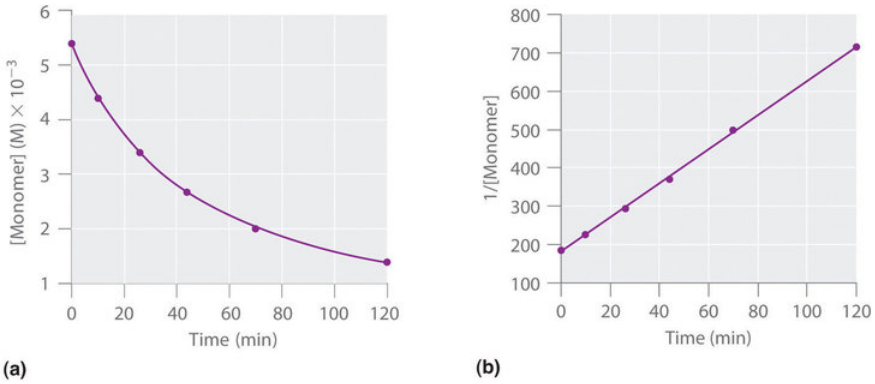


Figure 15.2.8: Dimerization of a Monomeric Compound, a Second-Order Reaction. These plots correspond to dimerization of the monomer in Figure 14.4.6 as (a) the experimentally determined concentration of monomer versus time and (b) 1/[monomer] versus time. The straight line in (b) is expected for a simple second-order reaction.

For two or more reactions of the same order, the reaction with the largest rate constant is the fastest. Because the units of the rate constants for zeroth-, first-, and second-order reactions are different, however, we cannot compare the magnitudes of rate constants for reactions that have different orders.

Example 15.2.3

At high temperatures, nitrogen dioxide decomposes to nitric oxide and oxygen.

$$2\text{NO}_2(\text{g}) \xrightarrow{\Delta} 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$$

Experimental data for the reaction at 300°C and four initial concentrations of NO_2 are listed in the following table:

Experimental data for the reaction at 300°C and four initial concentrations of NO2

Experiment	$[NO_2]_0$ (M)	Initial Rate (M/s)
1	0.015	1.22×10^{-4}

Experiment	$[NO_2]_0$ (M)	Initial Rate (M/s)
2	0.010	5.40×10^{-5}
3	0.0080	3.46×10^{-5}
4	0.0050	1.35×10^{-5}

Determine the reaction order and the rate constant.

Given: balanced chemical equation, initial concentrations, and initial rates

Asked for: reaction order and rate constant

Strategy:

A. From the experiments, compare the changes in the initial reaction rates with the corresponding changes in the initial concentrations. Determine whether the changes are characteristic of zeroth-, first-, or second-order reactions.

B. Determine the appropriate rate law. Using this rate law and data from any experiment, solve for the rate constant (k).

Solution

A We can determine the reaction order with respect to nitrogen dioxide by comparing the changes in NO_2 concentrations with the corresponding reaction rates. Comparing Experiments 2 and 4, for example, shows that doubling the concentration quadruples the reaction rate [$(5.40 \times 10^{-5}) \div (1.35 \times 10^{-5}) = 4.0$], which means that the reaction rate is proportional to $[NO_2]^2$. Similarly, comparing Experiments 1 and 4 shows that tripling the concentration increases the reaction rate by a factor of 9, again indicating that the reaction rate is proportional to $[NO_2]^2$. This behavior is characteristic of a second-order reaction.

B We have rate = $k[NO_2]^2$. We can calculate the rate constant (k) using data from any experiment in the table. Selecting Experiment 2, for example, gives the following:

$$\begin{aligned} \text{rate} &= k[\text{NO}_2]^2 \\ 5.40 \times 10^{-5}\ \text{M/s} &= k(0.010\ \text{M})^2 \\ 0.54\ \text{M}^{-1} \cdot \text{s}^{-1} &= k \end{aligned}$$

Exercise 15.2.3

When the highly reactive species HO_2 forms in the atmosphere, one important reaction that then removes it from the atmosphere is as follows:

$$2HO_{2(g)} \rightarrow H_2O_{2(g)} + O_{2(g)}$$

The kinetics of this reaction have been studied in the laboratory, and some initial rate data at 25°C are listed in the following table:

Some initial rate data at 25°C

Experiment	$[HO_2]_0$ (M)	Initial Rate (M/s)
1	1.1×10^{-8}	1.7×10^{-7}
2	2.5×10^{-8}	8.8×10^{-7}
3	3.4×10^{-8}	1.6×10^{-6}
4	5.0×10^{-8}	3.5×10^{-6}

Determine the reaction order and the rate constant.

Answer

second order in HO_2; $k = 1.4 \times 10^9\ \text{M}^{-1} \cdot \text{s}^{-1}$

If a plot of reactant concentration versus time is **not** linear, but a plot of 1/(reactant concentration) versus time is linear, then the reaction is second order.

Example 15.2.4

If a flask that initially contains 0.056 M NO_2 is heated at 300°C, what will be the concentration of NO_2 after 1.0 h? How long will it take for the concentration of NO_2 to decrease to 10% of the initial concentration? Use the integrated rate law for a second-order reaction (Equation 15.2.9) and the rate constant calculated above.

Given: balanced chemical equation, rate constant, time interval, and initial concentration

Asked for: final concentration and time required to reach specified concentration

Strategy:

A. Given *k*, *t*, and $[A]_0$, use the integrated rate law for a second-order reaction to calculate [A].

B. Setting [A] equal to 1/10 of $[A]_0$, use the same equation to solve for t.

Solution

A We know *k* and $[NO_2]_0$, and we are asked to determine $[NO_2]$ at *t* = 1 h (3600 s). Substituting the appropriate values into Equation 15.2.9,

$$\begin{aligned}\frac{1}{[NO_2]_{3600}} &= \frac{1}{[NO_2]_0} + kt \\ &= \frac{1}{0.056\ \text{M}} + [(0.54\ \text{M}^{-1}\cdot\text{s}^{-1})(3600\ \text{s})] \\ &= 2.0 \times 10^3\ \text{M}^{-1}\end{aligned}$$

Thus $[NO_2]_{3600} = 5.1 \times 10^{-4}$ M.

B In this case, we know *k* and $[NO_2]_0$, and we are asked to calculate at what time $[NO_2] = 0.1[NO_2]_0 = 0.1(0.056\ \text{M}) = 0.0056$ M. To do this, we solve Equation 15.2.9 for *t*, using the concentrations given.

$$\begin{aligned}t &= \frac{(1/[NO_2]) - (1/[NO_2]_0)}{k} \\ &= \frac{(1/0.0056\ \text{M}) - (1/0.056\ \text{M})}{0.54\ \text{M}^{-1}\cdot\text{s}^{-1}} \\ &= 3.0 \times 10^2\ \text{s} = 5.0\ \text{min}\end{aligned}$$

NO_2 decomposes very rapidly; under these conditions, the reaction is 90% complete in only 5.0 min.

Exercise 15.2.4

In the previous exercise, you calculated the rate constant for the decomposition of HO_2 as $k = 1.4 \times 10^9\ \text{M}^{-1}\cdot\text{s}^{-1}$. This high rate constant means that HO_2 decomposes rapidly under the reaction conditions given in the problem. In fact, the HO_2 molecule is so reactive that it is virtually impossible to obtain in high concentrations. Given a 0.0010 M sample of HO_2, calculate the concentration of HO_2 that remains after 1.0 h at 25°C. How long will it take for 90% of the HO_2 to decompose? Use the integrated rate law for a second-order reaction (Equation 15.2.9) and the rate constant calculated in the exercise in Example 15.2.3

Answer

2.0×10^{-13} M; 6.4×10^{-6} s

In addition to the simple second-order reaction and rate law we have just described, another very common second-order reaction has the general form $A + B \rightarrow products$, in which the reaction is first order in A and first order in B. The differential rate law for this reaction is as follows:

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

Because the reaction is first order both in A and in B, it has an overall reaction order of 2. (The integrated rate law for this reaction is rather complex, so we will not describe it.) We can recognize second-order reactions of this sort because the reaction rate is proportional to the concentrations of each reactant.

Summary

The reaction rate of a zeroth-order reaction is independent of the concentration of the reactants. The reaction rate of a first-order reaction is directly proportional to the concentration of one reactant. The reaction rate of a simple second-order reaction is proportional to the square of the concentration of one reactant. Knowing the rate law of a reaction gives clues to the reaction mechanism.

- **zeroth-order reaction:**

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

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

- **first-order reaction**:

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

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

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

- **second-order reaction:**

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]^2$$

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

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15.3: Reaction Mechanisms

Learning Objectives

- To determine the individual steps of a simple reaction.

One of the major reasons for studying chemical kinetics is to use measurements of the macroscopic properties of a system, such as the rate of change in the concentration of reactants or products with time, to discover the sequence of events that occur at the molecular level during a reaction. This molecular description is the mechanism of the reaction; it describes how individual atoms, ions, or molecules interact to form particular products. The stepwise changes are collectively called the reaction mechanism.

In an internal combustion engine, for example, isooctane reacts with oxygen to give carbon dioxide and water:

$$2\,C_8H_{18}(l) + 25\,O_2(g) \longrightarrow 16\,CO_2(g) + 18\,H_2O(g) \tag{15.3.1}$$

For this reaction to occur in a single step, 25 dioxygen molecules and 2 isooctane molecules would have to collide simultaneously and be converted to 34 molecules of product, which is very unlikely. It is more likely that a complex series of reactions takes place in a stepwise fashion. Each individual reaction, which is called an **elementary reaction**, involves one, two, or (rarely) three atoms, molecules, or ions. The overall sequence of elementary reactions is the **mechanism** of the reaction. The sum of the individual steps, or elementary reactions, in the mechanism must give the balanced chemical equation for the overall reaction.

> *The overall sequence of elementary reactions is the mechanism of the reaction.*

Molecularity and the Rate-Determining Step

To demonstrate how the analysis of elementary reactions helps us determine the overall reaction mechanism, we will examine the much simpler reaction of carbon monoxide with nitrogen dioxide.

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g) \tag{15.3.2}$$

From the balanced chemical equation, one might expect the reaction to occur via a collision of one molecule of NO_2 with a molecule of CO that results in the transfer of an oxygen atom from nitrogen to carbon. The experimentally determined rate law for the reaction, however, is as follows:

$$rate = k[NO_2]^2 \tag{15.3.3}$$

The fact that the reaction is second order in $[NO_2]$ and independent of $[CO]$ tells us that it does not occur by the simple collision model outlined previously. If it did, its predicted rate law would be

$$rate = k[NO_2][CO].$$

The following two-step mechanism is consistent with the rate law if step 1 is much slower than step 2:

two-step mechanism

step 1	$NO_2 + NO_2 \overset{\text{slow}}{\longrightarrow} NO_3 + NO$	elementary reaction
step 2	$\underline{NO_3 + CO \rightarrow NO_2 + CO_2}$	elementary reaction
sum	$NO_2 + CO \rightarrow NO + CO_2$	overall reaction

According to this mechanism, the overall reaction occurs in two steps, or elementary reactions. Summing steps 1 and 2 and canceling on both sides of the equation gives the overall balanced chemical equation for the reaction. The NO_3 molecule is an **intermediate** in the reaction, a species that does not appear in the balanced chemical equation for the overall reaction. It is formed as a product of the first step but is consumed in the second step.

> *The sum of the elementary reactions in a reaction mechanism **must** give the overall balanced chemical equation of the reaction.*

Using Molecularity to Describe a Rate Law

The **molecularity** of an elementary reaction is the number of molecules that collide during that step in the mechanism. If there is only a single reactant molecule in an elementary reaction, that step is designated as **unimolecular**; if there are two reactant molecules, it is **bimolecular**; and if there are three reactant molecules (a relatively rare situation), it is **termolecular**. Elementary reactions that involve the simultaneous collision of more than three molecules are highly improbable and have never been observed experimentally. (To understand why, try to make three or more marbles or pool balls collide with one another simultaneously!)

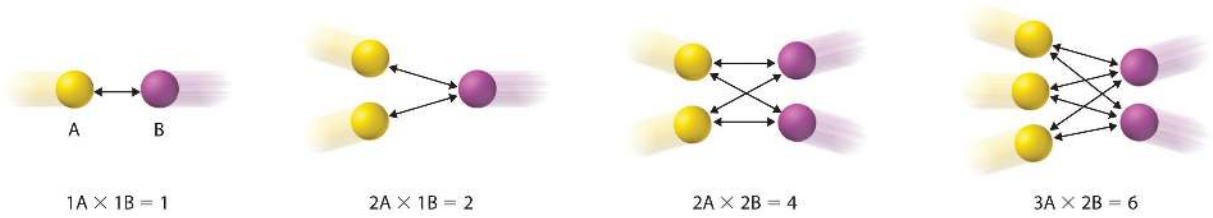


Figure 15.3.1: The Basis for Writing Rate Laws of Elementary Reactions. This diagram illustrates how the number of possible collisions per unit time between two reactant species, A and B, depends on the number of A and B particles present. The number of collisions between A and B particles increases as the product of the number of particles, not as the sum. This is why the rate law for an elementary reaction depends on the product of the concentrations of the species that collide in that step. (CC BY-NC-SA; anonymous)

Writing the rate law for an elementary reaction is straightforward because we know how many molecules must collide simultaneously for the elementary reaction to occur; hence the order of the elementary reaction is the same as its molecularity (Table 15.3.1). In contrast, the rate law for the reaction cannot be determined from the balanced chemical equation for the overall reaction. The general rate law for a unimolecular elementary reaction (A → products) is

$$rate = k[A].$$

For bimolecular reactions, the reaction rate depends on the number of collisions per unit time, which is proportional to the product of the concentrations of the reactants, as shown in Figure 15.3.1. For a bimolecular elementary reaction of the form A + B → products, the general rate law is

$$rate = k[A][B].$$

Table 15.3.1: Common Types of Elementary Reactions and Their Rate Laws

Elementary Reaction	Molecularity	Rate Law	Reaction Order
A → products	unimolecular	rate = k[A]	first
2A → products	bimolecular	rate = k[A]^2	second
A + B → products	bimolecular	rate = k[A][B]	second
2A + B → products	termolecular	rate = k[A]^2[B]	third
A + B + C → products	termolecular	rate = k[A][B][C]	third

> *For elementary reactions, the order of the elementary reaction is the same as its molecularity. In contrast, the rate law **cannot** be determined from the balanced chemical equation for the overall reaction (unless it is a single step mechanism and is therefore also an elementary step).*

Identifying the Rate-Determining Step

Note the important difference between writing rate laws for elementary reactions and the balanced chemical equation of the overall reaction. Because the balanced chemical equation does not necessarily reveal the individual elementary reactions by which the reaction occurs, we cannot obtain the rate law for a reaction from the overall balanced chemical equation alone. In fact, it is the rate law for the slowest overall reaction, which is the same as the rate law for the slowest step in the reaction mechanism, the **rate-determining step**, that must give the experimentally determined rate law for the overall reaction.This statement is true if one step is substantially slower than all the others, typically by a factor of 10 or more. If two or more slow steps have comparable rates, the

experimentally determined rate laws can become complex. Our discussion is limited to reactions in which one step can be identified as being substantially slower than any other. The reason for this is that any process that occurs through a sequence of steps can take place no faster than the slowest step in the sequence. In an automotive assembly line, for example, a component cannot be used faster than it is produced. Similarly, blood pressure is regulated by the flow of blood through the smallest passages, the capillaries. Because movement through capillaries constitutes the rate-determining step in blood flow, blood pressure can be regulated by medications that cause the capillaries to contract or dilate. A chemical reaction that occurs via a series of elementary reactions can take place no faster than the slowest step in the series of reactions.



Rate-determining step. The phenomenon of a rate-determining step can be compared to a succession of funnels. The smallest-diameter funnel controls the rate at which the bottle is filled, whether it is the first or the last in the series. Pouring liquid into the first funnel faster than it can drain through the smallest results in an overflow. (CC BY-NC-SA; anonymous)

Look at the rate laws for each elementary reaction in our example as well as for the overall reaction.

rate laws for each elementary reaction in our example as well as for the overall reaction.

step 1	$NO_2 + NO_2 \xrightarrow{k_1} NO_3 + NO$	$\text{rate} = k_1[NO_2]^2$ (predicted)
step 2	$NO_3 + CO \xrightarrow{k_2} NO_2 + CO_2$	$\text{rate} = k_2[NO_3][CO]$ (predicted)
sum	$NO_2 + CO \xrightarrow{k} NO + CO_2$	$\text{rate} = k[NO_2]^2$ (observed)

The experimentally determined rate law for the reaction of NO_2 with CO is the same as the predicted rate law for step 1. This tells us that the first elementary reaction is the rate-determining step, so k for the overall reaction must equal k_1. That is, NO_3 is formed slowly in step 1, but once it is formed, it reacts very rapidly with CO in step 2.

Sometimes chemists are able to propose two or more mechanisms that are consistent with the available data. If a proposed mechanism predicts the wrong experimental rate law, however, the mechanism must be incorrect.

Example 15.3.1: A Reaction with an Intermediate

In an alternative mechanism for the reaction of NO_2 with CO with N_2O_4 appearing as an intermediate.

alternative mechanism for the reaction of NO_2 with CO with N_2O_4 appearing as an intermediate.

step 1	$NO_2 + NO_2 \xrightarrow{k_1} N_2O_4$
step 2	$N_2O_4 + CO \xrightarrow{k_2} NO + NO_2 + CO_2$
sum	$NO_2 + CO \rightarrow NO + CO_2$

Write the rate law for each elementary reaction. Is this mechanism consistent with the experimentally determined rate law (rate = $k[NO_2]^2$)?

Given: elementary reactions

Asked for: rate law for each elementary reaction and overall rate law

Strategy:

A. Determine the rate law for each elementary reaction in the reaction.

B. Determine which rate law corresponds to the experimentally determined rate law for the reaction. This rate law is the one for the rate-determining step.

Solution

A The rate law for step 1 is rate = $k_1[NO_2]^2$; for step 2, it is rate = $k_2[N_2O_4][CO]$.

B If step 1 is slow (and therefore the rate-determining step), then the overall rate law for the reaction will be the same: rate = $k_1[NO_2]^2$. This is the same as the experimentally determined rate law. Hence this mechanism, with N_2O_4 as an intermediate, and the one described previously, with NO_3 as an intermediate, are kinetically indistinguishable. In this case, further experiments are needed to distinguish between them. For example, the researcher could try to detect the proposed intermediates, NO_3 and N_2O_4, directly.

? Exercise 15.3.1

Iodine monochloride (ICl) reacts with H_2 as follows:

$$2\,ICl(l) + H_2(g) \rightarrow 2\,HCl(g) + I_2(s)$$

The experimentally determined rate law is $rate = k[ICl][H_2]$. Write a two-step mechanism for this reaction using only bimolecular elementary reactions and show that it is consistent with the experimental rate law. (Hint: HI is an intermediate.)

Answer

Solutions to Exercise 14.6.1

step 1	$ICl + H_2 \xrightarrow{k_1} HCl + HI$	$\text{rate} = k_1[ICl][H_2]$ (slow)
step 2	$HI + ICl \xrightarrow{k_2} HCl + I_2$	$\text{rate} = k_2[HI][ICl]$ (fast)
sum	$2ICl + H_2 \rightarrow 2HCl + I_2$	

This mechanism is consistent with the experimental rate law if the first step is the rate-determining step.

✓ Example 15.3.2 : Nitrogen Oxide Reacting with Molecular Hydrogen

Assume the reaction between NO and H_2 occurs via a three-step process:

the reaction between NO and H_2 occurs via a three-step process

step 1	$NO + NO \xrightarrow{k_1} N_2O_2$	(fast)
step 2	$N_2O_2 + H_2 \xrightarrow{k_2} N_2O + H_2O$	(slow)
step 3	$N_2O + H_2 \xrightarrow{k_3} N_2 + H_2O$	(fast)

Write the rate law for each elementary reaction, write the balanced chemical equation for the overall reaction, and identify the rate-determining step. Is the rate law for the rate-determining step consistent with the experimentally derived rate law for the overall reaction:

$$\text{rate} = k[NO]^2[H_2]? \qquad \text{(observed)}$$

Answer

- Step 1: $rate = k_1[NO]^2$
- Step 2: $rate = k_2[N_2O_2][H_2]$

- Step 3: $rate = k_3[\mathrm{N_2O}][\mathrm{H_2}]$

The overall reaction is then

$$2\,\mathrm{NO(g)} + 2\,\mathrm{H_2(g)} \longrightarrow \mathrm{N_2(g)} + 2\,\mathrm{H_2O(g)}$$

- Rate Determining Step : #2
- Yes, because the rate of formation of $[\mathrm{N_2O_2}] = k_1[\mathrm{NO}]^2$. Substituting $k_1[\mathrm{NO}]^2$ for $[\mathrm{N_2O_2}]$ in the rate law for step 2 gives the experimentally derived rate law for the overall chemical reaction, where $k = k_1k_2$.



Reaction Mechanism (Slow step followed by fast step): Reaction Mechanism (Slow step Followed by Fast Step)(opens in new window) [youtu.be] (opens in new window)

Summary

A balanced chemical reaction does not necessarily reveal either the individual elementary reactions by which a reaction occurs or its rate law. A reaction mechanism is the microscopic path by which reactants are transformed into products. Each step is an elementary reaction. Species that are formed in one step and consumed in another are intermediates. Each elementary reaction can be described in terms of its *molecularity*, the number of molecules that collide in that step. The slowest step in a reaction mechanism is the rate-determining step.

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15.4: Effect of Temperature on Reaction Rates

Learning Objectives

- To understand why and how chemical reactions occur.

It is possible to use kinetics studies of a chemical system, such as the effect of changes in reactant concentrations, to deduce events that occur on a microscopic scale, such as collisions between individual particles. Such studies have led to the collision model of chemical kinetics, which is a useful tool for understanding the behavior of reacting chemical species. The collision model explains why chemical reactions often occur more rapidly at higher temperatures. For example, the reaction rates of many reactions that occur at room temperature approximately double with a temperature increase of only 10°C. In this section, we will use the collision model to analyze this relationship between temperature and reaction rates. Before delving into the relationship between temperature and reaction rate, we must discuss three microscopic factors that influence the observed macroscopic reaction rates.

Microscopic Factor 1: Collisional Frequency

Central to collision model is that a chemical reaction can occur only when the reactant molecules, atoms, or ions collide. Hence, the observed rate is influence by the frequency of collisions between the reactants. The **collisional frequency** is the average rate in which two reactants collide for a given system and is used to express the average number of collisions per unit of time in a defined system. While deriving the collisional frequency (Z_{AB}) between two species in a gas is straightforward, it is beyond the scope of this text and the equation for collisional frequency of A and B is the following:

$$Z_{AB} = N_A N_B (r_A + r_B)^2 \sqrt{\frac{8\pi k_B T}{\mu_{AB}}} \tag{15.4.1}$$

with

- N_A and N_B are the numbers of A and B molecules in the system, respectively
- r_a and r_b are the radii of molecule A and B, respectively
- k_B is the Boltzmann constant k_B = 1.380 x 10^{-23} Joules Kelvin
- T is the temperature in Kelvin
- μ_{AB} is calculated via $\mu_{AB} = \frac{m_A m_B}{m_A + m_B}$

The specifics of Equation 15.4.1 are not important for this conversation, but it is important to identify that Z_{AB} increases with increasing density (i.e., increasing N_A and N_B), with increasing reactant size (r_a and r_b), with increasing velocities (predicted via Kinetic Molecular Theory), and with increasing temperature (although weakly because of the square root function).



A Video Discussing Collision Theory of Kinetics: Collusion Theory of Kinetics (opens in new window) [youtu.be]

Microscopic Factor 2: Activation Energy

Previously, we discussed the kinetic molecular theory of gases, which showed that the average kinetic energy of the particles of a gas increases with increasing temperature. Because the speed of a particle is proportional to the square root of its kinetic energy, increasing the temperature will also increase the number of collisions between molecules per unit time. What the kinetic molecular theory of gases does not explain is why the reaction rate of most reactions approximately doubles with a 10°C temperature increase. This result is surprisingly large considering that a 10°C increase in the temperature of a gas from 300 K to 310 K increases the kinetic energy of the particles by only about 4%, leading to an increase in molecular speed of only about 2% and a correspondingly small increase in the number of bimolecular collisions per unit time.

The collision model of chemical kinetics explains this behavior by introducing the concept of **activation energy** (E_a). We will define this concept using the reaction of NO with ozone, which plays an important role in the depletion of ozone in the ozone layer:

$$\mathrm{NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)}$$

Increasing the temperature from 200 K to 350 K causes the rate constant for this particular reaction to increase by a factor of more than 10, whereas the increase in the frequency of bimolecular collisions over this temperature range is only 30%. Thus something other than an increase in the collision rate must be affecting the reaction rate.

Experimental rate law for this reaction is

$$\mathrm{rate} = k[\mathrm{NO}][\mathrm{O_3}]$$

and is used to identify how the reaction rate (not the rate constant) vares with concentration. The rate constant, however, does vary with temperature. Figure 15.4.1 shows a plot of the rate constant of the reaction of NO with $\mathrm{O_3}$ at various temperatures. The relationship is not linear but instead resembles the relationships seen in graphs of vapor pressure versus temperature (e.g, the Clausius-Claperyon equation). In all three cases, the shape of the plots results from a distribution of kinetic energy over a population of particles (electrons in the case of conductivity; molecules in the case of vapor pressure; and molecules, atoms, or ions in the case of reaction rates). Only a fraction of the particles have sufficient energy to overcome an energy barrier.

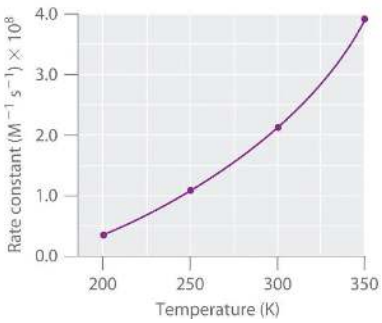


Figure 15.4.1: Rate Constant versus Temperature for the Reaction of NO with $\mathrm{O_3}$The nonlinear shape of the curve is caused by a distribution of kinetic energy over a population of molecules. Only a fraction of the particles have enough energy to overcome an energy barrier, but as the temperature is increased, the size of that fraction increases. (CC BY-SA-NC; anonymous)

In the case of vapor pressure, particles must overcome an energy barrier to escape from the liquid phase to the gas phase. This barrier corresponds to the energy of the intermolecular forces that hold the molecules together in the liquid. In conductivity, the barrier is the energy gap between the filled and empty bands. In chemical reactions, the energy barrier corresponds to the amount of energy the particles must have to react when they collide. This energy threshold, called the **activation energy**, was first postulated in 1888 by the Swedish chemist Svante Arrhenius (1859–1927; Nobel Prize in Chemistry 1903). It is the minimum amount of energy needed for a reaction to occur. Reacting molecules must have enough energy to overcome electrostatic repulsion, and a minimum amount of energy is required to break chemical bonds so that new ones may be formed. Molecules that collide with less than the threshold energy bounce off one another chemically unchanged, with only their direction of travel and their speed altered by the collision. Molecules that are able to overcome the energy barrier are able to react and form an arrangement of atoms called the **activated complex** or the **transition state** of the reaction. The activated complex is not a reaction intermediate; it does not last long enough to be detected readily.

> *Any phenomenon that depends on the distribution of thermal energy in a population of particles has a nonlinear temperature dependence.*

We can graph the energy of a reaction by plotting the potential energy of the system as the reaction progresses. Figure 15.4.2 shows a plot for the NO–O_3 system, in which the vertical axis is potential energy and the horizontal axis is the reaction coordinate, which indicates the progress of the reaction with time. The activated complex is shown in brackets with an asterisk. The overall change in potential energy for the reaction (ΔE) is negative, which means that the reaction releases energy. (In this case, ΔE is −200.8 kJ/mol.) To react, however, the molecules must overcome the energy barrier to reaction (E_a is 9.6 kJ/mol). That is, 9.6 kJ/mol must be put into the system as the activation energy. Below this threshold, the particles do not have enough energy for the reaction to occur.

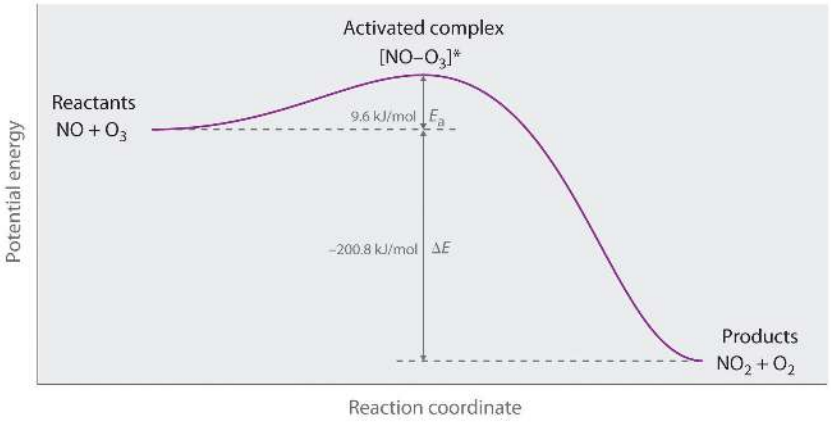


Figure 15.4.2: Energy of the Activated Complex for the NO–O_3 System. The diagram shows how the energy of this system varies as the reaction proceeds from reactants to products. Note the initial increase in energy required to form the activated complex. (CC BY-SA-NC; anonymous)

Figure 15.4.3*a* illustrates the general situation in which the products have a lower potential energy than the reactants. In contrast, Figure 15.4.3*b* illustrates the case in which the products have a higher potential energy than the reactants, so the overall reaction requires an input of energy; that is, it is energetically uphill, and \($\Delta E > 0$\). Although the energy changes that result from a reaction can be positive, negative, or even zero, in most cases an energy barrier must be overcome before a reaction can occur. This means that the activation energy is almost always positive; there is a class of reactions called barrierless reactions, but those are discussed elsewhere.

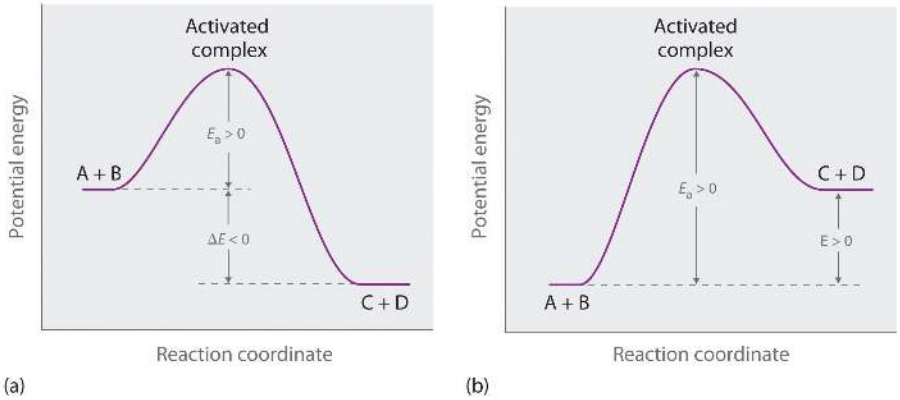


Figure 15.4.3: Differentiating between E_a and ΔE. The potential energy diagrams for a reaction with (a) ΔE < 0 and (b) ΔE > 0 illustrate the change in the potential energy of the system as reactants are converted to products. In both cases, E_a is positive. For a reaction such as the one shown in (b), E_a must be greater than ΔE. (CC BY-SA-NC; anonymous)

> *For similar reactions under comparable conditions, the one with the smallest E_a will occur most rapidly.*

Whereas ΔE is related to the tendency of a reaction to occur spontaneously, E_a gives us information about the reaction rate and how rapidly the reaction rate changes with temperature. For two similar reactions under comparable conditions, the reaction with

the smallest E_a will occur more rapidly.

Figure 15.4.4shows both the kinetic energy distributions and a potential energy diagram for a reaction. The shaded areas show that at the lower temperature (300 K), only a small fraction of molecules collide with kinetic energy greater than E_a; however, at the higher temperature (500 K) a much larger fraction of molecules collide with kinetic energy greater than E_a. Consequently, the reaction rate is much slower at the lower temperature because only a relatively few molecules collide with enough energy to overcome the potential energy barrier.

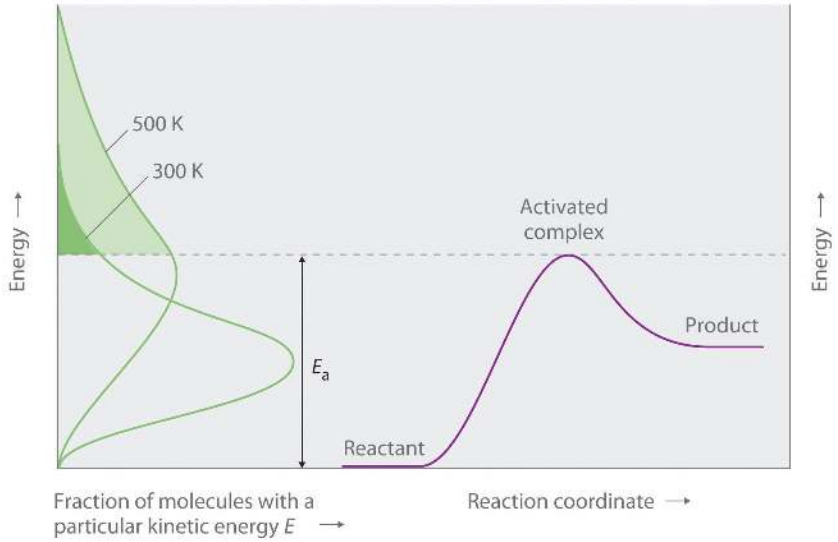


Figure 15.4.4: Surmounting the Energy Barrier to a Reaction. This chart juxtaposes the energy distributions of lower-temperature (300 K) and higher-temperature (500 K) samples of a gas against the potential energy diagram for a reaction. Only those molecules in the shaded region of the energy distribution curve have E > E_a and are therefore able to cross the energy barrier separating reactants and products. The fraction of molecules with $E > E_a$ is much greater at 500 K than at 300 K, so the reaction will occur much more rapidly at 500 K. (CC BY-SA-NC; anonymous)

Energy is on the y axis while reaction coordinate and fraction of molecules with a particular kinetic energy E are on the x axis.



Video Discussing Transition State Theory: Transition State Theory(opens in new window) [youtu.be]

Microscopic Factor 3: Sterics

Even when the energy of collisions between two reactant species is greater than E_a, most collisions do not produce a reaction. The probability of a reaction occurring depends not only on the collision energy but also on the spatial orientation of the molecules when they collide. For NO and O_3 to produce NO_2 and O_2, a terminal oxygen atom of O_3 must collide with the nitrogen atom of NO at an angle that allows O_3 to transfer an oxygen atom to NO to produce NO_2 (Figure 15.4.4). All other collisions produce no reaction. Because fewer than 1% of all possible orientations of NO and O_3 result in a reaction at kinetic energies greater than E_a, most collisions of NO and O_3 are unproductive. The fraction of orientations that result in a reaction is called the **steric factor** (ρ) and its value can range from $\rho = 0$ (no orientations of molecules result in reaction) to $\rho = 1$ (all orientations result in reaction).

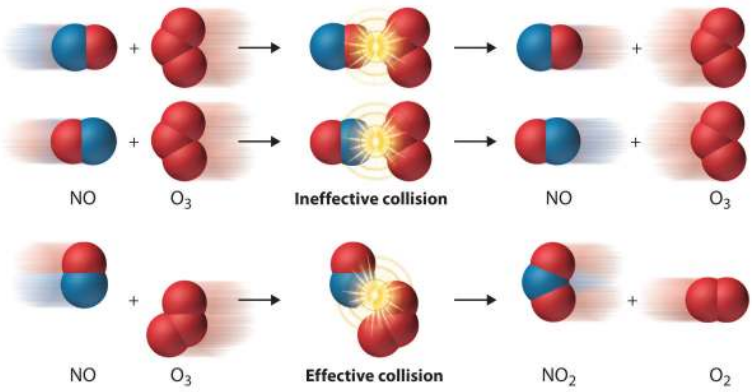


Figure 15.4.4: The Effect of Molecular Orientation on the Reaction of NO and O_3. Most collisions of NO and O_3 molecules occur with an incorrect orientation for a reaction to occur. Only those collisions in which the N atom of NO collides with one of the terminal O atoms of O_3 are likely to produce NO_2 and O_2, even if the molecules collide with $E > E_a$. (CC BY-SA-NC; anonymous)

Macroscopic Behavior: The Arrhenius Equation

The collision model explains why most collisions between molecules do not result in a chemical reaction. For example, nitrogen and oxygen molecules in a single liter of air at room temperature and 1 atm of pressure collide about 10^{30} times per second. If every collision produced two molecules of NO, the atmosphere would have been converted to NO and then NO_2 a long time ago. Instead, in most collisions, the molecules simply bounce off one another without reacting, much as marbles bounce off each other when they collide.

For an $A + B$ elementary reaction, all three microscopic factors discussed above that affect the reaction rate can be summarized in a single relationship:

$$\text{rate} = (\text{collision frequency}) \times (\text{steric factor}) \times (\text{fraction of collisions with } E > E_a)$$

where

$$\text{rate} = k[A][B] \tag{15.4.2}$$

Arrhenius used these relationships to arrive at an equation that relates the magnitude of the rate constant for a reaction to the temperature, the activation energy, and the constant, A, called the **frequency factor**:

$$k = Ae^{-E_a/RT} \tag{15.4.3}$$

The frequency factor is used to convert concentrations to collisions per second (scaled by the steric factor). Because the frequency of collisions depends on the temperature, A is actually not constant (Equation 15.4.1). Instead, A increases slightly with temperature as the increased kinetic energy of molecules at higher temperatures causes them to move slightly faster and thus undergo more collisions per unit time.

Equation 15.4.3 is known as the **Arrhenius equation** and summarizes the collision model of chemical kinetics, where T is the absolute temperature (in K) and R is the ideal gas constant [8.314 J/(K·mol)]. E_a indicates the sensitivity of the reaction to changes in temperature. The reaction rate with a large E_a increases rapidly with increasing temperature, whereas the reaction rate with a smaller E_a increases much more slowly with increasing temperature.

If we know the reaction rate at various temperatures, we can use the Arrhenius equation to calculate the activation energy. Taking the natural logarithm of both sides of Equation 15.4.3,

$$\ln k = \ln A + \left(-\frac{E_a}{RT}\right) \tag{15.4.4}$$

$$= \ln A + \left[\left(-\frac{E_a}{R}\right)\left(\frac{1}{T}\right)\right] \tag{15.4.5}$$

Equation 15.4.5 is the equation of a straight line,

$$y = mx + b$$

where $y = \ln k$ and $x = 1/T$. This means that a plot of $\ln k$ versus $1/T$ is a straight line with a slope of $-E_a/R$ and an intercept of $\ln A$. In fact, we need to measure the reaction rate at only two temperatures to estimate E_a.

Knowing the E_a at one temperature allows us to predict the reaction rate at other temperatures. This is important in cooking and food preservation, for example, as well as in controlling industrial reactions to prevent potential disasters. The procedure for determining E_a from reaction rates measured at several temperatures is illustrated in Example 15.4.1.



A Video Discussing The Arrhenius Equation: The Arrhenius Equation(opens in new window) [youtu.be]

Example 15.4.1: Chirping Tree Crickets

Many people believe that the rate of a tree cricket's chirping is related to temperature. To see whether this is true, biologists have carried out accurate measurements of the rate of tree cricket chirping (f) as a function of temperature (T). Use the data in the following table, along with the graph of ln[chirping rate] versus $1/T$ to calculate E_a for the biochemical reaction that controls cricket chirping. Then predict the chirping rate on a very hot evening, when the temperature is 308 K (35°C, or 95°F).

Chirping Tree Crickets Frequency Table

Frequency (f; chirps/min)	ln f	T (K)	1/T (K)
200	5.30	299	3.34×10^{-3}
179	5.19	298	3.36×10^{-3}
158	5.06	296	3.38×10^{-3}
141	4.95	294	3.40×10^{-3}
126	4.84	293	3.41×10^{-3}
112	4.72	292	3.42×10^{-3}
100	4.61	290	3.45×10^{-3}
89	4.49	289	3.46×10^{-3}
79	4.37	287	3.48×10^{-3}

Given: chirping rate at various temperatures

Asked for: activation energy and chirping rate at specified temperature

Strategy:

A. From the plot of ln f versus $1/T$, calculate the slope of the line ($-E_a/R$) and then solve for the activation energy.
B. Express Equation 15.4.5 in terms of k_1 and T_1 and then in terms of k_2 and T_2.
C. Subtract the two equations; rearrange the result to describe k_2/k_1 in terms of T_2 and T_1.

D. Using measured data from the table, solve the equation to obtain the ratio k_2/k_1. Using the value listed in the table for k_1, solve for k_2.

Solution

A If cricket chirping is controlled by a reaction that obeys the Arrhenius equation, then a plot of $\ln f$ versus $1/T$ should give a straight line (Figure 15.4.6).

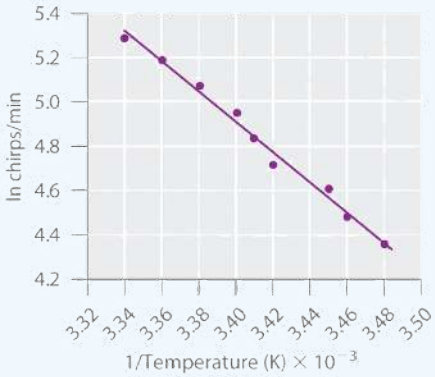


Figure 15.4.6: Graphical Determination of E_a for Tree Cricket Chirping. When the natural logarithm of the rate of tree cricket chirping is plotted versus 1/T, a straight line results. The slope of the line suggests that the chirping rate is controlled by a single reaction with an E_a of 55 kJ/mol. (CC BY-SA-NC; anonymous)

Also, the slope of the plot of $\ln f$ versus $1/T$ should be equal to $-E_a/R$. We can use the two endpoints in Figure 15.4.6 to estimate the slope:

$$\begin{aligned}\text{slope} &= \frac{\Delta \ln f}{\Delta(1/T)} \\ &= \frac{5.30 - 4.37}{3.34 \times 10^{-3}\ \text{K}^{-1} - 3.48 \times 10^{-3}\ \text{K}^{-1}} \\ &= \frac{0.93}{-0.14 \times 10^{-3}\ \text{K}^{-1}} \\ &= -6.6 \times 10^{3}\ \text{K}\end{aligned}$$

A computer best-fit line through all the points has a slope of −6.67 × 10^3 K, so our estimate is very close. We now use it to solve for the activation energy:

$$\begin{aligned}E_\text{a} &= -(\text{slope})(R) \\ &= -(-6.6 \times 10^{3}\ \text{K}) \left(\frac{8.314\ \text{J}}{\text{K} \cdot \text{mol}}\right) \left(\frac{1\ \text{KJ}}{1000\ \text{J}}\right) \\ &= \frac{55\ \text{kJ}}{\text{mol}}\end{aligned}$$

B If the activation energy of a reaction and the rate constant at one temperature are known, then we can calculate the reaction rate at any other temperature. We can use Equation 15.4.5 to express the known rate constant (k_1) at the first temperature (T_1) as follows:

$$\ln k_1 = \ln A - \frac{E_\text{a}}{RT_1}$$

Similarly, we can express the unknown rate constant (k_2) at the second temperature (T_2) as follows:

$$\ln k_2 = \ln A - \frac{E_\text{a}}{RT_2}$$

C These two equations contain four known quantities (E_a, T_1, T_2, and k_1) and two unknowns (A and k_2). We can eliminate A by subtracting the first equation from the second:

$$\ln k_2 - \ln k_1 = \left(\ln A - \frac{E_a}{RT_2}\right) - \left(\ln A - \frac{E_a}{RT_1}\right)$$
$$= -\frac{E_a}{RT_2} + \frac{E_a}{RT_1}$$

Then

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

D To obtain the best prediction of chirping rate at 308 K (T_2), we try to choose for T_1 and k_1 the measured rate constant and corresponding temperature in the data table that is closest to the best-fit line in the graph. Choosing data for T_1 = 296 K, where f = 158, and using the E_a calculated previously,

$$\ln \frac{k_{T_2}}{k_{T_1}} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$
$$= \frac{55\ \text{kJ/mol}}{8.314\ \text{J/(K·mol)}}\left(\frac{1000\ \text{J}}{1\ \text{kJ}}\right)\left(\frac{1}{296\ \text{K}} - \frac{1}{308\ \text{K}}\right)$$
$$= 0.87$$

Thus k_{308}/k_{296} = 2.4 and k_{308} = (2.4)(158) = 380, and the chirping rate on a night when the temperature is 308 K is predicted to be 380 chirps per minute.

Exercise 15.4.1A

The equation for the decomposition of NO_2 to NO and O_2 is second order in NO_2:

$$2\,NO_2(g) \rightarrow 2\,NO(g) + O_2(g)$$

Data for the reaction rate as a function of temperature are listed in the following table. Calculate E_a for the reaction and the rate constant at 700 K.

Data for the reaction rate as a function of temperature

T (K)	k ($M^{-1}·s^{-1}$)
592	522
603	755
627	1700
652	4020
656	5030

Answer

E_a = 114 kJ/mol; k_{700}= 18,600 $M^{-1}·s^{-1}$ = 1.86 × 10^4 $M^{-1}·s^{-1}$.

Exercise 15.4.1B

What E_a results in a doubling of the reaction rate with a 10°C increase in temperature from 20° to 30°C?

Answer

about 51 kJ/mol



A Video Discussing Graphing Using the Arrhenius Equation: Graphing Using the Arrhenius Equation (opens in new window) [youtu.be] (opens in new window)

Summary

For a chemical reaction to occur, an energy threshold must be overcome, and the reacting species must also have the correct spatial orientation. The Arrhenius equation is $k = Ae^{-E_a/RT}$. A minimum energy (activation energy,vE_a) is required for a collision between molecules to result in a chemical reaction. Plots of potential energy for a system versus the reaction coordinate show an energy barrier that must be overcome for the reaction to occur. The arrangement of atoms at the highest point of this barrier is the activated complex, or transition state, of the reaction. At a given temperature, the higher the E_a, the slower the reaction. The fraction of orientations that result in a reaction is the steric factor. The frequency factor, steric factor, and activation energy are related to the rate constant in the Arrhenius equation: $k = Ae^{-E_a/RT}$. A plot of the natural logarithm of k versus $1/T$ is a straight line with a slope of $-E_a/R$.

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15.5: A Deeper Look- Reaction Dynamics

under construction

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15.6: Kinetics of Catalysis

Learning Objectives

- To understand how catalysts increase the reaction rate and the selectivity of chemical reactions.

Catalysts are substances that increase the reaction rate of a chemical reaction without being consumed in the process. A catalyst, therefore, does not appear in the overall stoichiometry of the reaction it catalyzes, but it must appear in at least one of the elementary reactions in the mechanism for the catalyzed reaction. The catalyzed pathway has a lower E_a, but the net change in energy that results from the reaction (the difference between the energy of the reactants and the energy of the products) is not affected by the presence of a catalyst (Figure 15.6.1). Nevertheless, because of its lower E_a, the reaction rate of a catalyzed reaction is faster than the reaction rate of the uncatalyzed reaction at the same temperature. Because a catalyst decreases the height of the energy barrier, its presence increases the reaction rates of both the forward and the reverse reactions by the same amount. In this section, we will examine the three major classes of catalysts: heterogeneous catalysts, homogeneous catalysts, and enzymes.

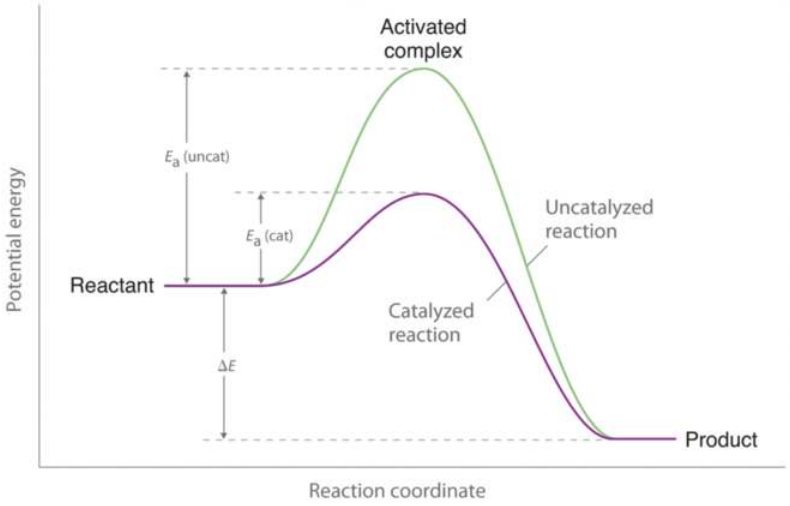


Figure 15.6.1: Lowering the Activation Energy of a Reaction by a Catalyst. This graph compares potential energy diagrams for a single-step reaction in the presence and absence of a catalyst. The only effect of the catalyst is to lower the activation energy of the reaction. The catalyst does not affect the energy of the reactants or products (and thus does not affect ΔE). (CC BY-NC-SA; anonymous)

The green line represents the uncatalyzed reaction. The purple line represent the catalyzed reaction .

> *A catalyst affects E_a, not ΔE.*

Heterogeneous Catalysis

In **heterogeneous catalysis**, the catalyst is in a different phase from the reactants. At least one of the reactants interacts with the solid surface in a physical process called adsorption in such a way that a chemical bond in the reactant becomes weak and then breaks. Poisons are substances that bind irreversibly to catalysts, preventing reactants from adsorbing and thus reducing or destroying the catalyst's efficiency.

An example of heterogeneous catalysis is the interaction of hydrogen gas with the surface of a metal, such as Ni, Pd, or Pt. As shown in part (a) in Figure 15.6.2, the hydrogen–hydrogen bonds break and produce individual adsorbed hydrogen atoms on the surface of the metal. Because the adsorbed atoms can move around on the surface, two hydrogen atoms can collide and form a molecule of hydrogen gas that can then leave the surface in the reverse process, called desorption. Adsorbed H atoms on a metal surface are substantially more reactive than a hydrogen molecule. Because the relatively strong H–H bond (dissociation energy = 432 kJ/mol) has already been broken, the energy barrier for most reactions of H_2 is substantially lower on the catalyst surface.

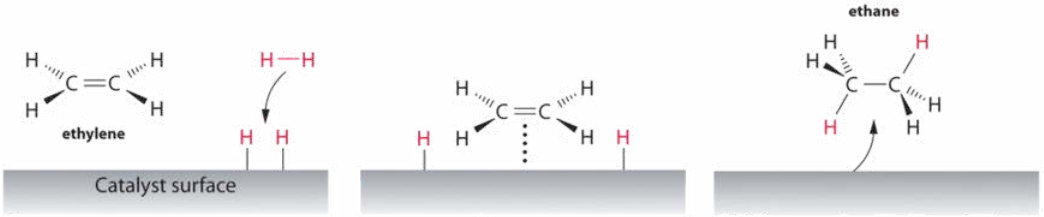


Figure 15.6.2: Hydrogenation of Ethylene on a Heterogeneous Catalyst. When a molecule of hydrogen adsorbs to the catalyst surface, the H–H bond breaks, and new M–H bonds are formed. The individual H atoms are more reactive than gaseous H_2. When a molecule of ethylene interacts with the catalyst surface, it reacts with the H atoms in a stepwise process to eventually produce ethane, which is released. (CC BY-NC-SA; anonymous)

Figure 15.6.2 shows a process called *hydrogenation*, in which hydrogen atoms are added to the double bond of an alkene, such as ethylene, to give a product that contains C–C single bonds, in this case ethane. Hydrogenation is used in the food industry to convert vegetable oils, which consist of long chains of alkenes, to more commercially valuable solid derivatives that contain alkyl chains. Hydrogenation of some of the double bonds in polyunsaturated vegetable oils, for example, produces margarine, a product with a melting point, texture, and other physical properties similar to those of butter.

Several important examples of industrial heterogeneous catalytic reactions are in Table 15.6.1. Although the mechanisms of these reactions are considerably more complex than the simple hydrogenation reaction described here, they all involve adsorption of the reactants onto a solid catalytic surface, chemical reaction of the adsorbed species (sometimes via a number of intermediate species), and finally desorption of the products from the surface.

Table 15.6.1: Some Commercially Important Reactions that Employ Heterogeneous Catalysts

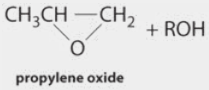
Commercial Process	Catalyst	Initial Reaction	Final Commercial Product
contact process	V_2O_5 or Pt	$2SO_2 + O_2 \rightarrow 2SO_3$	H_2SO_4
Haber process	Fe, K_2O, Al_2O_3	$N_2 + 3H_2 \rightarrow 2NH_3$	NH_3
Ostwald process	Pt and Rh	$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$	HNO_3
water–gas shift reaction	Fe, Cr_2O_3, or Cu	$CO + H_2O \rightarrow CO_2 + H_2$	H_2 for NH_3, CH_3OH, and other fuels
steam reforming	Ni	$CH_4 + H_2O \rightarrow CO + 3H_2$	H_2
methanol synthesis	ZnO and Cr_2O_3	$CO + 2H_2 \rightarrow CH_3OH$	CH_3OH
Sohio process	bismuth phosphomolybdate	$CH_2{=}CHCH_3 + NH_3 + \frac{3}{2}O_2 \rightarrow CH_2{=}CHCN + 3H_2O$	$CH_2{=}CHCN$ (acrylonitrile)
catalytic hydrogenation	Ni, Pd, or Pt	RCH=CHR′ + H2 → RCH_2—CH_2R'	partially hydrogenated oils for margarine, and so forth

Homogeneous Catalysis

In **homogeneous catalysis**, the catalyst is in the same phase as the reactant(s). The number of collisions between reactants and catalyst is at a maximum because the catalyst is uniformly dispersed throughout the reaction mixture. Many homogeneous catalysts in industry are transition metal compounds (Table 15.6.2), but recovering these expensive catalysts from solution has been a major challenge. As an added barrier to their widespread commercial use, many homogeneous catalysts can be used only at relatively low temperatures, and even then they tend to decompose slowly in solution. Despite these problems, a number of commercially viable processes have been developed in recent years. High-density polyethylene and polypropylene are produced by homogeneous catalysis.

Table 15.6.2: Some Commercially Important Reactions that Employ Homogeneous Catalysts

Commercial Process	Catalyst	Reactants	Final Product

Commercial Process	Catalyst	Reactants	Final Product
Union Carbide	$[Rh(CO)_2I_2]^-$	$CO + CH_3OH$	CH_3CO_2H
hydroperoxide process	Mo(VI) complexes	$CH_3CH{=}CH_2 + R{-}O{-}O{-}H$	 propylene oxide
hydroformylation	Rh/PR_3 complexes	$RCH{=}CH_2 + CO + H_2$	RCH_2CH_2CHO
adiponitrile process	Ni/PR_3complexes	$2HCN + CH_2{=}CHCH{=}CH_2$	$NCCH_2CH_2CH_2CH_2CN$ used to synthesize nylon
olefin polymerization	$(RC_5H_5)_2ZrCl_2$	$CH_2{=}CH_2$	$-(CH_2CH_2-)_n$: high-density polyethylene

Enzymes

Enzymes, catalysts that occur naturally in living organisms, are almost all protein molecules with typical molecular masses of 20,000–100,000 amu. Some are homogeneous catalysts that react in aqueous solution within a cellular compartment of an organism. Others are heterogeneous catalysts embedded within the membranes that separate cells and cellular compartments from their surroundings. The reactant in an enzyme-catalyzed reaction is called a **substrate**.

Because enzymes can increase reaction rates by enormous factors (up to 10^{17} times the uncatalyzed rate) and tend to be very specific, typically producing only a single product in quantitative yield, they are the focus of active research. At the same time, enzymes are usually expensive to obtain, they often cease functioning at temperatures greater than 37 °C, have limited stability in solution, and have such high specificity that they are confined to turning one particular set of reactants into one particular product. This means that separate processes using different enzymes must be developed for chemically similar reactions, which is time-consuming and expensive. Thus far, enzymes have found only limited industrial applications, although they are used as ingredients in laundry detergents, contact lens cleaners, and meat tenderizers. The enzymes in these applications tend to be proteases, which are able to cleave the amide bonds that hold amino acids together in proteins. Meat tenderizers, for example, contain a protease called papain, which is isolated from papaya juice. It cleaves some of the long, fibrous protein molecules that make inexpensive cuts of beef tough, producing a piece of meat that is more tender. Some insects, like the bombadier beetle, carry an enzyme capable of catalyzing the decomposition of hydrogen peroxide to water (Figure 15.6.3).



Figure 15.6.3: A Catalytic Defense Mechanism. The scalding, foul-smelling spray emitted by this bombardier beetle is produced by the catalytic decomposition of H_2O_2.

Enzyme inhibitors cause a decrease in the reaction rate of an enzyme-catalyzed reaction by binding to a specific portion of an enzyme and thus slowing or preventing a reaction from occurring. Irreversible inhibitors are therefore the equivalent of poisons in heterogeneous catalysis. One of the oldest and most widely used commercial enzyme inhibitors is aspirin, which selectively inhibits one of the enzymes involved in the synthesis of molecules that trigger inflammation. The design and synthesis of related molecules that are more effective, more selective, and less toxic than aspirin are important objectives of biomedical research.

Summary

Catalysts participate in a chemical reaction and increase its rate. They do not appear in the reaction's net equation and are not consumed during the reaction. Catalysts allow a reaction to proceed via a pathway that has a lower activation energy than the uncatalyzed reaction. In heterogeneous catalysis, catalysts provide a surface to which reactants bind in a process of adsorption. In homogeneous catalysis, catalysts are in the same phase as the reactants. Enzymes are biological catalysts that produce large

increases in reaction rates and tend to be specific for certain reactants and products. The reactant in an enzyme-catalyzed reaction is called a substrate. Enzyme inhibitors cause a decrease in the reaction rate of an enzyme-catalyzed reaction.

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