OT - PDX - METRO: GENERAL CHEMISTRY II



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OT - PDX - Metro: General Chemistry II

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This text was compiled on 01/12/2026

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Licensing

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

CHAPTER OVERVIEW

1: The Quantum Mechanical Model of the Atom

Unit Objectives

By the end of this unit, you should be able to:

- Explain the basic behavior of waves, including travelling waves and standing waves
- Describe the wave nature of light
- Use appropriate equations to calculate related light-wave properties such as period, frequency, wavelength, and energy
- Distinguish between line and continuous emission spectra
- Describe the particle nature of light
- Extend the concept of wave–particle duality that was observed in electromagnetic radiation to matter as well
- Calculate deBroglie wavelengths

1.1: The Nature of Light

1.1.1: The Nature of Light (Problems)

1.2: Atomic Spectroscopy and the deBroglie Wavelength

1.2.1: Atomic Spectroscopy and the deBroglie Wavelength (Problems)

1.3: Coulomb's Law and the Electrostatic Potential

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1.4: Atomic Orbitals and Quantum Numbers

1.4.1: Atomic Orbitals and Quantum Numbers (Problems)

1.5: Atomic Orbitals and the Bohr Model

1.5.1: Atomic Orbitals and the Bohr Model (Problems)

Thumbnail: 3D views of some the 2s atomic orbitals showing probability density and phase. Image used with permission (CC BY-AS 4.0; Geek3).

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1.1: The Nature of Light

Skills to Develop

- 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, and energy



Video* 1.1.1*: *Is light a particle or a wave? This section will explore the answers to this question.*

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.



Video* 1.1.2*: *An exploration of light as a wave.*

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 **1.1.1**, 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.

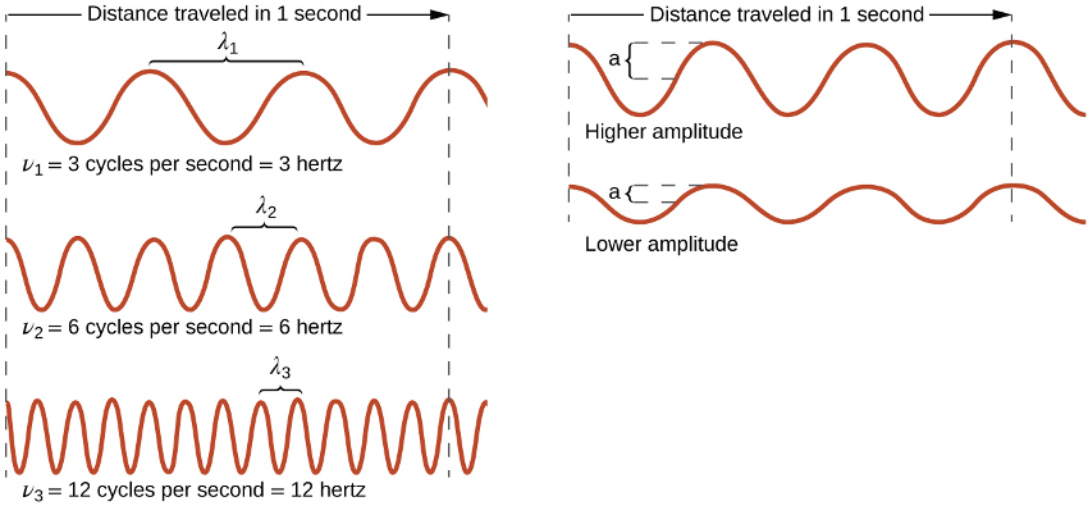


Figure* 1.1.1*: *One-dimensional sinusoidal waves show the relationship among wavelength, frequency, and speed. The wave with the shortest wavelength has the highest frequency. Amplitude is one-half the height of the wave from peak to trough.*

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:

$$c = 2.998 \times 10^8\ \mathrm{ms}^{-1} = \lambda\nu \tag{1.1.1}$$

Wavelength and frequency are inversely proportional: As the wavelength increases, the frequency decreases. The inverse proportionality is illustrated in Figure **1.1.2**. 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).

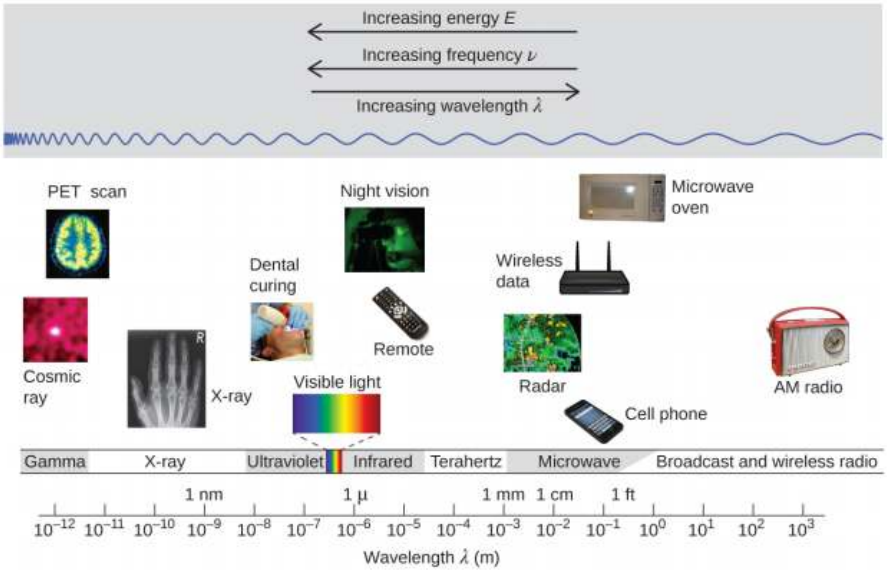


Figure* 1.1.2*: *Portions of the electromagnetic spectrum are shown in order of decreasing frequency and increasing wavelength. Examples of some applications for various wavelengths include positron emission tomography (PET) scans, X-ray imaging, remote controls, wireless Internet, cellular telephones, 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)

The TeraHertz Region

Terahertz radiation is a region of the electromagnetic spectrum with frequencies of 0.3 to 3 THz (or 1 mm to 0.1 mm), and was previously defined as microwave radio waves or the far IR. Because of its seat into beteen microwaves and IR, scientists have begin refering to the region as the "TeraHertz gap" Due to the ability of several atmospheric gases to absorb energy in this region of the spectrum, it is unsuitable for radio communications, but a lot of research into uses of technology in this area of the spectrum have emerged over the last decade. To read more about it visit here or here.

Example 1.1.1: 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 1.1.1 to solve for the frequency:

$$\nu = \frac{c}{\lambda} \tag{1.1.2}$$

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

$$\nu = \left(\frac{2.998 \times 10^{8}\ \cancel{\text{m}}\,\text{s}^{-1}}{589\ \cancel{\text{nm}}}\right)\left(\frac{1 \times 10^{9}\ \cancel{\text{nm}}}{1\ \cancel{\text{m}}}\right) = 5.09 \times 10^{14}\,\text{s}^{-1} \tag{1.1.3}$$

Exercise 1.1.1

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



***Video* 1.1.3:** *A summary of light's behavior as a wave.*

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 1.1.5). In FM radio, by contrast, the amplitude is constant and the instantaneous frequency varies.



Figure* 1.1.3*: *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.

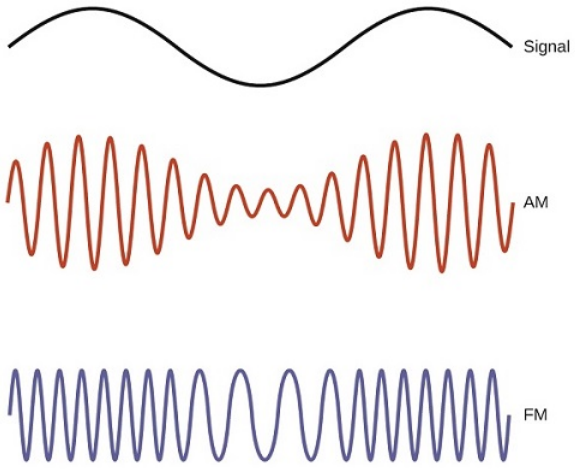


Figure* 1.1.4*: *This schematic depicts how amplitude modulation (AM) and frequency modulation (FM) can be used to transmit a radio wave.*

One particularly characteristic phenomenon of waves results when two or more waves come into contact: They interfere with each other. Figure 1.1.5 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 1.1.5 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.

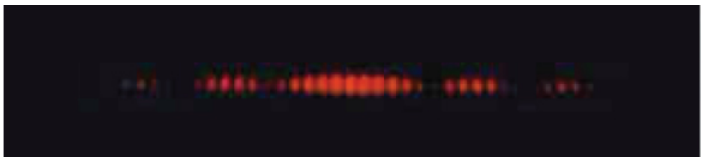


Figure* 1.1.5*: *Interference fringe patterns are shown for light passing through two closely spaced, narrow slits. The spacing of the fringes depends on the wavelength, with the fringes being more closely spaced for the shorter-wavelength blue light. (credit: PASCO)*

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 **1.1.6** 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 **1.1.6**. 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.

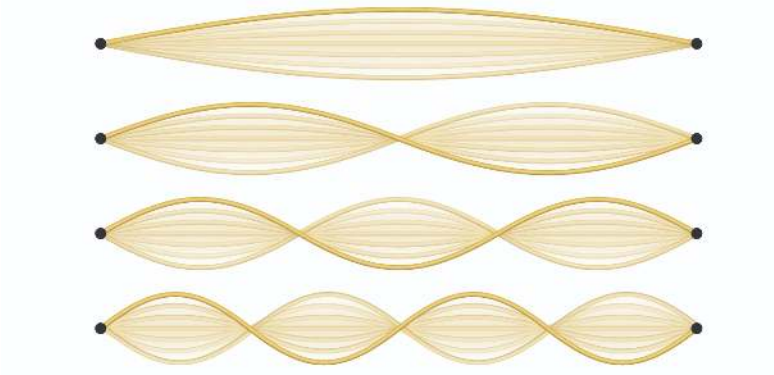


Figure* 1.1.6*: A vibrating string shows some one-dimensional standing waves. Since the two end points of the string are held fixed, only waves having an integer number of half-wavelengths can form. The points on the string between the end points that are not moving are called the nodes.

An example of two-dimensional standing waves is shown in Figure **1.1.7** 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 **1.1.7** shows two radial nodes, while the image in the lower right shows the vibrational pattern associated with three radial nodes and two angular nodes.

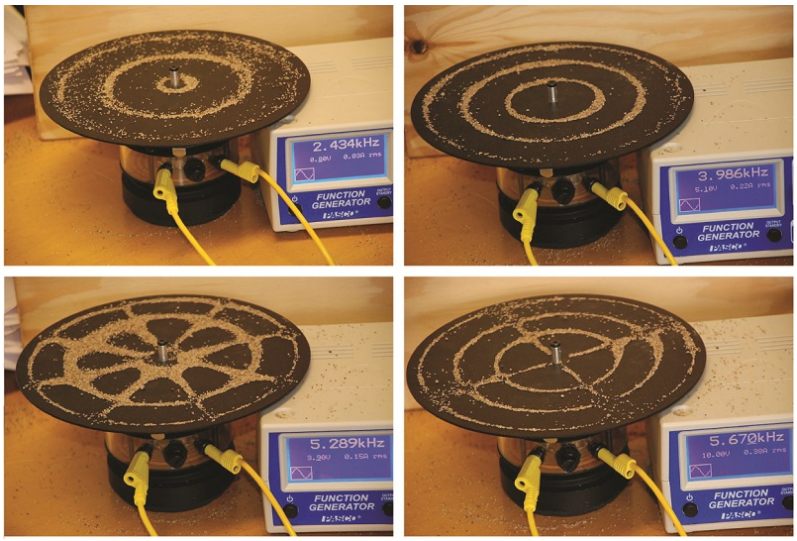


***Figure* 1.1.7:** *Two-dimensional standing waves can be visualized on a vibrating surface. The surface has been sprinkled with a powder that collects near the nodal lines. There are two types of nodes visible: radial nodes (circles) and angular nodes (radii).*
For a more animated video, check this link out.

Radial Nodes & Imogen Heap

You can watch the formation of various radial nodes below as singer Imogen Heap projects her voice across a kettle drum.

Video* 1.1.4*: *Singer Imogen Heap projects her voice across a kettle drum.*

Blackbody Radiation and the Ultraviolet Catastrophe

The last few decades of the nineteenth century witnessed intense research activity in commercializing newly discovered electric lighting. This required obtaining a better understanding of the distributions of light emitted from various sources being considered. Artificial lighting is usually designed to mimic natural sunlight within the limitations of the underlying technology. Such lighting consists of a range of broadly distributed frequencies that form a continuous spectrum. Figure 1.1.8 shows the wavelength distribution for sunlight. The most intense radiation is in the visible region, with the intensity dropping off rapidly for shorter wavelength ultraviolet (UV) light, and more slowly for longer wavelength infrared (IR) light.

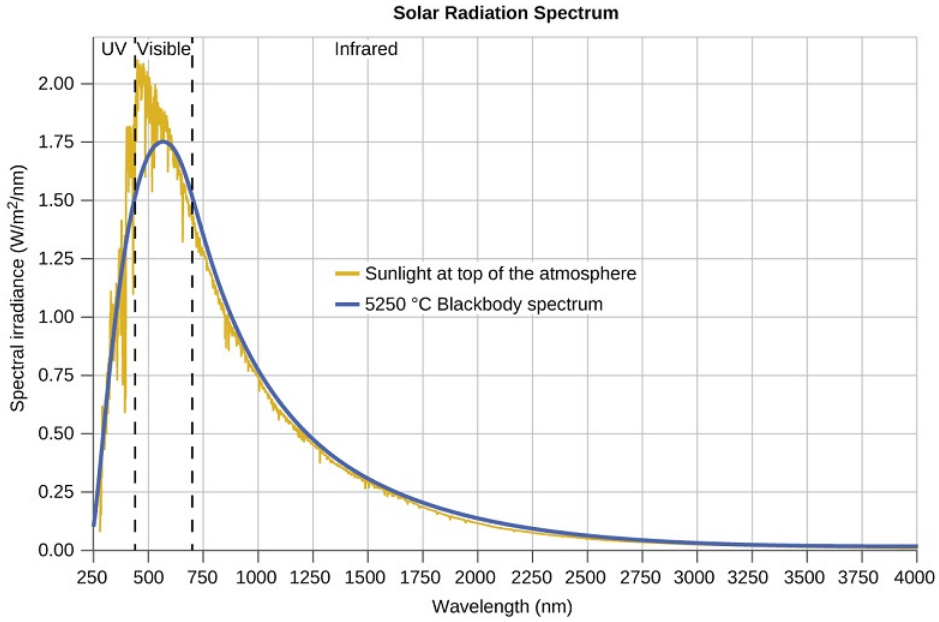


Figure* 1.1.8*: *The spectral distribution (light intensity vs. wavelength) of sunlight reaches the Earth's atmosphere as UV light, visible light, and IR light. The unabsorbed sunlight at the top of the atmosphere has a distribution that approximately matches the theoretical distribution of a blackbody at 5250 °C, represented by the blue curve. (credit: modification of work by American Society for Testing and Materials (ASTM) Terrestrial Reference Spectra for Photovoltaic Performance Evaluation)*

In Figure 1.1.8, the solar distribution is compared to a representative distribution, called a blackbody spectrum, that corresponds to a temperature of 5250 °C. The blackbody spectrum matches the solar spectrum quite well. A blackbody is a convenient, ideal emitter that approximates the behavior of many materials when heated. It is “ideal” in the same sense that an ideal gas is a convenient, simple representation of real gases that works well, provided that the pressure is not too high nor the temperature too low. A good approximation of a blackbody that can be used to observe blackbody radiation is a metal oven that can be heated to very high temperatures. The oven has a small hole allowing for the light being emitted within the oven to be observed with a spectrometer so that the wavelengths and their intensities can be measured. Figure 1.1.8 shows the resulting curves for some representative temperatures. Each distribution depends only on a single parameter: the temperature. The maxima in the blackbody curves, λ_{max}, shift to shorter wavelengths as the temperature increases, reflecting the observation that metals being heated to high temperatures begin to glow a darker red that becomes brighter as the temperature increases, eventually becoming white hot at very high temperatures as the intensities of all of the visible wavelengths become appreciable. This common observation was at the heart of the first paradox that showed the fundamental limitations of classical physics that we will examine.

Physicists derived mathematical expressions for the blackbody curves using well-accepted concepts from the theories of classical mechanics and classical electromagnetism. The theoretical expressions as functions of temperature fit the observed experimental blackbody curves well at longer wavelengths, but showed significant discrepancies at shorter wavelengths. Not only did the theoretical curves not show a peak, they absurdly showed the intensity becoming infinitely large as the wavelength became smaller, which would imply that everyday objects at room temperature should be emitting large amounts of UV light. This became known

as the “ultraviolet catastrophe” because no one could find any problems with the theoretical treatment that could lead to such unrealistic short-wavelength behavior. Finally, around 1900, Max Planck derived a theoretical expression for blackbody radiation that fit the experimental observations exactly (within experimental error). Planck developed his theoretical treatment by extending the earlier work that had been based on the premise that the atoms composing the oven vibrated at increasing frequencies (or decreasing wavelengths) as the temperature increased, with these vibrations being the source of the emitted electromagnetic radiation. But where the earlier treatments had allowed the vibrating atoms to have any energy values obtained from a continuous set of energies (perfectly reasonable, according to classical physics), Planck found that by restricting the vibrational energies to discrete values for each frequency, he could derive an expression for blackbody radiation that correctly had the intensity dropping rapidly for the short wavelengths in the UV region.

$$E = nh\nu,\ n = 1, 2, 3,\ \ldots \tag{1.1.4}$$

The quantity h is a constant now known as Planck's constant, in his honor. Although Planck was pleased he had resolved the blackbody radiation paradox, he was disturbed that to do so, he needed to assume the vibrating atoms required quantized energies, which he was unable to explain. The value of Planck's constant is very small, 6.626×10^{-34} joule seconds (J s), which helps explain why energy quantization had not been observed previously in macroscopic phenomena.

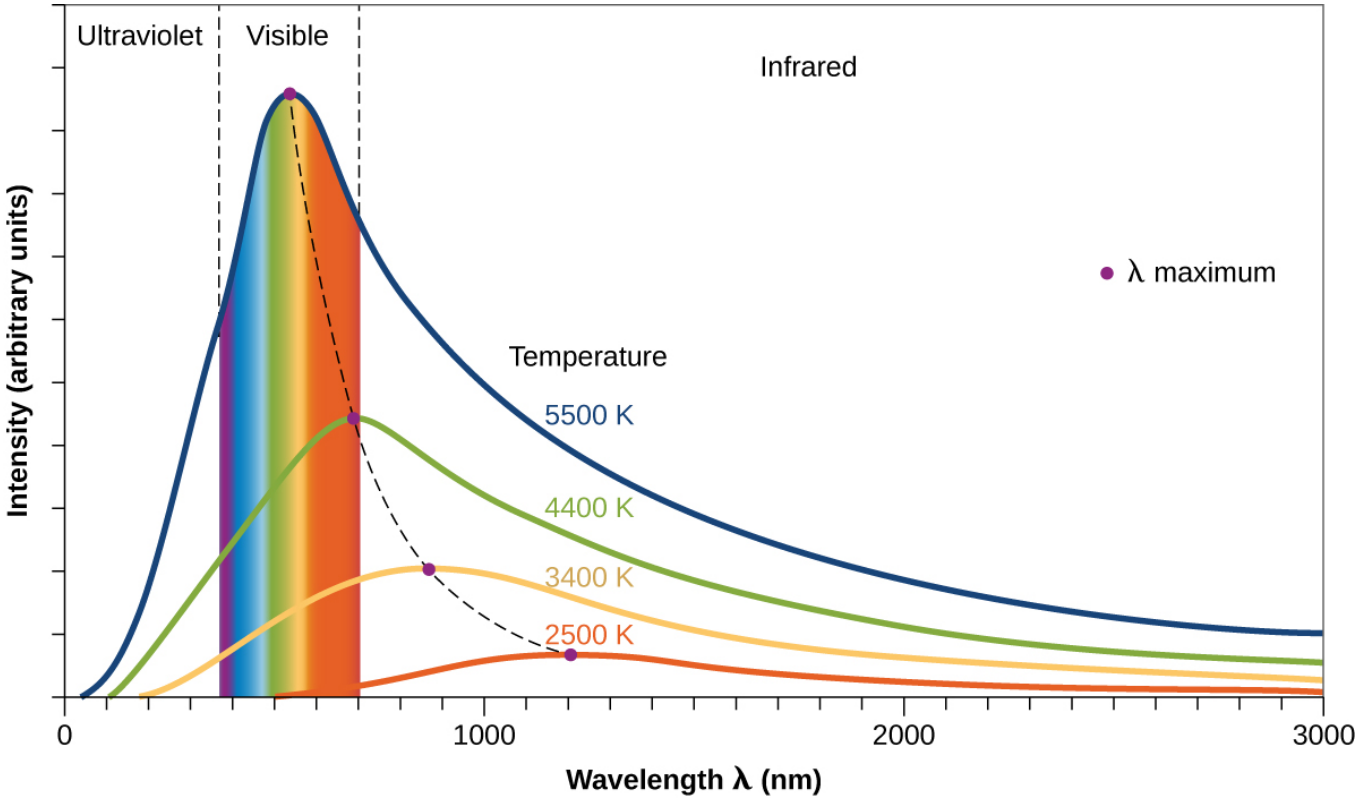
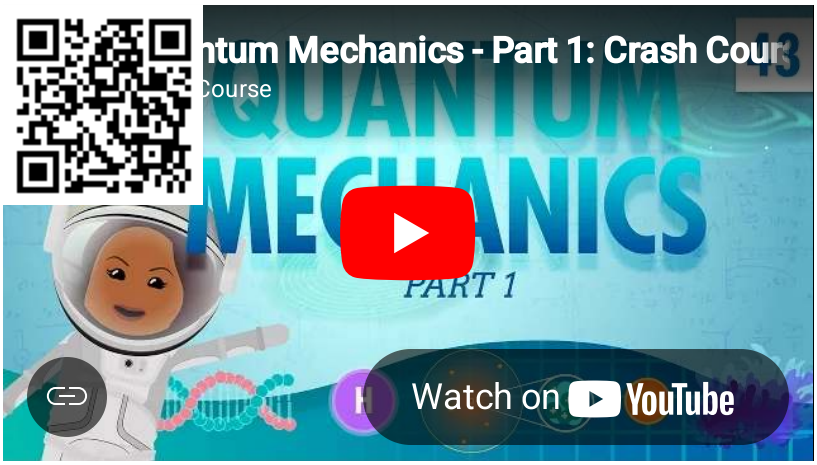


Figure* 1.1.9*: *Blackbody spectral distribution curves are shown for some representative temperatures.*



Video* 1.1.5*: *An overview of the Ultraviolet Catastrophe.*

The Photoelectric Effect

The next paradox in the classical theory to be resolved concerned the photoelectric effect (Figure **1.1.10**). It had been observed that electrons could be ejected from the clean surface of a metal when light having a frequency greater than some threshold frequency was shone on it. Surprisingly, the kinetic energy of the ejected electrons did not depend on the brightness of the light, but increased with increasing frequency of the light. Since the electrons in the metal had a certain amount of binding energy keeping them there, the incident light needed to have more energy to free the electrons. According to classical wave theory, a wave's energy depends on its intensity (which depends on its amplitude), not its frequency. One part of these observations was that the number of electrons ejected within in a given time period was seen to increase as the brightness increased. In 1905, Albert Einstein was able to resolve the paradox by incorporating Planck's quantization findings into the discredited particle view of light (Einstein actually won his Nobel prize for this work, and not for his theories of relativity for which he is most famous).

Einstein argued that the quantized energies that Planck had postulated in his treatment of blackbody radiation could be applied to the light in the photoelectric effect so that the light striking the metal surface should not be viewed as a wave, but instead as a stream of particles (later called photons) whose energy depended on their frequency, according to Planck's formula, $E = h\nu$ (or, in terms of wavelength using $c = \nu\lambda$, $\boldsymbol{E = \frac{hc}{\lambda}}$). Electrons were ejected when hit by photons having sufficient energy (a frequency greater than the threshold). The greater the frequency, the greater the kinetic energy imparted to the escaping electrons by the collisions. Einstein also argued that the light intensity did not depend on the amplitude of the incoming wave, but instead corresponded to the number of photons striking the surface within a given time period. This explains why the number of ejected electrons increased with increasing brightness, since the greater the number of incoming photons, the greater the likelihood that they would collide with some of the electrons.

With Einstein's findings, the nature of light took on a new air of mystery. Although many light phenomena could be explained either in terms of waves or particles, certain phenomena, such as the interference patterns obtained when light passed through a double slit, were completely contrary to a particle view of light, while other phenomena, such as the photoelectric effect, were completely contrary to a wave view of light. Somehow, at a deep fundamental level still not fully understood, light is both wavelike and particle-like. This is known as wave-particle duality.

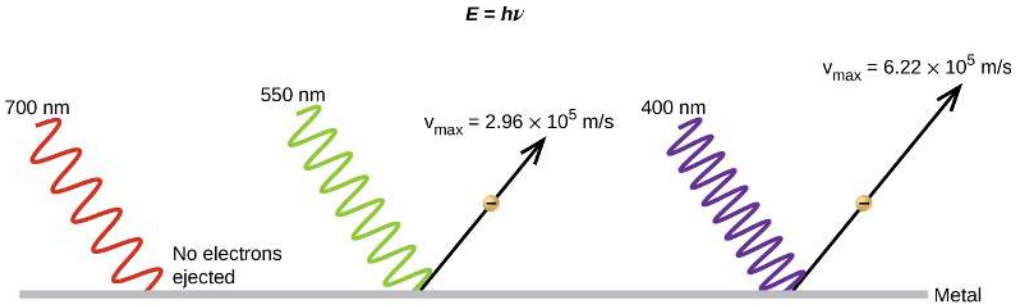


Figure 1.1.10*: Photons with low frequencies do not have enough energy to cause electrons to be ejected via the photoelectric effect. For any frequency of light above the threshold frequency, the kinetic energy of an ejected electron will increase linearly with the energy of the incoming photon.*

Example 1.1.2: 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.

$$E = \frac{hc}{\lambda}$$

$$E = \frac{(6.626 \times 10^{-34}\ \text{J}\cancel{s})(2.998 \times 10^{8}\ \text{m}\cancel{s^{-1}})}{(640\ \cancel{\text{nm}}) \left(\frac{1\ \text{m}}{10^{9}\ \cancel{\text{nm}}} \right)}$$

$$E = 3.10 \times 10^{-19}\ \text{J}$$

Exercise 1.1.2

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

Answer

2×10^{-24} J

Example 1.1.3: Photoelectric Effect

Identify which of the following statements are false and, where necessary, change the italicized word or phrase to make them true, consistent with Einstein's explanation of the photoelectric effect.

a. Increasing the brightness of incoming light *increases* the kinetic energy of the ejected electrons.
b. Increasing the *wavelength* of incoming light increases the kinetic energy of the ejected electrons.
c. Increasing the brightness of incoming light *increases* the number of ejected electrons.
d. Increasing the *frequency* of incoming light can increase the number of ejected electrons.

Solution

a. False. Increasing the brightness of incoming light *has no effect* on the kinetic energy of the ejected electrons. Only energy, not the number or amplitude, of the photons influences the kinetic energy of the electrons.
b. False. Increasing the *frequency* of incoming light increases the kinetic energy of the ejected electrons. Frequency is proportional to energy and inversely proportional to wavelength. Frequencies above the threshold value transfer the excess energy into the kinetic energy of the electrons.
c. True. Because the number of collisions with photons increases with brighter light, the number of ejected electrons increases.
d. True with regard to the threshold energy binding the electrons to the metal. Below this threshold, electrons are not emitted and above it they are. Once over the threshold value, further increasing the frequency does not increase the number of ejected electrons

Exercise 1.1.3

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

$3.94\ kJ/mol$



Video* 1.1.6*: *An overview of the photoelectric effect.*

Summary



Video* 1.1.7*: *An overview of the wave nature of light.*

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. Electromagnetic radiation that passes through two closely spaced narrow slits having dimensions roughly similar to the wavelength will show an interference pattern that is a result of constructive and destructive interference of the waves. Electromagnetic radiation also 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 $\boldsymbol{E = \frac{hc}{\lambda}}$), 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). Continuous spectra often have distributions that can be approximated as blackbody radiation at some appropriate temperature. The line spectrum of hydrogen can be obtained by passing the light from an electrified tube of hydrogen gas through a prism. This line spectrum was simple enough that an empirical formula called the Rydberg formula could be derived from the spectrum. Three historically important paradoxes from the late 19th and early 20th centuries that could not be explained within the existing framework of classical mechanics and classical electromagnetism were the blackbody problem, the photoelectric effect, and the

discrete spectra of atoms. The resolution of these paradoxes ultimately led to quantum theories that superseded the classical theories.

Preview of Section 1.2



Video* 1.1.8*: *Looking toward the next section...*

Key Equations

- $c = \lambda\nu$
- $E = h\nu = \frac{hc}{\lambda}$, where $h = 6.626 \times 10^{-34}$ J s

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

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

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1.1.1: The Nature of Light (Problems)

PROBLEM 1.1.1.1

An FM radio station found at 103.1 on the FM dial broadcasts at a frequency of $1.031 \times 10^8\ s^{-1}$ (103.1 MHz). What is the wavelength of these radio waves in meters?

Answer

2.908 m

PROBLEM 1.1.1.2

FM-95, an FM radio station, broadcasts at a frequency of $9.51 \times 10^7\ s^{-1}$ (95.1 MHz). What is the wavelength of these radio waves in meters?

Answer

3.15 m

Click here to see a video of the solution



PROBLEM 1.1.1.3

Light with a wavelength of 614.5 nm looks orange. What is the energy, in joules, per photon of this orange light? What is the energy in eV (1 eV = 1.602×10^{-19} J)?

Answer

$3.233 \times 10^{-19} J$

2.018 eV

PROBLEM 1.1.1.4

Heated lithium atoms emit photons of light with an energy of 2.961×10^{-19} J. Calculate the frequency and wavelength of one of these photons. What is the total energy in 1 mole of these photons? What is the color of the emitted light?

Answer

Frequency: $4.469 \times 10^{14} Hz$

Wavelength: $6.709 \times 10^{-7} m$ = **Red Light**

Total energy: $1.783 \times 10^5 J$

Click here to see a video of the solution

PROBLEM 1.1.1.5

A photon of light produced l … cy and wavelength of the photon. What is the total ene …

Answer

$\nu = 4.568 \times 10^{14}$ s; λ = 65 …

PROBLEM 1.1.1.6

One of the radiographic devi … m. What is the energy, in joules, and frequency of this …

Answer

$E = 9.502 \times 10^{-15}$ J; ν = 1 …

Click here to see a video of the solution

PROBLEM 1.1.1.7

The eyes of certain reptiles pass a single visual signal to the brain when the visual receptors are struck by photons of a wavelength of 850 nm. If a total energy of 3.15×10^{-14} J is required to trip the signal, what is the minimum number of photons that must strike the receptor?

Answer

$1.3 \times 10^{5}\ photons$

PROBLEM 1.1.1.8

Answer the following questions about a Blu-ray laser:

a. The laser on a Blu-ray player has a wavelength of 405 nm. In what region of the electromagnetic spectrum is this radiation? What is its frequency?
b. A Blu-ray laser has a power of 5 milliwatts (1 watt = 1 J s^{-1}). How many photons of light are produced by the laser in 1 hour?
c. The ideal resolution of a player using a laser (such as a Blu-ray player), which determines how close together data can be stored on a compact disk, is determined using the following formula: Resolution = 0.60(λ/NA), where λ is the wavelength of the laser (in nm) and NA is the numerical aperture (dimensionless). Numerical aperture is a measure of the size of the spot of

light on the disk; the larger the NA, the smaller the spot. In a typical Blu-ray system, NA = 0.95. If the 405-nm laser is used in a Blu-ray player, what is the closest that information can be stored on a Blu-ray disk?

d. The data density of a Blu-ray disk using a 405-nm laser is 1.5×10^7 bits mm^{-2}. Disks have an outside diameter of 120 mm and a hole of 15-mm diameter. How many data bits can be contained on the disk? If a Blu-ray disk can hold 9,400,000 pages of text, how many data bits are needed for a typed page? (Hint: Determine the area of the disk that is available to hold data. The area inside a circle is given by $A = \pi r^2$, where the radius r is one-half of the diameter.)

Answer a

7.40×10^{14} s^{-1}

Answer b

3.67×10^{19} photons

Answer c

255 nm

Answer d

1.67×10^{11} bits

17,765 bits/page

Click here to see a video of the solution



PROBLEM 1.1.1.9

What is the threshold frequency for sodium metal if a photon with frequency 6.66×10^{14} s^{-1} ejects a photon with 7.74×10^{-20} J kinetic energy? Will the photoelectric effect be observed if sodium is exposed to orange light?

Answer

5.49×10^{14} s^{-1}; no

Contributors

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- Adelaide Clark, Oregon Institute of Technology

Feedback

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1.2: Atomic Spectroscopy and the deBroglie Wavelength

Skills to Develop

- Distinguish between line and continuous emission spectra
- Describe the particle nature of light
- Extend the concept of wave–particle duality that was observed in electromagnetic radiation to matter as well
- Calculate deBroglie wavelengths

Line Spectra



Video* 1.2.1*: *A brief review of how wavelength and frequency affect the colors of light.*

Another paradox within the classical electromagnetic theory that scientists in the late nineteenth century struggled with concerned the light emitted from atoms and molecules. When solids, liquids, or condensed gases are heated sufficiently, they radiate some of the excess energy as light. Photons produced in this manner have a range of energies, and thereby produce a continuous spectrum in which an unbroken series of wavelengths is present. Most of the light generated from stars (including our sun) is produced in this fashion. You can see all the visible wavelengths of light present in sunlight by using a prism to separate them. As can be seen in Figure 1.1.8 in the previous section, sunlight also contains UV light (shorter wavelengths) and IR light (longer wavelengths) that can be detected using instruments but that are invisible to the human eye. Incandescent (glowing) solids such as tungsten filaments in incandescent lights also give off light that contains all wavelengths of visible light. These continuous spectra can often be approximated by blackbody radiation curves at some appropriate temperature, such as those shown in the previous section.

In contrast to continuous spectra, light can also occur as discrete or line spectra having very narrow line widths interspersed throughout the spectral regions such as those shown in Figure **1.2.2**. Exciting a gas at low partial pressure using an electrical current, or heating it, will produce line spectra. Fluorescent light bulbs and neon signs operate in this way (Figure **1.2.1**). Each element displays its own characteristic set of lines, as do molecules, although their spectra are generally much more complicated.



Figure* 1.2.1*: *Neon signs operate by exciting a gas at low partial pressure using an electrical current. This sign shows the elaborate artistic effects that can be achieved. (credit: Dave Shaver)*

Each emission line consists of a single wavelength of light, which implies that the light emitted by a gas consists of a set of discrete energies. For example, when an electric discharge passes through a tube containing hydrogen gas at low pressure, the H_2 molecules are broken apart into separate H atoms, and we see a blue-pink color. Passing the light through a prism produces a line spectrum, indicating that this light is composed of photons of four visible wavelengths, as shown in Figure **1.2.2**.

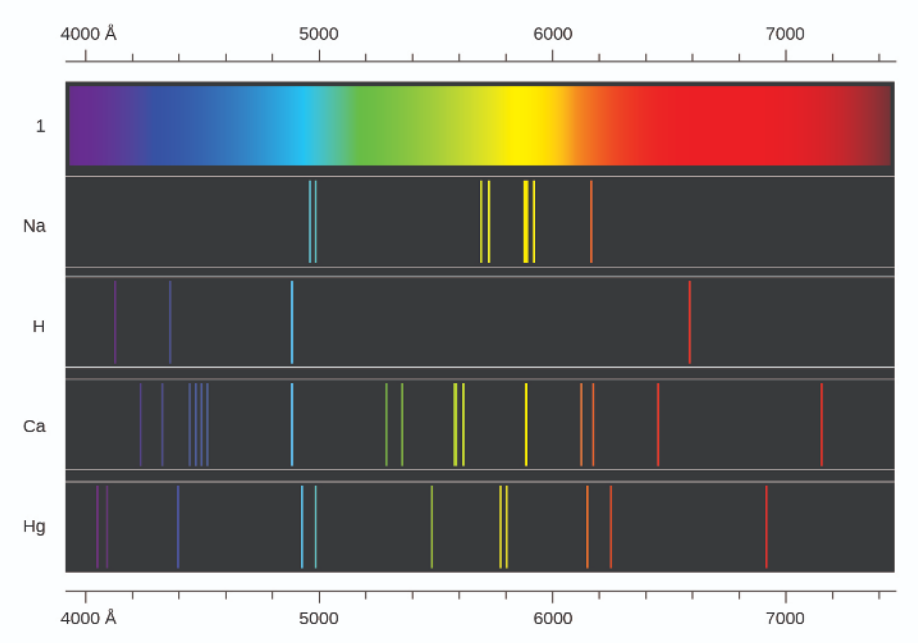


Figure* 1.2.2*: *Line spectra of select gas. Compare the two types of emission spectra: continuous spectrum of white light (top) and the line spectra of the light from excited sodium, hydrogen, calcium, and mercury atoms.*

The origin of discrete spectra in atoms and molecules was extremely puzzling to scientists in the late nineteenth century, since according to classical electromagnetic theory, only continuous spectra should be observed. Even more puzzling, in 1885, Johann Balmer was able to derive an empirical equation that related the four visible wavelengths of light emitted by hydrogen atoms to whole integers. That equation is the following one, in which k is a constant:

$$\frac{1}{\lambda} = k\left(\frac{1}{4} - \frac{1}{n^2}\right), \; n = 3,\, 4,\, 5,\, 6 \tag{1.2.1}$$

Other discrete lines for the hydrogen atom were found in the UV and IR regions. Johannes Rydberg generalized Balmer's work and developed an empirical formula that predicted all of hydrogen's emission lines, not just those restricted to the visible range, where, n_1 and n_2 are integers, $n_1 < n_2$, and R_∞ is the Rydberg constant (1.097×10^7 m^{-1}).

$$\frac{1}{\lambda} = R_\infty \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \tag{1.2.2}$$

Even in the late nineteenth century, spectroscopy was a very precise science, and so the wavelengths of hydrogen were measured to very high accuracy, which implied that the Rydberg constant could be determined very precisely as well. That such a simple formula as the Rydberg formula could account for such precise measurements seemed astounding at the time, but it was the eventual explanation for emission spectra by Neils Bohr in 1913 that ultimately convinced scientists to abandon classical physics and spurred the development of modern quantum mechanics.



Video* 1.2.2*: *Emissions of electrons and the colors of elements.*

Looking Further



Figure* 1.2.3*: *Dr. Neil Degrasse Tyson. Photo Credit: NASA/Bill Ingalls*

In his book, *Astrophysics for People in a Hurry*, Neil Degrasse Tyson talks about the origins of the universe and how we've used atomic spectroscopy and line spectra to determine what elements are present in various celestial bodies. Read versions of these essays by clicking the links below:

"Over the Rainbow" - A look at Spectroscopy and it's role in learning more about our universe.

"The Periodic Table of the Cosmos" - A look at the origin of the elements (from space!)

Behavior in the Microscopic World

We know how matter behaves in the macroscopic world—objects that are large enough to be seen by the naked eye follow the rules of classical physics. A billiard ball moving on a table will behave like a particle: It will continue in a straight line unless it collides with another ball or the table cushion, or is acted on by some other force (such as friction). The ball has a well-defined position and velocity (or a well-defined momentum, $p = mv$, defined by mass m and velocity v) at any given moment. In other words, the ball is moving in a classical trajectory. This is the typical behavior of a classical object.

When waves interact with each other, they show interference patterns that are not displayed by macroscopic particles such as the billiard ball. For example, interacting waves on the surface of water can produce interference patters similar to those shown on Figure 1.2.4. This is a case of wave behavior on the macroscopic scale, and it is clear that particles and waves are very different phenomena in the macroscopic realm.

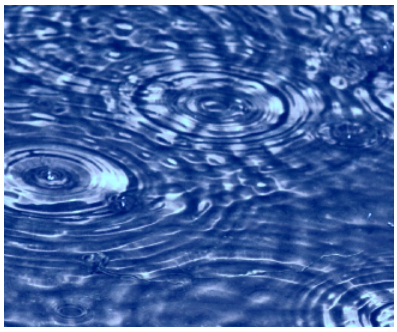


***Figure* 1.2.4**: *An interference pattern on the water surface is formed by interacting waves. The waves are caused by reflection of water from the rocks. (credit: modification of work by Sukanto Debnath)*

As technological improvements allowed scientists to probe the microscopic world in greater detail, it became increasingly clear by the 1920s that very small pieces of matter follow a different set of rules from those we observe for large objects. The unquestionable separation of waves and particles was no longer the case for the microscopic world.

One of the first people to pay attention to the special behavior of the microscopic world was Louis de Broglie. He asked the question: If electromagnetic radiation can have particle-like character, can electrons and other submicroscopic particles exhibit wavelike character? In his 1925 doctoral dissertation, de Broglie extended the wave–particle duality of light that Einstein used to resolve the photoelectric-effect paradox to material particles. He predicted that a particle with mass m and velocity v (that is, with linear momentum p) should also exhibit the behavior of a wave with a wavelength value λ, given by this expression in which h is the familiar Planck's constant

$$\lambda = \frac{h}{mv} = \frac{h}{p} \tag{1.2.3}$$

This is called the *de Broglie wavelength*. Unlike the other values of λ discussed in this chapter, the de Broglie wavelength is a characteristic of particles and other bodies, not electromagnetic radiation (note that this equation involves velocity [v, m/s], not frequency [ν, Hz]. Although these two symbols are identical, they mean very different things). Where Bohr had postulated the electron as being a particle orbiting the nucleus in quantized orbits, de Broglie argued that Bohr's assumption of quantization can be explained if the electron is considered not as a particle, but rather as a circular standing wave such that only an integer number of wavelengths could fit exactly within the orbit (Figure 1.2.5).

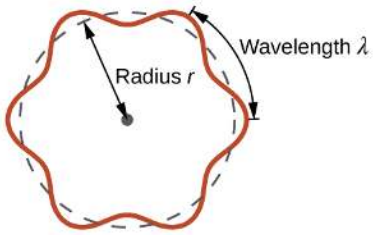


***Figure* 1.2.5**: *If an electron is viewed as a wave circling around the nucleus, an integer number of wavelengths must fit into the orbit for this standing wave behavior to be possible.*

For a circular orbit of radius r, the circumference is 2πr, and so de Broglie's condition is:

$$2\pi r = n\lambda \tag{1.2.4}$$

with $n = 1, 2, 3, ...$

Shortly after de Broglie proposed the wave nature of matter, two scientists at Bell Laboratories, C. J. Davisson and L. H. Germer, demonstrated experimentally that electrons can exhibit wavelike behavior by showing an interference pattern for electrons travelling through a regular atomic pattern in a crystal. The regularly spaced atomic layers served as slits, as used in other interference experiments. Since the spacing between the layers serving as slits needs to be similar in size to the wavelength of the tested wave for an interference pattern to form, Davisson and Germer used a crystalline nickel target for their "slits," since the spacing of the atoms within the lattice was approximately the same as the de Broglie wavelengths of the electrons that they used. Figure 1.2.6 shows an interference pattern.

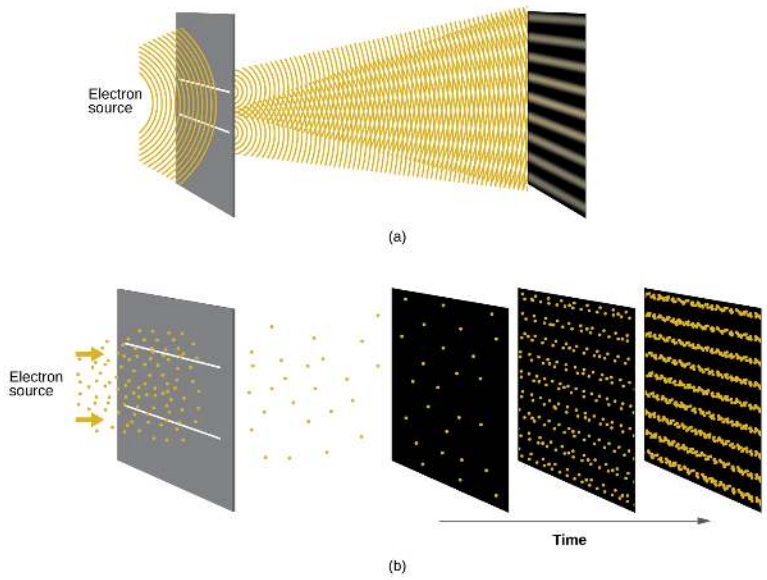


***Figure* 1.2.6:** *(a) The interference pattern for electrons passing through very closely spaced slits demonstrates that quantum particles such as electrons can exhibit wavelike behavior. (b) The experimental results illustrated here demonstrate the wave–particle duality in electrons. The electrons pass through very closely spaced slits, forming an interference pattern, with increasing numbers of electrons being recorded from the left image to the right. With only a few electrons recorded, it is clear that the electrons arrive as individual localized "particles," but in a seemingly random pattern. As more electrons arrive, a wavelike interference pattern begins to emerge. Note that the probability of the final electron location is still governed by the wave-type distribution, even for a single electron, but it can be observed more easily if many electron collisions have been recorded.*

The wave–particle duality of matter can be seen by observing what happens if electron collisions are recorded over a long period of time. Initially, when only a few electrons have been recorded, they show clear particle-like behavior, having arrived in small localized packets that appear to be random. As more and more electrons arrived and were recorded, a clear interference pattern that is the hallmark of wavelike behavior emerged. Thus, it appears that while electrons are small localized particles, their motion does not follow the equations of motion implied by classical mechanics, but instead it is governed by some type of a wave equation that governs a probability distribution even for a single electron's motion. Thus the wave–particle duality first observed with photons is actually a fundamental behavior intrinsic to all quantum particles.



***Video* 1.2.3:** *View the Dr. Quantum – Double Slit Experiment cartoon for an easy-to-understand description of wave–particle duality and the associated experiments.*

Example 1.2.1: Calculating the Wavelength of a Particle

If an electron travels at a velocity of 1.000×10^7 m s^{-1} and has a mass of 9.109×10^{-28} g, what is its wavelength?

Solution

We can use de Broglie's equation to solve this problem, but we first must do a unit conversion of Planck's constant. You learned earlier that 1 J = 1 kg m^2/s^2. Thus, we can write $h = 6.626 \times 10^{-34}$ J s as 6.626×10^{-34} kg m^2/s.

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

$$= \frac{6.626 \times 10^{-34}\ \text{kg m}^2/\text{s}}{(9.109 \times 10^{-31}\ \text{kg})(1.000 \times 10^{7}\ \text{m/s})}$$
$$= 7.274 \times 10^{-11}\ \text{m}$$

This is a small value, but it is significantly larger than the size of an electron in the classical (particle) view. This size is the same order of magnitude as the size of an atom. This means that electron wavelike behavior is going to be noticeable in an atom.

Exercise 1.2.1

Calculate the wavelength of a softball with a mass of 100 g traveling at a velocity of 35 m s^{-1}, assuming that it can be modeled as a single particle.

Answer

1.9×10^{-34} m.

We never think of a thrown softball having a wavelength, since this wavelength is so small it is impossible for our senses or any known instrument to detect (strictly speaking, the wavelength of a real baseball would correspond to the wavelengths of its constituent atoms and molecules, which, while much larger than this value, would still be microscopically tiny). The de Broglie wavelength is only appreciable for matter that has a very small mass and/or a very high velocity.

Werner Heisenberg considered the limits of how accurately we can measure properties of an electron or other microscopic particles. He determined that there is a fundamental limit to how accurately one can measure both a particle's position and its momentum simultaneously. The more accurately we measure the momentum of a particle, the less accurately we can determine its position at that time, and vice versa. This is summed up in what we now call the Heisenberg uncertainty principle: *It is fundamentally impossible to determine simultaneously and exactly both the momentum and the position of a particle*. For a particle of mass m moving with velocity v_x in the x direction (or equivalently with momentum p_x), the product of the uncertainty in the position, Δx, and the uncertainty in the momentum, Δp_x , must be greater than or equal to $\frac{\hbar}{2}$ (recall that $\hbar = \frac{h}{2\pi}$, the value of Planck's constant divided by 2π).

$$\Delta x \times \Delta p_x = (\Delta x)(m\Delta v) \geq \frac{\hbar}{2} \tag{1.2.5}$$

This equation allows us to calculate the limit to how precisely we can know both the simultaneous position of an object and its momentum. For example, if we improve our measurement of an electron's position so that the uncertainty in the position (Δx) has a value of, say, 1 pm (10^{-12} m, about 1% of the diameter of a hydrogen atom), then our determination of its momentum must have an uncertainty with a value of at least

$$\left[\Delta p = m\Delta v = \frac{h}{(2\Delta x)}\right] = \frac{(1.055 \times 10^{-34}\ \text{kg m}^2/\text{s})}{(2 \times 1 \times 10^{-12}\ \text{m})} = 5 \times 10^{-23}\ \text{kg m/s}. \tag{1.2.6}$$

The value of $\hbar$ is not large, so the uncertainty in the position or momentum of a macroscopic object like a baseball is too insignificant to observe. However, the mass of a microscopic object such as an electron is small enough that the uncertainty can be large and significant.

It should be noted that Heisenberg's uncertainty principle is not just limited to uncertainties in position and momentum, but it also links other dynamical variables. For example, when an atom absorbs a photon and makes a transition from one energy state to another, the uncertainty in the energy and the uncertainty in the time required for the transition are similarly related, as $\Delta E\ \Delta t \geq \frac{\hbar}{2}$. As will be discussed later, even the vector components of angular momentum cannot all be specified exactly simultaneously.

Heisenberg's principle imposes ultimate limits on what is knowable in science. The uncertainty principle can be shown to be a consequence of wave–particle duality, which lies at the heart of what distinguishes modern quantum theory from classical mechanics. Recall that the equations of motion obtained from classical mechanics are trajectories where, at any given instant in time, both the position and the momentum of a particle can be determined exactly. Heisenberg's uncertainty principle implies that such a view is untenable in the microscopic domain and that there are fundamental limitations governing the motion of quantum particles. This does not mean that microscopic particles do not move in trajectories, it is just that measurements of trajectories are limited in their precision. In the realm of quantum mechanics, measurements introduce changes into the system that is being observed.



***Video* 1.2.4:** *VAn overview of the deBroglie wavelength.*

Summary

Macroscopic objects act as particles. Microscopic objects (such as electrons) have properties of both a particle and a wave. Their exact trajectories cannot be determined. The quantum mechanical model of atoms describes the three-dimensional position of the electron in a *probabilistic* manner according to a mathematical function called a wavefunction, often denoted as ψ. Atomic wavefunctions are also called orbitals. The squared magnitude of the wavefunction describes the distribution of the probability of finding the electron in a particular region in space. Therefore, atomic orbitals describe the areas in an atom where electrons are most likely to be found.

Key Equation

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

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1.2.1: Atomic Spectroscopy and the deBroglie Wavelength (Problems)

PROBLEM 1.2.1.1

Assume the mass of an electron is 9.11 x 10^{-31} kg.

a. Calculate the wavelength of an electron traveling with a speed of 2.65 x 10^{6} m/s.

b. What would the wavelength of the helium atom be if it were traveling at the same speed as the electron in part a (1 amu = 1.6606 x 10^{-24} g)?

Answer a

2.74 x 10^{-10} m

Answer b

3.77 x 10^{-14} m

PROBLEM 1.2.1.2

What is the de Broglie wavelength of a 46 g baseball traveling at 94 mph?

Answer

3.43 x 10^{-34} m

Click here for a video of the solution



PROBLEM 1.2.1.3

Which of the following equations describe particle-like behavior? Which describe wavelike behavior?

a. $c = \lambda\nu$

b. $E = \frac{m\nu^2}{2}$

c. $r = \frac{n^2 a_0}{Z}$

d. $E = h\nu$

e. $\lambda = \frac{h}{m\nu}$

Answer

e. describes particle-like behavior

a&d describe wavelike behavior

PROBLEM 1.2.1.4

RGB color television and computer displays use cathode ray tubes that produce colors by mixing red, green, and blue light. If we look at the screen with a magnifying glass, we can see individual dots turn on and off as the colors change. Using a spectrum of visible light, determine the approximate wavelength of each of these colors. What is the frequency and energy of a photon of each of these colors

Answer

Red: 660 nm; 4.54×10^{14} Hz; 3.01×10^{-19} J. Green: 520 nm; 5.77×10^{14} Hz; 3.82×10^{-19} J. Blue: 440 nm; 6.81×10^{14} Hz; 4.51×10^{-19} J.

PROBLEM 1.2.1.5

A bright violet line occurs at 435.8 nm in the emission spectrum of mercury vapor. What amount of energy, in joules, must be released by an electron in a mercury atom to produce a photon of this light?

Answer

$4.56 \times 10^{-19} J$

PROBLEM 1.2.1.6

When rubidium ions are heated to a high temperature, two lines are observed in its line spectrum at wavelengths (a) 7.9×10^{-7} m and (b) 4.2×10^{-7} m. What are the frequencies of the two lines? What color do we see when we heat a rubidium compound?

Answer

The frequency of (a) would be 3.79×10^{14} s^{-1}.

The frequency of (b) would be 7.13×10^{14} s^{-1}.

Because (a) would be in the near-IR, the compound would appear purple/blue based on the wavelength of (b).

Click here to see a video of the solution



PROBLEM 1.2.1.7

The emission spectrum of cesium contains two lines whose frequencies are (a) 3.45×10^{14} Hz and (b) 6.53×10^{14} Hz. What are the wavelengths and energies per photon of the two lines? What color are the lines?

Answer a

$\lambda = 8.69 \times 10^{-7}$ m; $E = 2.29 \times 10^{-19}$ J; red

Answer b

$\lambda = 4.59 \times 10^{-7}$ m; $E = 4.33 \times 10^{-19}$ J; blue

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1.3: Coulomb's Law and the Electrostatic Potential

Skills to Develop

- Use Coulomb's Law to explain electrostatic potential and bonding

Through the work of scientists in the late 18th century, the main features of the **electrostatic force**—the existence of two types of charge, the observation that like charges repel, unlike charges attract, and the decrease of force with distance—were eventually refined, and expressed as a mathematical formula. The mathematical formula for the electrostatic force is called **Coulomb's law** after the French physicist Charles Coulomb (1736–1806), who performed experiments and first proposed a formula to calculate it.



Figure 1.3.1: *This NASA image of Arp 87 shows the result of a strong gravitational attraction between two galaxies. In contrast, at the subatomic level, the electrostatic attraction between two objects, such as an electron and a proton, is far greater than their mutual attraction due to gravity. (credit: NASA/HST)*

Following the work of Ernest Rutherford and his colleagues in the early twentieth century, the picture of atoms consisting of tiny dense nuclei surrounded by lighter and even tinier electrons continually moving about the nucleus was well established. This picture was called the planetary model, since it pictured the atom as a miniature "solar system" with the electrons orbiting the nucleus like planets orbiting the sun. The simplest atom is hydrogen, consisting of a single proton as the nucleus about which a single electron moves. The electrostatic force attracting the electron to the proton depends only on the distance between the two particles, based on Coulomb's Law:

$$F_{gravity} = G\frac{m_1 m_2}{r^2} \tag{1.3.1}$$

with

- G is a gravitational constant
- m_1 and m_2 are the masses of particle 1 and 2, respectively
- r is the distance between the two particles

The electrostatic force has the same form as the gravitational force between two mass particles except that the electrostatic force depends on the magnitudes of the charges on the particles (+1 for the proton and −1 for the electron) instead of the magnitudes of the particle masses that govern the gravitational force.

$$F_{electrostatic} = k\frac{m_1 m_2}{r^2} \tag{1.3.2}$$

with

- k is a constant
- m_1 and m_2 are the masses of particle 1 and 2, respectively
- r is the distance between the two particles

The electrostatic force is a vector quantity and is expressed in units of newtons. The force is understood to be along the line joining the two charges. (Figure 1.3.2)

Although the formula for Coulomb's law is simple, it was no mean task to prove it. The experiments Coulomb did, with the primitive equipment then available, were difficult. Modern experiments have verified Coulomb's law to great precision. For example, it has been shown that the force is inversely proportional to distance between two objects squared ($F \propto 1/r^2$) to an accuracy of 1 part in 10^{16}. No exceptions have ever been found, even at the small distances within the atom.

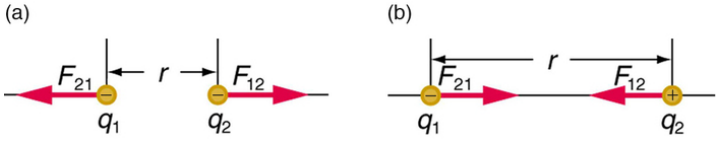
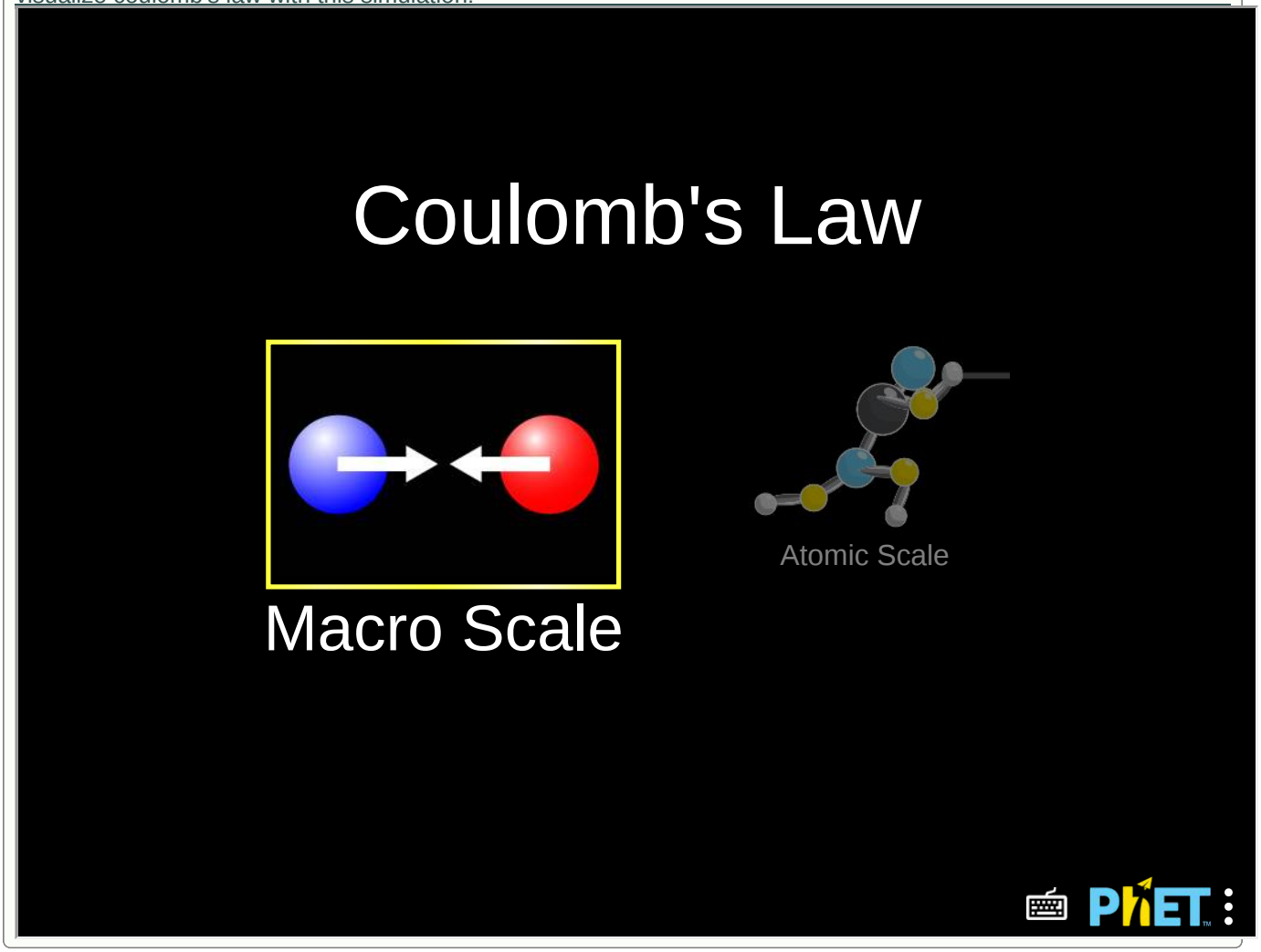


Figure 1.3.2: *The magnitude of the electrostatic force* F *between point charges* q_1 *and* q_2 *separated by a distance* r *is given by Coulomb's law. Note that Newton's third law (every force exerted creates an equal and opposite force) applies as usual—the force on* q_1 *is equal in magnitude and opposite in direction to the force it exerts on* q_2*. (a) Like charges. (b) Unlike charges.*

Since forces can be derived from potentials, it is convenient to work with potentials instead, since they are forms of energy. The electrostatic potential is also called the *Coulomb potential*. Because the electrostatic potential has the same form as the gravitational potential, according to classical mechanics, the equations of motion should be similar, with the electron moving around the nucleus in circular or elliptical orbits (hence the label “planetary” model of the atom). Potentials of the form $V(r)$ that depend only on the radial distance r are known as central potentials. Central potentials have spherical symmetry, and so rather than specifying the position of the electron in the usual Cartesian coordinates (x, y, z), it is more convenient to use polar spherical coordinates centered at the nucleus, consisting of a linear coordinate r and two angular coordinates, usually specified by the Greek letters theta (θ) and phi (Φ). These coordinates are similar to the ones used in GPS devices and most smart phones that track positions on our (nearly) spherical earth, with the two angular coordinates specified by the latitude and longitude, and the linear coordinate specified by sea-level elevation. Because of the spherical symmetry of central potentials, the energy and angular momentum of the classical hydrogen atom are constants, and the orbits are constrained to lie in a plane like the planets orbiting the sun. This classical mechanics description of the atom is incomplete, however, since an electron moving in an elliptical orbit would be accelerating (by changing direction) and, according to classical electromagnetism, it should continuously emit electromagnetic radiation. This loss in orbital energy should result in the electron’s orbit getting continually smaller until it spirals into the nucleus, implying that atoms are inherently unstable.

visualize coulomb's law with this simulation!



Summary



***Video* 1.3.1:** *A review of Coulomb's Law.*

Frenchman Charles Coulomb was the first to publish the mathematical equation that describes the electrostatic force between two objects. Coulomb's law gives the magnitude of the force between point charges. It is $F = k\frac{|q_1 q_2|}{r^2}$, where q_1 and q_2 are two point charges separated by a distance r, and $k \approx 8.99 \times 10^9 N \cdot m^2/C^2$. This Coulomb force is extremely basic, since most charges are due to point-like particles. It is responsible for all electrostatic effects and underlies most macroscopic forces. The Coulomb force is extraordinarily strong compared with the gravitational force, another basic force—but unlike gravitational force it can cancel, since it can be either attractive or repulsive. The electrostatic force between two subatomic particles is far greater than the gravitational force between the same two particles.

Glossary

Coulomb's law
: the mathematical equation calculating the electrostatic force vector between two charged particles

Coulomb force
: another term for the electrostatic force

electrostatic force
: the amount and direction of attraction or repulsion between two charged bodies

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1.3.1: Coulomb's Law and the Electrostatic Potential (Problems)

PROBLEM 1.3.1.1

Would you expect two like charges close together to have a relative potential energy above or below 0?

Answer

Like charges should have energies above 0.

PROBLEM 1.3.1.2

Would you expect two like charges far apart to have a relative potential energy above or below 0?

Answer

Like charges should have energies above 0.

PROBLEM 1.3.1.3

Would you expect two opposite charges far apart to have a relative potential energy above or below 0?

Answer

opposite charges should have energies below 0.

PROBLEM 1.3.1.4

Rank the following scenarios from HIGHEST (most positive) to LOWEST (most negative) relative potential energy.

a. +3, -2 charges, 100 angstroms apart

b. +1, -1 charges, 200 angstroms apart

c. +1, +1 charges, 200 angstroms apart

d. -3, -3 charges, 100 angstroms apart

Answer

d, c, b, a

Click here for a video of the solution



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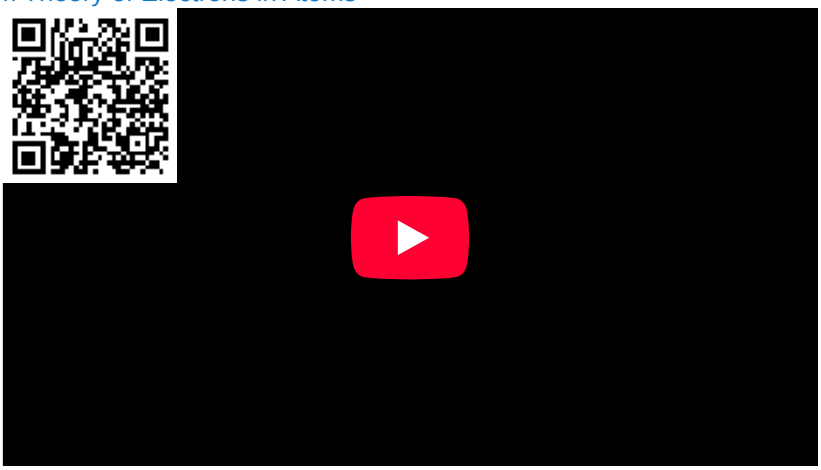
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1.4: Atomic Orbitals and Quantum Numbers

Skills to Develop

- Understand the general idea of the quantum mechanical description of electrons in an atom, and that it uses the notion of three-dimensional wave functions, or orbitals, that define the distribution of probability to find an electron in a particular part of space
- List and describe traits of the four quantum numbers that form the basis for completely specifying the state of an electron in an atom

Understanding Quantum Theory of Electrons in Atoms



***Video* 1.4.1**: *A preview of electrons in orbitals.*

The goal of this section is to understand the electron orbitals (location of electrons in atoms), their different energies, and other properties. The use of quantum theory provides the best understanding to these topics. This knowledge is a precursor to chemical bonding.

As was described previously, electrons in atoms can exist only on discrete energy levels but not between them. It is said that the energy of an electron in an atom is quantized, that is, it can be equal only to certain specific values and can jump from one energy level to another but not transition smoothly or stay between these levels.

The energy levels are labeled with an n value, where n = 1, 2, 3, …. Generally speaking, the energy of an electron in an atom is greater for greater values of n. This number, n, is referred to as the principal quantum number. The principal quantum number defines the location of the energy level. It is essentially the same concept as the n in the Bohr atom description. Another name for the principal quantum number is the shell number. The shells of an atom can be thought of concentric circles radiating out from the nucleus. The electrons that belong to a specific shell are most likely to be found within the corresponding circular area. The further we proceed from the nucleus, the higher the shell number, and so the higher the energy level (Figure **1.4.1**). The positively charged protons in the nucleus stabilize the electronic orbitals by electrostatic attraction between the positive charges of the protons and the negative charges of the electrons. So the further away the electron is from the nucleus, the greater the energy it has.

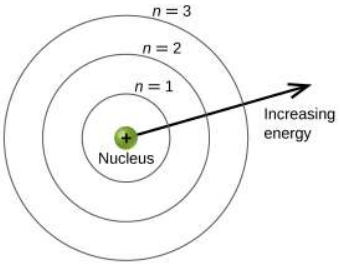


***Figure* 1.4.1**: *Different shells are numbered by principal quantum numbers.*

This quantum mechanical model for where electrons reside in an atom can be used to look at electronic transitions, the events when an electron moves from one energy level to another. If the transition is to a higher energy level, energy is absorbed, and the energy change has a positive value. To obtain the amount of energy necessary for the transition to a higher energy level, a photon is absorbed by the atom. A transition to a lower energy level involves a release of energy, and the energy change is negative. This process is accompanied by emission of a photon by the atom. The following equation summarizes these relationships and is based on the hydrogen atom:

$$\begin{aligned}\Delta E &= E_{\text{final}} - E_{\text{initial}} \\ &= -2.18 \times 10^{-18} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \text{ J}\end{aligned}$$

The values n_f and n_i are the final and initial energy states of the electron.

The principal quantum number is one of three quantum numbers used to characterize an orbital. An atomic orbital, which is distinct from an *orbit*, is a general region in an atom within which an electron is most probable to reside. The quantum mechanical model specifies the probability of finding an electron in the three-dimensional space around the nucleus and is based on solutions of the Schrödinger equation. In addition, the principal quantum number defines the energy of an electron in a hydrogen or hydrogen-like atom or an ion (an atom or an ion with only one electron) and the general region in which discrete energy levels of electrons in a multi-electron atoms and ions are located.

Another quantum number is l, the angular momentum quantum number. It is an integer that defines the shape of the orbital, and takes on the values, l = 0, 1, 2, …, n – 1. This means that an orbital with n = 1 can have only one value of l, l = 0, whereas n = 2 permits l = 0 and l = 1, and so on. The principal quantum number defines the general size and energy of the orbital. The l value specifies the shape of the orbital. Orbitals with the same value of l form a subshell. In addition, the greater the angular momentum quantum number, the greater is the angular momentum of an electron at this orbital.

Orbitals with l = 0 are called *s* orbitals (or the *s* subshells). The value l = 1 corresponds to the *p* orbitals. For a given *n*, *p* orbitals constitute a *p* subshell (e.g., 3*p* if n = 3). The orbitals with l = 2 are called the *d* orbitals, followed by the *f*-, *g*-, *and h*-orbitals for l = 3, 4, 5, and there are higher values we will not consider.

There are certain distances from the nucleus at which the probability density of finding an electron located at a particular orbital is zero. In other words, the value of the wavefunction ψ is zero at this distance for this orbital. Such a value of radius r is called a radial node. The number of radial nodes in an orbital is $n - l - 1$.

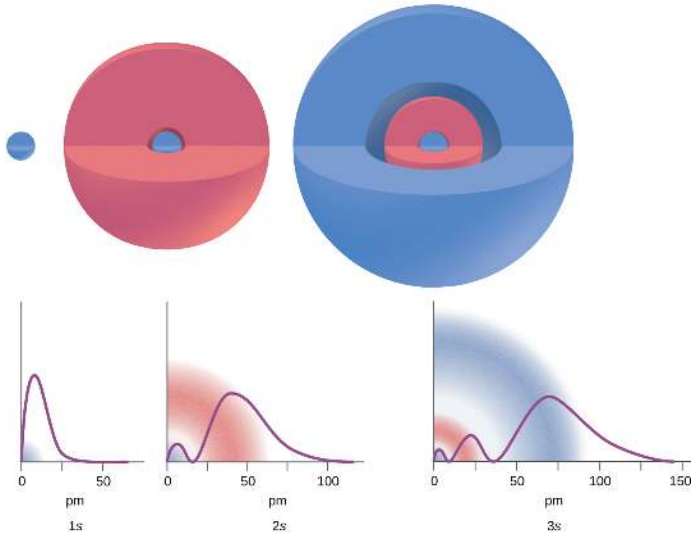
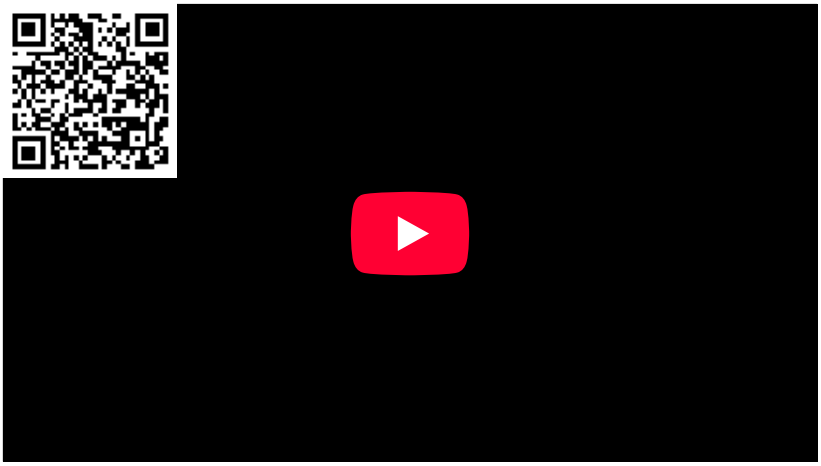


***Figure* 1.4.2**: *The graphs show the probability (y axis) of finding an electron for the 1s, 2s, 3s orbitals as a function of distance from the nucleus.*



***Video* 1.4.2**: Looking into the probability of finding electrons.

Consider the examples in Figure **1.4.3**. The orbitals depicted are of the *s* type, thus l = 0 for all of them. It can be seen from the graphs of the probability densities that there are 1 – 0 – 1 = 0 places where the density is zero (nodes) for 1*s* (n = 1), 2 – 0 – 1 = 1 node for 2*s*, and 3 – 0 – 1 = 2 nodes for the 3*s* orbitals.

The *s* subshell electron density distribution is spherical and the *p* subshell has a dumbbell shape. The *d* and *f* orbitals are more complex. These shapes represent the three-dimensional regions within which the electron is likely to be found.

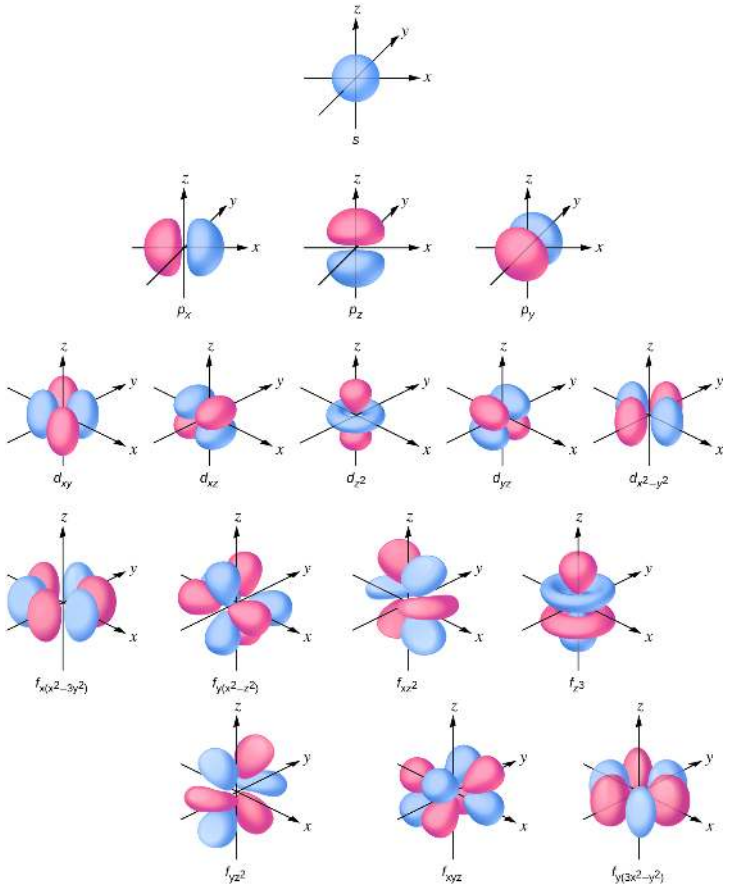


***Figure* 1.4.3**: *Shapes of s, p, d, and f orbitals.*

If an electron has an angular momentum ($l \neq 0$), then this vector can point in different directions. In addition, the *z* component of the angular momentum can have more than one value. This means that if a magnetic field is applied in the *z* direction, orbitals with different values of the *z* component of the angular momentum will have different energies resulting from interacting with the field. The magnetic quantum number, called m_l, specifies the *z* component of the angular momentum for a particular orbital. For example, for an *s* orbital, $l = 0$, and the only value of m_l is zero. For *p* orbitals, $l = 1$, and m_l can be equal to –1, 0, or +1. Generally speaking, m_l can be equal to $-l$, $-(l - 1)$, …, –1, 0, +1, …, $(l - 1)$, l. The total number of possible orbitals with the same value of l (a subshell) is $2l + 1$. Thus, there is one *s*-orbital for $ml = 0$, there are three *p*-orbitals for $ml = 1$, five *d*-orbitals for $ml = 2$, seven *f*-orbitals for $ml = 3$, and so forth. The principal quantum number defines the general value of the electronic energy. The angular momentum quantum number determines the shape of the orbital. And the magnetic quantum number specifies orientation of the orbital in space, as can be seen in Figure **1.4.3**.

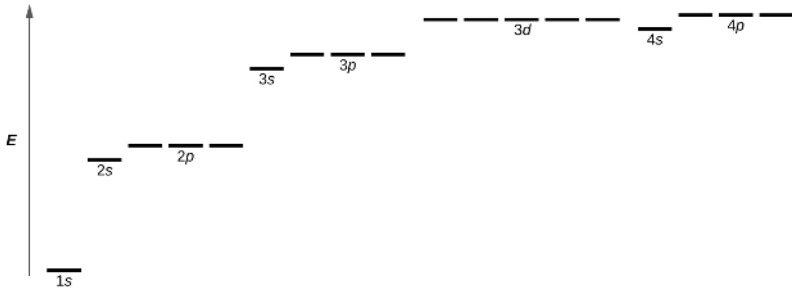


***Figure* 1.4.4**: *The chart shows the energies of electron orbitals in a multi-electron atom.*

Figure **1.4.4** illustrates the energy levels for various orbitals. The number before the orbital name (such as 2*s*, 3*p*, and so forth) stands for the principal quantum number, *n*. The letter in the orbital name defines the subshell with a specific angular momentum quantum number $l = 0$ for *s* orbitals, 1 for *p* orbitals, 2 for *d* orbitals. Finally, there are more than one possible orbitals for $l \geq 1$, each corresponding to a specific value of m_l. In the case of a hydrogen atom or a one-electron ion (such as He^+, Li^{2+}, and so on), energies of all the orbitals with the same *n* are the same. This is called a

degeneracy, and the energy levels for the same principal quantum number, n, are called degenerate energy levels. However, in atoms with more than one electron, this degeneracy is eliminated by the electron–electron interactions, and orbitals that belong to different subshells have different energies. Orbitals within the same subshell (for example ns, np, nd, nf, such as $2p$, $3s$) are still degenerate and have the same energy.

While the three quantum numbers discussed in the previous paragraphs work well for describing electron orbitals, some experiments showed that they were not sufficient to explain all observed results. It was demonstrated in the 1920s that when hydrogen-line spectra are examined at extremely high resolution, some lines are actually not single peaks but, rather, pairs of closely spaced lines. This is the so-called fine structure of the spectrum, and it implies that there are additional small differences in energies of electrons even when they are located in the same orbital. These observations led Samuel Goudsmit and George Uhlenbeck to propose that electrons have a fourth quantum number. They called this the spin quantum number, or m_s.

The other three quantum numbers, n, l, and m_l, are properties of specific atomic orbitals that also define in what part of the space an electron is most likely to be located. Orbitals are a result of solving the Schrödinger equation for electrons in atoms. The electron spin is a different kind of property. It is a completely quantum phenomenon with no analogues in the classical realm. In addition, it cannot be derived from solving the Schrödinger equation and is not related to the normal spatial coordinates (such as the Cartesian x, y, and z). Electron spin describes an intrinsic electron "rotation" or "spinning." Each electron acts as a tiny magnet or a tiny rotating object with an angular momentum, even though this rotation cannot be observed in terms of the spatial coordinates.

The magnitude of the overall electron spin can only have one value, and an electron can only "spin" in one of two quantized states. One is termed the α state, with the z component of the spin being in the positive direction of the z axis. This corresponds to the spin quantum number $m_s = \frac{1}{2}$. The other is called the β state, with the z component of the spin being negative and $m_s = -\frac{1}{2}$. Any electron, regardless of the atomic orbital it is located in, can only have one of those two values of the spin quantum number. The energies of electrons having $m_s = -\frac{1}{2}$ and $m_s = \frac{1}{2}$ are different if an external magnetic field is applied.

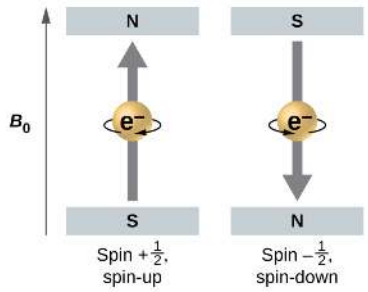


***Figure* 1.4.5**: *Electrons with spin values \(±\ce{1/2}\) in an external magnetic field.*

Figure **1.4.5** illustrates this phenomenon. An electron acts like a tiny magnet. Its moment is directed up (in the positive direction of the z axis) for the $\frac{1}{2}$ spin quantum number and down (in the negative z direction) for the spin quantum number of $-\frac{1}{2}$. A magnet has a lower energy if its magnetic moment is aligned with the external magnetic field (the left electron) and a higher energy for the magnetic moment being opposite to the applied field. This is why an electron with $m_s = \frac{1}{2}$ has a slightly lower energy in an external field in the positive z direction, and an electron with $m_s = -\frac{1}{2}$ has a slightly higher energy in the same field. This is true even for an electron occupying the same orbital in an atom. A spectral line corresponding to a transition for electrons from the same orbital but with different spin quantum numbers has two possible values of energy; thus, the line in the spectrum will show a fine structure splitting.



***Video* 1.4.3**: The uncertainty of the location of electrons.

An electron in an atom is completely described by four quantum numbers: n, l, m_l, and m_s. The first three quantum numbers define the orbital and the fourth quantum number describes the intrinsic electron property called spin. An Austrian physicist Wolfgang Pauli formulated a general principle that gives the last piece of information that we need to understand the general behavior of electrons in atoms. The Pauli exclusion principle can be formulated as follows: No two electrons in the same atom can have exactly the same set of all the four quantum numbers. What this means is that electrons can share the same orbital (the same set of the quantum numbers n, l, and m_l), but only if their spin quantum numbers m_s have different values. Since the spin quantum number can only have two values $\left(\pm\frac{1}{2}\right)$, no more than two electrons can occupy the same orbital (and if two electrons are located in the same orbital, they must have opposite spins). Therefore, any atomic orbital can be populated by only zero, one, or two electrons. The properties and meaning of the quantum numbers of electrons in atoms are briefly summarized in Table **1.4.1**.

***Table* 1.4.1**: *Quantum Numbers, Their Properties, and Significance*

Name	Symbol	Allowed values	Physical meaning
principal quantum number	n	1, 2, 3, 4, ….	shell, the general region for the value of energy for an electron on the orbital
angular momentum or azimuthal quantum number	l	$0 \le l \le n-1$	subshell, the shape of the orbital
magnetic quantum number	m_l	$-l \le m_l \le l$	orientation of the orbital
spin quantum number	m_s	$\frac{1}{2}, -\frac{1}{2}$	direction of the intrinsic quantum "spinning" of the electron

Example 1.4.1: Working with Shells and Subshells

Indicate the number of subshells, the number of orbitals in each subshell, and the values of l and m_l for the orbitals in the $n = 4$ shell of an atom.

Solution

For $n = 4$, l can have values of 0, 1, 2, and 3. Thus, *s*, *p*, *d*, and *f* subshells are found in the $n = 4$ shell of an atom. For $l = 0$ (the *s* subshell), m_l can only be 0. Thus, there is only one 4*s* orbital. For $l = 1$ (*p*-type orbitals), m can have values of –1, 0, +1, so we find three 4*p* orbitals. For $l = 2$ (*d*-type orbitals), m_l can have values of –2, –1, 0, +1, +2, so we have five 4*d* orbitals. When $l = 3$ (*f*-type orbitals), m_l can have values of –3, –2, –1, 0, +1, +2, +3, and we can have seven 4*f* orbitals. Thus, we find a total of 16 orbitals in the $n = 4$ shell of an atom.

Exercise 1.4.1

Identify the subshell in which electrons with the following quantum numbers are found:

a. $n = 3$, $l = 1$;
b. $n = 5$, $l = 3$;
c. $n = 2$, $l = 0$.

Answer a

3*p*

Answer b

5*f*

Answer c

2s

Example 1.4.2: Maximum Number of Electrons

Calculate the maximum number of electrons that can occupy a shell with (a) $n = 2$, (b) $n = 5$, and (c) n as a variable. Note you are only looking at the orbitals with the specified n value, not those at lower energies.

Solution

(a) When $n = 2$, there are four orbitals (a single 2*s* orbital, and three orbitals labeled 2*p*). These four orbitals can contain eight electrons.

(b) When $n = 5$, there are five subshells of orbitals that we need to sum:

1 orbital labeled 5*s*
3 orbitals labeled 5*p*
5 orbitals labeled 5*d*
7 orbitals labeled 5*f*
+9 orbitals labeled 5*g*
25 orbitals total

Again, each orbital holds two electrons, so 50 electrons can fit in this shell.

(c) The number of orbitals in any shell *n* will equal n^2. There can be up to two electrons in each orbital, so the maximum number of electrons will be $2 \times n^2$

Exercise 1.4.2

If a shell contains a maximum of 32 electrons, what is the principal quantum number, *n*?

Answer

n = 4

Example 1.4.3: Working with Quantum Numbers

Complete the following table for atomic orbitals:

Orbital	*n*	*l*	m_l degeneracy	Radial nodes (no.)
4*f*				
	4	1		
	7		7	3
5*d*				

Solution

The table can be completed using the following rules:

- The orbital designation is *nl*, where *l* = 0, 1, 2, 3, 4, 5, … is mapped to the letter sequence s, *p*, *d*, *f*, *g*, *h*, …,
- The m_l degeneracy is the number of orbitals within an *l* subshell, and so is $2l + 1$ (there is one *s* orbital, three *p* orbitals, five *d* orbitals, seven *f* orbitals, and so forth).
- The number of radial nodes is equal to $n - l - 1$.

Orbital	***n***	***l***	**m_l degeneracy**	**Radial nodes (no.)**
4*f*	4	3	7	0
4*p*	4	1	3	2
7*f*	7	3	7	3
5*d*	5	2	5	2

Exercise 1.4.3

How many orbitals have *l* = 2 and *n* = 3?

Answer

The five degenerate 3*d* orbitals

Summary



***Video* 1.4.4**: *An overview of orbitals.*

An atomic orbital is characterized by three quantum numbers. The principal quantum number, n, can be any positive integer. The general region for value of energy of the orbital and the average distance of an electron from the nucleus are related to n. Orbitals having the same value of n are said to be in the same shell. The angular momentum quantum number, l, can have any integer value from 0 to $n – 1$. This quantum number describes the shape or type of the orbital. Orbitals with the same principal quantum number and the same l value belong to the same subshell. The magnetic quantum number, m_l, with $2l + 1$ values ranging from $–l$ to $+l$, describes the orientation of the orbital in space. In addition, each electron has a spin quantum number, m_s, that can be equal to $\pm\frac{1}{2}$. No two electrons in the same atom can have the same set of values for all the four quantum numbers.

Glossary

angular momentum quantum number (l)
quantum number distinguishing the different shapes of orbitals; it is also a measure of the orbital angular momentum

wavefunction (ψ)
mathematical description of an atomic orbital that describes the shape of the orbital; it can be used to calculate the probability of finding the electron at any given location in the orbital, as well as dynamical variables such as the energy and the angular momentum

subshell
set of orbitals in an atom with the same values of n and l

spin quantum number (m_s)
number specifying the electron spin direction, either $+\frac{1}{2}$ or $-\frac{1}{2}$

shell
set of orbitals with the same principal quantum number, n

***s* orbital**
spherical region of space with high electron density, describes orbitals with $l = 0$. An electron in this orbital is called an s electron

quantum mechanics
field of study that includes quantization of energy, wave-particle duality, and the Heisenberg uncertainty principle to describe matter

principal quantum number (n)
quantum number specifying the shell an electron occupies in an atom

Pauli exclusion principle
specifies that no two electrons in an atom can have the same value for all four quantum numbers

***p* orbital**
dumbbell-shaped region of space with high electron density, describes orbitals with $l = 1$. An electron in this orbital is called a p electron

magnetic quantum number (m_l)
quantum number signifying the orientation of an atomic orbital around the nucleus; orbitals having different values of m_l but the same subshell value of l have the same energy (are degenerate), but this degeneracy can be removed by application of an external magnetic field

Heisenberg uncertainty principle
rule stating that it is impossible to exactly determine both certain conjugate dynamical properties such as the momentum and the position of a particle at the same time. The uncertainty principle is a consequence of quantum particles exhibiting wave–particle duality

***f* orbital**
multilobed region of space with high electron density, describes orbitals with $l = 3$. An electron in this orbital is called an f electron

electron density

a measure of the probability of locating an electron in a particular region of space, it is equal to the squared absolute value of the wave function ψ

***d* orbital**

region of space with high electron density that is either four lobed or contains a dumbbell and torus shape; describes orbitals with $l = 2$. An electron in this orbital is called a *d* electron

atomic orbital

mathematical function that describes the behavior of an electron in an atom (also called the wavefunction), it can be used to find the probability of locating an electron in a specific region around the nucleus, as well as other dynamical variables

Contributors

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1.4.1: Atomic Orbitals and Quantum Numbers (Problems)

PROBLEM 1.4.1.1

What are the allowed values for each of the four quantum numbers: n, l, m_l, and m_s?

Answer

n: non-zero integer

l: 0 to n-1

m_l : -l to l

m_s : $\frac{1}{2}$ or $\frac{-1}{2}$

PROBLEM 1.4.1.2

Describe the properties of an electron associated with each of the following four quantum numbers: n, l, m_l, and m_s.

Answer

n determines the general range for the value of energy and the probable distances that the electron can be from the nucleus. l determines the shape of the orbital. m_l determines the orientation of the orbitals of the same l value with respect to one another. m_s determines the spin of an electron

PROBLEM 1.4.1.3

Identify the subshell in which electrons with the following quantum numbers are found:

a. $n = 2$, $l = 1$
b. $n = 4$, $l = 2$
c. $n = 6$, $l = 0$

Answer a

2p

Answer b

4d

Answer c

6s

PROBLEM 1.4.1.4

Identify the subshell in which electrons with the following quantum numbers are found:

a. $n = 3$, $l = 2$
b. $n = 1$, $l = 0$
c. $n = 4$, $l = 3$

Answer a

3d

Answer b

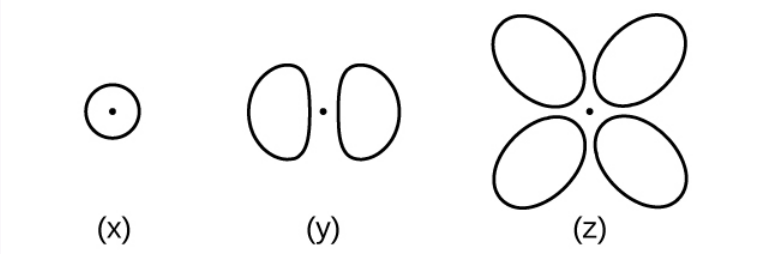
1s

Answer c

4f

PROBLEM 1.4.1.5

Consider the orbitals shown here in outline.



a. What is the maximum number of electrons contained in an orbital of type (x)? Of type (y)? Of type (z)?
b. How many orbitals of type (x) are found in a shell with $n = 2$? How many of type (y)? How many of type (z)?
c. Write a set of quantum numbers for an electron in an orbital of type (x) in a shell with $n = 4$. Of an orbital of type (y) in a shell with $n = 2$. Of an orbital of type (z) in a shell with $n = 3$.
d. What is the smallest possible n value for an orbital of type (x)? Of type (y)? Of type (z)?
e. What are the possible l and m_l values for an orbital of type (x)? Of type (y)? Of type (z)?

Answer a

x. 2

y. 2

z. 2

Answer b

x. 1

y. 3

z. 0

Answer c

x. 4 0 0 $\frac{1}{2}$

y. 2 1 0 $\frac{1}{2}$

z. 3 2 0 $\frac{1}{2}$

Answer d

x. 1

y. 2

z. 3

Answer e

x. $l = 0$, $m_l = 0$

y. $l = 1$, $m_l = -1$, 0, or +1

z. $l = 2$, $m_l = -2, -1, 0, +1, +2$

PROBLEM 1.4.1.6

How many electrons could be held in the second shell of an atom if the spin quantum number m_s could have three values instead of just two? (Hint: Consider the Pauli exclusion principle.)

Answer

12

PROBLEM 1.4.1.7

Write a set of quantum numbers for each of the electrons with an n of 4 in a Se atom.

Answer

n	l	m_l	s
4	0	0	$+\frac{1}{2}$
4	0	0	$-\frac{1}{2}$
4	1	−1	$+\frac{1}{2}$
4	1	0	$+\frac{1}{2}$
4	1	+1	$+\frac{1}{2}$
4	1	−1	$-\frac{1}{2}$

PROBLEM 1.4.1.8

Answer the following questions:

a. Without using quantum numbers, describe the differences between the shells, subshells, and orbitals of an atom.
b. How do the quantum numbers of the shells, subshells, and orbitals of an atom differ?

Answer a

shell: set of orbitals in the same energy level

subshell: set of orbitals in the same energy level and same shape (s, p, d, or f)

orbital: can hold up to 2 electrons

Answer b

shell: set of orbitals with same n

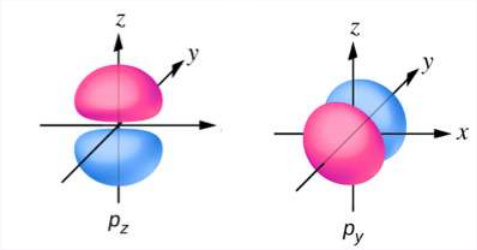
subshell: set of orbitals in an atom with the same values of n and l

orbital: shape defined by l quantum number

PROBLEM 1.4.1.9

Sketch the boundary surface of a p_z and a p_y orbital. Be sure to show and label the axes.

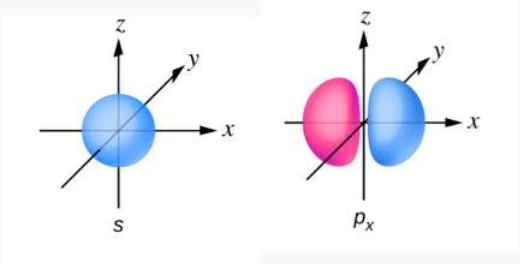
Answer



PROBLEM 1.4.1.10

Sketch the p_x and s orbitals. Be sure to show and label the coordinates.

Answer



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1.5: Atomic Orbitals and the Bohr Model

Skills to Develop

- Describe the Bohr model of the hydrogen atom
- Use the Rydberg equation to calculate energies of light emitted or absorbed by hydrogen atoms
- Understand the general idea of the quantum mechanical description of electrons in an atom, and that it uses the notion of three-dimensional wave functions, or orbitals, that define the distribution of probability to find an electron in a particular part of space

The Bohr Model and Spectroscopy



Video* 1.5.1*: *An introduction to the Bohr Model of the Atom.*

In 1913, Niels Bohr attempted to resolve the atomic paradox by ignoring classical electromagnetism's prediction that the orbiting electron in hydrogen would continuously emit light. Instead, he incorporated into the classical mechanics description of the atom Planck's ideas of quantization and Einstein's finding that light consists of photons whose energy is proportional to their frequency. Bohr assumed that the electron orbiting the nucleus would not normally emit any radiation (the stationary state hypothesis), but it would emit or absorb a photon if it moved to a different orbit. The energy absorbed or emitted would reflect differences in the orbital energies according to this equation:

$$|\Delta E| = |E_f - E_i| = h\nu = \frac{hc}{\lambda} \tag{1.5.1}$$

In this equation, h is Planck's constant and E_i and E_f are the initial and final orbital energies, respectively. The absolute value of the energy difference is used, since frequencies and wavelengths are always positive. Instead of allowing for continuous values for the angular momentum, energy, and orbit radius, Bohr assumed that only discrete values for these could occur (actually, quantizing any one of these would imply that the other two are also quantized). Bohr's expression for the quantized energies is:

$$E_n = -\frac{k}{n^2} \tag{1.5.2}$$

with $n = 1, 2, 3, \ldots$

In this expression, k is a constant comprising fundamental constants such as the electron mass and charge and Planck's constant. Inserting the expression for the orbit energies into the equation for ΔE gives

$$\Delta E = k\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = \frac{hc}{\lambda} \tag{1.5.3}$$

or

$$\frac{1}{\lambda} = \frac{k}{hc}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \tag{1.5.4}$$

$$\Delta E = E_1 - E_2 = 2.179 \times 10^{-18}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \tag{1.5.5}$$

This formula should look familiar - we talked about it in the previous section when we talked about the principle quantum number. The lowest few energy levels are shown in Figure 1.5.1. One of the fundamental laws of physics is that matter is most stable with the lowest possible energy. Thus, the electron in a hydrogen atom usually moves in the $n = 1$ orbit, the orbit in which it has the lowest energy. When the electron is in this lowest energy orbit, the atom is said to be in its ground electronic state (or simply ground state). If the atom receives energy from an outside source, it is possible for the electron to move to an orbit with a higher n value and the atom is now in an excited electronic state (or simply an excited state) with a higher energy. When an electron transitions from an excited state (higher energy orbit) to a less excited state, or ground state, the difference in energy is emitted as a photon. Similarly, if a photon is absorbed by an atom, the energy of the photon moves an electron from a lower energy orbit up to a more excited one.

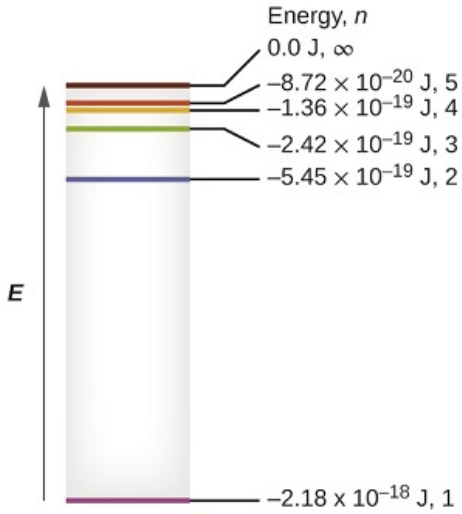


Figure 1.5.1*: Quantum numbers and energy levels in a hydrogen atom. The more negative the calculated value, the lower the energy.*

We can relate the energy of electrons in atoms to what we learned previously about energy. The law of conservation of energy says that we can neither create nor destroy energy. Thus, if a certain amount of external energy is required to excite an electron from one energy level to another, that same amount of energy will be liberated when the electron returns to its initial state (Figure 1.5.2). In effect, an atom can "store" energy by using it to promote an electron to a state with a higher energy and release it when the electron returns to a lower state. The energy can be released as one quantum of energy, as the electron returns to its ground state (say, from $n = 5$ to $n = 1$), or it can be released as two or more smaller quanta as the electron falls to an intermediate state, then to the ground state (say, from $n = 5$ to $n = 4$, emitting one quantum, then to $n = 1$, emitting a second quantum).

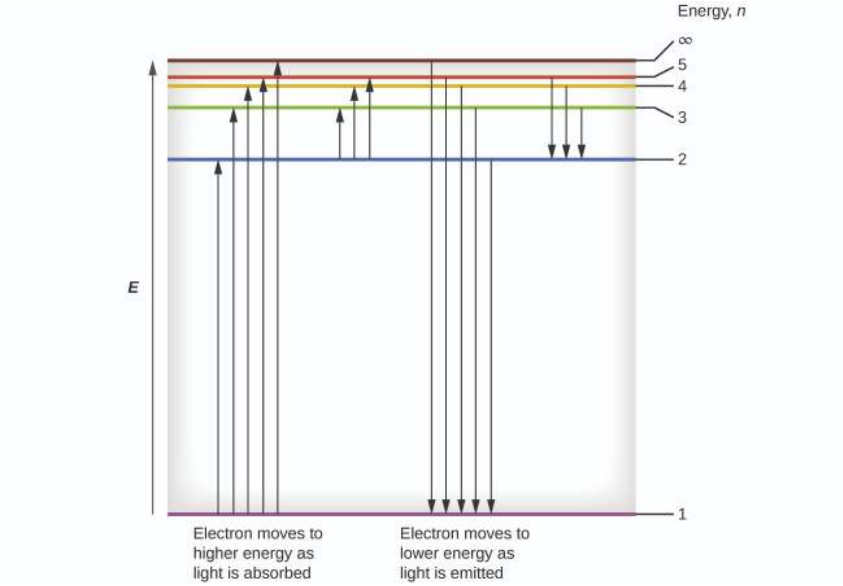


***Figure* 1.5.2**: *The horizontal lines show the relative energy of orbits in the Bohr model of the hydrogen atom, and the vertical arrows depict the energy of photons absorbed (left) or emitted (right) as electrons move between these orbits.*

Since Bohr's model involved only a single electron, it could also be applied to the single electron ions He^{+}, Li^{2+}, Be^{3+}, and so forth, which differ from hydrogen only in their nuclear charges, and so one-electron atoms and ions are collectively referred to as *hydrogen-like* or *hydrogenic* atoms. The energy expression for hydrogen-like atoms is a generalization of the hydrogen atom energy, in which Z is the nuclear charge (+1 for hydrogen, +2 for He, +3 for Li, and so on) and k has a value of $2.179 \times 10^{-18}\ J$.

$$E_n = -\frac{kZ^2}{n^2} \tag{1.5.6}$$

The sizes of the circular orbits for hydrogen-like atoms are given in terms of their radii by the following expression, in which a_o is a constant called the Bohr radius, with a value of $5.292 \times 10^{-11}\ m$:

$$r = \frac{n^2}{Z} a_0 \tag{1.5.7}$$

The equation also shows us that as the electron's energy increases (as n increases), the electron is found at greater distances from the nucleus. This is implied by the inverse dependence on r in the Coulomb potential, since, as the electron moves away from the nucleus, the electrostatic attraction between it and the nucleus decreases, and it is held less tightly in the atom. Note that as n gets larger and the orbits get larger, their energies get closer to zero, and so the limits $n \longrightarrow \infty$ and $r \longrightarrow \infty$ imply that $E = 0$ corresponds to the ionization limit where the electron is completely removed from the nucleus. Thus, for hydrogen in the ground state $n = 1$, the ionization energy would be:

$$\Delta E = E_{n \longrightarrow \infty} - E_1 = 0 + k = k \tag{1.5.8}$$

With three extremely puzzling paradoxes now solved (blackbody radiation, the photoelectric effect, and the hydrogen atom), and all involving Planck's constant in a fundamental manner, it became clear to most physicists at that time that the classical theories that worked so well in the macroscopic world were fundamentally flawed and could not be extended down into the microscopic domain of atoms and molecules. Unfortunately, despite Bohr's remarkable achievement in deriving a theoretical expression for the Rydberg constant, he was unable to extend his theory to the next simplest atom, He, which only has two electrons. Bohr's model was severely flawed, since it was still based on the classical mechanics notion of precise orbits, a concept that was later found to be untenable in the microscopic domain, when a proper model of quantum mechanics was developed to supersede classical mechanics.

Example 1.5.1: Calculating the Energy of an Electron in a Bohr Orbit

Early researchers were very excited when they were able to predict the energy of an electron at a particular distance from the nucleus in a hydrogen atom. If a spark promotes the electron in a hydrogen atom into an orbit with $n = 3$, what is the calculated

energy, in joules, of the electron?

Solution

The energy of the electron is given by Equation 1.5.6:

$$E = \frac{-kZ^2}{n^2} \tag{1.5.9}$$

The atomic number, Z, of hydrogen is 1; $k = 2.179 \times 10^{-18}\ J$; and the electron is characterized by an n value of 3. Thus,

$$E = \frac{-(2.179 \times 10^{-18}\ J) \times (1)^2}{(3)^2} = -2.421 \times 10^{-19}\ J \tag{1.5.10}$$

Exercise 1.5.1

The electron in Example 1.5.1 in the $n = 3$ state is promoted even further to an orbit with $n = 6$. What is its new energy?

Answer

TBD

Example 1.5.2: Calculating Electron Transitions in a One–electron System

What is the energy (in joules) and the wavelength (in meters) of the line in the spectrum of hydrogen that represents the movement of an electron from Bohr orbit with n = 4 to the orbit with n = 6? In what part of the electromagnetic spectrum do we find this radiation?

Solution

In this case, the electron starts out with $n = 4$, so $n_1 = 4$. It comes to rest in the $n = 6$ orbit, so $n_2 = 6$. The difference in energy between the two states is given by this expression:

$$\Delta E = E_1 - E_2 = 2.179 \times 10^{-18} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \tag{1.5.11}$$

$$\Delta E = 2.179 \times 10^{-18} \left(\frac{1}{4^2} - \frac{1}{6^2} \right) J \tag{1.5.12}$$

$$\Delta E = 2.179 \times 10^{-18} \left(\frac{1}{16} - \frac{1}{36} \right) J \tag{1.5.13}$$

$$\Delta E = 7.566 \times 10^{-20}\ J \tag{1.5.14}$$

This energy difference is *positive*, indicating a photon enters the system (is absorbed) to excite the electron from the n = 4 orbit up to the $n = 6$ orbit. The wavelength of a photon with this energy is found by the expression $E = hc\lambda$. Rearrangement gives:

$$\lambda = \frac{hc}{E} \tag{1.5.15}$$

From the figure of electromagnetic radiation, we can see that this wavelength is found in the infrared portion of the electromagnetic spectrum.

Exercise 1.5.2

What is the energy in joules and the wavelength in meters of the photon produced when an electron falls from the $n = 5$ to the $n = 3$ level in a He^+ ion ($Z = 2$ for He^+)?

Answer

$6.198 \times 10^{-19}\ J$ and $3.205 \times 10^{-7}\ m$

Bohr's model of the hydrogen atom provides insight into the behavior of matter at the microscopic level, but it is does not account for electron–electron interactions in atoms with more than one electron. It does introduce several important features of all models used to describe the distribution of electrons in an atom. These features include the following:

- The energies of electrons (energy levels) in an atom are quantized, described by quantum numbers: integer numbers having only specific allowed value and used to characterize the arrangement of electrons in an atom.
- An electron's energy increases with increasing distance from the nucleus.
- The discrete energies (lines) in the spectra of the elements result from quantized electronic energies.

Of these features, the most important is the postulate of quantized energy levels for an electron in an atom. As a consequence, the model laid the foundation for the quantum mechanical model of the atom. Bohr won a Nobel Prize in Physics for his contributions to our understanding of the structure of atoms and how that is related to line spectra emissions.



***Video* 1.5.2:** *An overview of the Bohr Model of the Atom.*

Bohr's model explained the experimental data for the hydrogen atom and was widely accepted, but it also raised many questions. Why did electrons orbit at only fixed distances defined by a single quantum number n = 1, 2, 3, and so on, but never in between? Why did the model work so well describing hydrogen and one-electron ions, but could not correctly predict the emission spectrum for helium or any larger atoms? To answer these questions, scientists needed to completely revise the way they thought about matter.

The Quantum–Mechanical Model of an Atom

Shortly after de Broglie published his ideas that the electron in a hydrogen atom could be better thought of as being a circular standing wave instead of a particle moving in quantized circular orbits, as Bohr had argued, Erwin Schrödinger extended de Broglie's work by incorporating the de Broglie relation into a wave equation, deriving what is today known as the Schrödinger equation. When Schrödinger applied his equation to hydrogen-like atoms, he was able to reproduce Bohr's expression for the energy and, thus, the Rydberg formula governing hydrogen spectra, and he did so without having to invoke Bohr's assumptions of stationary states and quantized orbits, angular momenta, and energies; quantization in Schrödinger's theory was a natural consequence of the underlying mathematics of the wave equation. Like de Broglie, Schrödinger initially viewed the electron in hydrogen as being a physical wave instead of a particle, but where de Broglie thought of the electron in terms of circular stationary waves, Schrödinger properly thought in terms of three-dimensional stationary waves, or wavefunctions, represented by the Greek letter psi, ψ. A few years later, Max Born proposed an interpretation of the wavefunction ψ that is still accepted today: Electrons are still particles, and so the waves represented by ψ are not physical waves but, instead, are complex probability amplitudes. The square of the magnitude of a wavefunction $|\psi|^2$ describes the probability of the quantum particle being present near a certain location in space. This means that wavefunctions can be used to determine the distribution of the electron's density with respect to the nucleus in an atom. In the most general form, the Schrödinger equation can be written as:

$$\hat{H}\psi = E\psi \tag{1.5.16}$$

$\hat{H}$ is the Hamiltonian operator, a set of mathematical operations representing the total energy of the quantum particle (such as an electron in an atom), ψ is the wavefunction of this particle that can be used to find the special distribution of the probability of finding the particle, and E is the actual value of the total energy of the particle.

Schrödinger's work, as well as that of Heisenberg and many other scientists following in their footsteps, is generally referred to as quantum mechanics.



***Video* 1.5.3:** *You may also have heard of Schrödinger because of his famous thought experiment. This story explains the concepts of superposition and entanglement as related to a cat in a box with poison.*



***Video* 1.5.4:** *What can we learn about Quantum Mechanics from the cat experiment?*



Video \(\PageIndex{5}\): *More on the thought experiment.*

Key Equations

- $$\Delta E = E_1 - E_2 = 2.179 \times 10^{-18} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \tag{1.5.17}$$

Summary

Bohr incorporated Planck's and Einstein's quantization ideas into a model of the hydrogen atom that resolved the paradox of atom stability and discrete spectra. The Bohr model of the hydrogen atom explains the connection between the quantization of photons and the quantized emission from atoms. Bohr described the hydrogen atom in terms of an electron moving in a circular orbit about a nucleus. He postulated that the electron was restricted to certain orbits characterized by discrete energies. Transitions between these allowed orbits result in the absorption or emission of photons. When an electron moves from a higher-energy orbit to a more stable one, energy is emitted in the form of a photon. To move an electron from a stable orbit to a more excited one, a photon of energy must be absorbed. Using the Bohr model, we can calculate the energy of an electron and the radius of its orbit in any one-electron system.

Glossary

Bohr's model of the hydrogen atom
: structural model in which an electron moves around the nucleus only in circular orbits, each with a specific allowed radius; the orbiting electron does not normally emit electromagnetic radiation, but does so when changing from one orbit to another.

excited state
: state having an energy greater than the ground-state energy

ground state
: state in which the electrons in an atom, ion, or molecule have the lowest energy possible

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

quantum number
: integer number having only specific allowed values and used to characterize the arrangement of electrons in an atom

Contributors

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1.5.1: Atomic Orbitals and the Bohr Model (Problems)

PROBLEM 1.5.1.1

Why is the electron in a Bohr hydrogen atom bound less tightly when it's electron is in energy level 3 than when it is in energy level 1?

Answer

An n of 3 indicated that the 1 electron in the hydrogen atom is in the third energy level, which is further from the nucleus than the first energy level (n=1), and therefore will not be as tightly bound.

PROBLEM 1.5.1.2

The electron volt (eV) is a convenient unit of energy for expressing atomic-scale energies. It is the amount of energy that an electron gains when subjected to a potential of 1 volt; $1\ eV = 1.602 \times 10^{-19}\ J$. Using the Bohr model, determine the energy, in electron volts, of the photon produced when an electron in a hydrogen atom moves from the orbit with $n = 5$ to the orbit with $n = 2$.

Answer

2.856 eV

PROBLEM 1.5.1.3

Using the Bohr model, determine the energy in joules of the photon produced when an electron in a He^+ ion moves from the orbit with n = 5 to the orbit with n = 2.

Answer

-4.58×10^{-19} J

Click here to see a video of the solution



PROBLEM 1.5.1.4

Using the Bohr model, determine the energy in joules of the photon produced when an electron in a Li^{2+} ion moves from the orbit with n = 2 to the orbit with n = 1.

Answer

1.471×10^{-17} J

PROBLEM 1.5.1.5

Consider a large number of hydrogen atoms with electrons randomly distributed in the n = 1, 2, 3, and 4 orbits

a. How many different wavelengths of light are emitted by these atoms as the electrons fall into lower-energy orbitals?
b. Calculate the lowest and highest energies of light produced by the transitions described in part (a).
c. Calculate the frequencies and wavelengths of the light produced by the transitions described in part (b).

Answer a

6 possible falls producing 6 wavelengths

Answer b

Highest: n=4 to n=1; -2.04×10^{-18} J

Lowest: n=4 to n=3; -1.06×10^{-19} J

Answer c

Highest: 9.73×10^{-8} m; 3.08×10^{15} s^{-1}

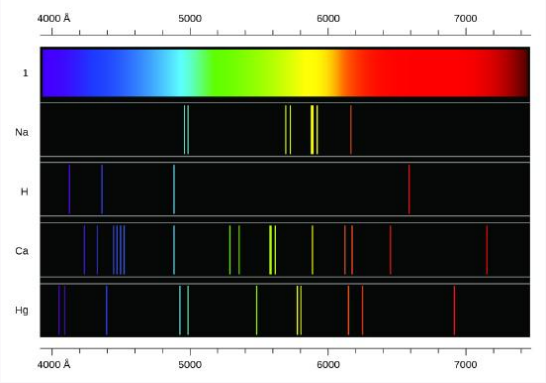
Lowest: 1.87×10^{-6} m; 1.60×10^{14} s^{-1}

Click here to see a video of the solution



PROBLEM 1.5.1.6

The spectra of hydrogen and of calcium are shown below. What causes the lines in these spectra? Why are the colors of the lines different? Suggest a reason for the observation that the spectrum of calcium is more complicated than the spectrum of hydrogen.



Answer

Both involve a relatively heavy nucleus with electrons moving around it, although strictly speaking, the Bohr model works only for one-electron atoms or ions. According to classical mechanics, the Rutherford model predicts a miniature “solar system” with electrons moving about the nucleus in circular or elliptical orbits that are confined to planes. If the requirements of classical electromagnetic theory that electrons in such orbits would emit electromagnetic radiation are

ignored, such atoms would be stable, having constant energy and angular momentum, but would not emit any visible light (contrary to observation). If classical electromagnetic theory is applied, then the Rutherford atom would emit electromagnetic radiation of continually increasing frequency (contrary to the observed discrete spectra), thereby losing energy until the atom collapsed in an absurdly short time (contrary to the observed long-term stability of atoms). The Bohr model retains the classical mechanics view of circular orbits confined to planes having constant energy and angular momentum, but restricts these to quantized values dependent on a single quantum number, n. The orbiting electron in Bohr's model is assumed not to emit any electromagnetic radiation while moving about the nucleus in its stationary orbits, but the atom can emit or absorb electromagnetic radiation when the electron changes from one orbit to another. Because of the quantized orbits, such "quantum jumps" will produce discrete spectra, in agreement with observations.

PROBLEM 1.5.1.7

How are the Bohr model and the quantum mechanical model of the hydrogen atom similar? How are they different?

Answer

Both models have a central positively charged nucleus with electrons moving about the nucleus in accordance with the Coulomb electrostatic potential. The Bohr model *assumes* that the electrons move in circular orbits that have quantized energies, angular momentum, and radii that are specified by a single quantum number, $n = 1, 2, 3, \ldots$, but this quantization is an ad hoc assumption made by Bohr to incorporate quantization into an essentially classical mechanics description of the atom. Bohr also assumed that electrons orbiting the nucleus normally do not emit or absorb electromagnetic radiation, but do so when the electron switches to a different orbit. In the quantum mechanical model, the electrons do not move in precise orbits (such orbits violate the Heisenberg uncertainty principle) and, instead, a probabilistic interpretation of the electron's position at any given instant is used, with a mathematical function ψ called a wavefunction that can be used to determine the electron's spatial probability distribution. These wavefunctions, or orbitals, are three-dimensional stationary waves that can be specified by three quantum numbers that arise naturally from their underlying mathematics (no ad hoc assumptions required): the principal quantum number, n (the same one used by Bohr), which specifies shells such that orbitals having the same n all have the same energy and approximately the same spatial extent; the angular momentum quantum number l, which is a measure of the orbital's angular momentum and corresponds to the orbitals' general shapes, as well as specifying subshells such that orbitals having the same l (and n) all have the same energy; and the orientation quantum number m, which is a measure of the z component of the angular momentum and corresponds to the orientations of the orbitals. The Bohr model gives the same expression for the energy as the quantum mechanical expression and, hence, both properly account for hydrogen's discrete spectrum (an example of getting the right answers for the wrong reasons, something that many chemistry students can sympathize with), but gives the wrong expression for the angular momentum (Bohr orbits necessarily all have non-zero angular momentum, but some quantum orbitals [s orbitals] can have zero angular momentum).

Contributors

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- Adelaide Clark, Oregon Institute of Technology

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CHAPTER OVERVIEW

2: Periodic Patterns

Unit Objectives

- Derive the predicted ground-state electron configurations of atoms
- Identify and explain exceptions to predicted electron configurations for atoms and ions
- Relate electron configurations to element classifications in the periodic table
- Describe and explain the observed trends in atomic size of the elements
- Describe and explain the observed trends in ionization energy of the elements
- Describe and explain the observed trends in electron affinity and metallic character of the elements
- To recognize the inverse relationship of ionization energies and electron affinities

2.1: Electron Configurations

2.1.1: Electron Configurations (Problems)

2.2: Trends in Size

2.2.1: Trends in Size (Problems)

2.3: Trends in Ionization Energy

2.3.1: Trends in Ionization Energy (Problems)

2.4: Trends in Electron Affinity and Metallic Character

2.4.1: Trends in Electron Affinity and Metallic Character (Problems)

2.5: Trends in Electronegativity

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2.1: Electron Configurations

Skills to Develop

- Derive the predicted ground-state electron configurations of atoms
- Identify and explain exceptions to predicted electron configurations for atoms and ions
- Predict the charge of common metallic and nonmetallic elements, and write their electron configurations
- Relate electron configurations to element classifications in the periodic table

Having introduced the basics of atomic structure and quantum mechanics, we can use our understanding of quantum numbers to determine how atomic orbitals relate to one another. This allows us to determine which orbitals are occupied by electrons in each atom. The specific arrangement of electrons in orbitals of an atom determines many of the chemical properties of that atom.

Orbital Energies and Atomic Structure

The energy of atomic orbitals increases as the principal quantum number, n, increases. In any atom with two or more electrons, the repulsion between the electrons makes energies of subshells with different values of l differ so that the energy of the orbitals increases within a shell in the order $s < p < d < f$. Figure **2.1.1** depicts how these two trends in increasing energy relate. The 1*s* orbital at the bottom of the diagram is the orbital with electrons of lowest energy. The energy increases as we move up to the 2*s* and then 2*p*, 3*s*, and 3*p* orbitals, showing that the increasing *n* value has more influence on energy than the increasing *l* value for small atoms. However, this pattern does not hold for larger atoms. The 3*d* orbital is higher in energy than the 4*s* orbital. Such overlaps continue to occur frequently as we move up the chart.

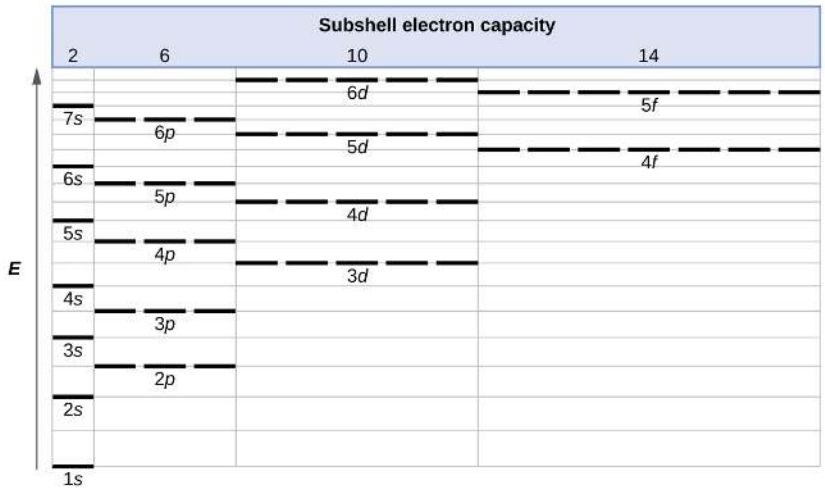


***Figure* 2.1.1**: *Generalized energy-level diagram for atomic orbitals in an atom with two or more electrons (not to scale).*

Electrons in successive atoms on the periodic table tend to fill low-energy orbitals first. Thus, many students find it confusing that, for example, the 5*p* orbitals fill immediately after the 4*d*, and immediately before the 6*s*. The filling order is based on observed experimental results, and has been confirmed by theoretical calculations. As the principal quantum number, *n*, increases, the size of the orbital increases and the electrons spend more time farther from the nucleus. Thus, the attraction to the nucleus is weaker and the energy associated with the orbital is higher (less stabilized). But this is not the only effect we have to take into account. Within each shell, as the value of *l* increases, the electrons are less penetrating (meaning there is less electron density found close to the nucleus), in the order $s > p > d > f$. Electrons that are closer to the nucleus slightly repel electrons that are farther out, offsetting the more dominant electron–nucleus attractions slightly (recall that all electrons have −1 charges, but nuclei have $+Z$ charges). This phenomenon is called shielding and will be discussed in more detail in the next section. Electrons in orbitals that experience more shielding are less stabilized and thus higher in energy. For small orbitals (1*s* through 3*p*), the increase in energy due to *n* is more significant than the increase due to *l*; however, for larger orbitals the two trends are comparable and cannot be simply predicted. We will discuss methods for remembering the observed order.

The arrangement of electrons in the orbitals of an atom is called the electron configuration of the atom. We describe an electron configuration with a symbol that contains three pieces of information (Figure **2.1.2**):

1. The number of the principal quantum shell, *n*,
2. The letter that designates the orbital type (the subshell, *l*), and
3. A superscript number that designates the number of electrons in that particular subshell.

For example, the notation $2p^4$ (read "two–p–four") indicates four electrons in a *p* subshell ($l = 1$) with a principal quantum number (n) of 2. The notation $3d^8$ (read "three–d–eight") indicates eight electrons in the *d* subshell (i.e., $l = 2$) of the principal shell for which $n = 3$.

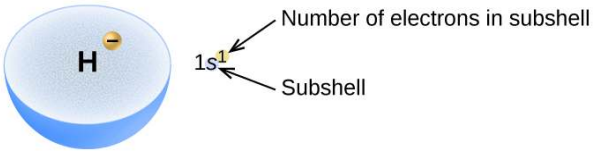


***Figure* 2.1.2**: *The diagram of an electron configuration specifies the subshell (n and l value, with letter symbol) and superscript number of electrons.*

The Aufbau Principle

To determine the electron configuration for any particular atom, we can “build” the structures in the order of atomic numbers. Beginning with hydrogen, and continuing across the periods of the periodic table, we add one proton at a time to the nucleus and one electron to the proper subshell until we have described the electron configurations of all the elements. This procedure is called the Aufbau principle, from the German word *Aufbau* (“to build up”). Each added electron occupies the subshell of lowest energy available (in the order shown in Figure **2.1.3**), subject to the limitations imposed by the allowed quantum numbers according to the Pauli exclusion principle. Electrons enter higher-energy subshells only after lower-energy subshells have been filled to capacity. Figure **2.1.3** illustrates the traditional way to remember the filling order for atomic orbitals.

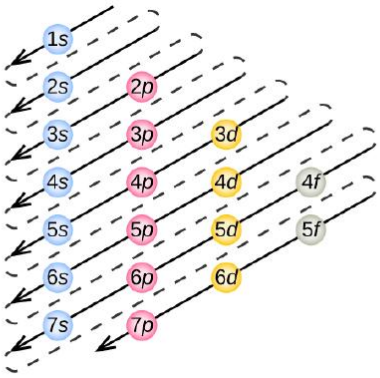


***Figure* 2.1.3**: *The arrow leads through each subshell in the appropriate filling order for electron configurations. This chart is straightforward to construct. Simply make a column for all the s orbitals with each n shell on a separate row. Repeat for p, d, and f. Be sure to only include orbitals allowed by the quantum numbers (no 1p or 2d, and so forth). Finally, draw diagonal lines from top to bottom as shown.*

Since the arrangement of the periodic table is based on the electron configurations, Figure **2.1.4** provides an alternative method for determining the electron configuration. The filling order simply begins at hydrogen and includes each subshell as you proceed in increasing *Z* order. For example, after filling the 3*p* block up to Ar, we see the orbital will be 4s (K, Ca), followed by the 3*d* orbitals.

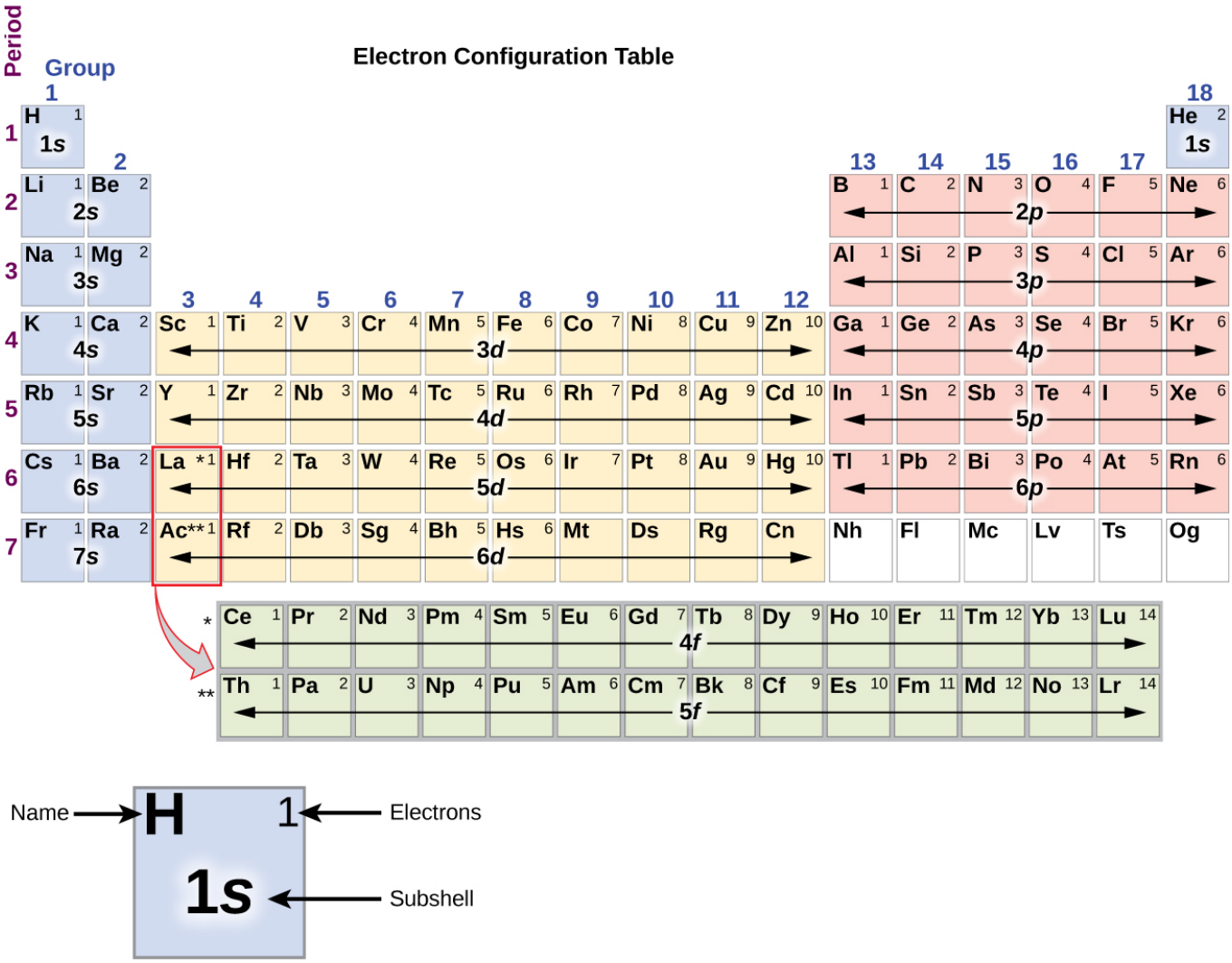
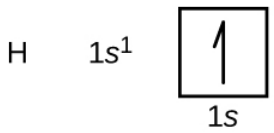


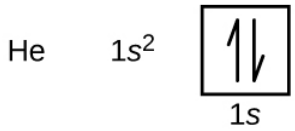
***Figure* 2.1.4**: *This periodic table shows the electron configuration for each subshell. By "building up" from hydrogen, this table can be used to determine the electron configuration for any atom on the periodic table.*

We will now construct the ground-state electron configuration and orbital diagram for a selection of atoms in the first and second periods of the periodic table. Orbital diagrams are pictorial representations of the electron configuration, showing the individual orbitals and the pairing arrangement of electrons. We start with a single hydrogen atom (atomic number 1), which consists of one proton and one electron. Referring to either Figure **2.1.3** or **2.1.4**, we would expect to find the electron in the 1*s* orbital. By convention, the $m_s = +\frac{1}{2}$ value is usually filled first. The electron configuration and the orbital diagram are:



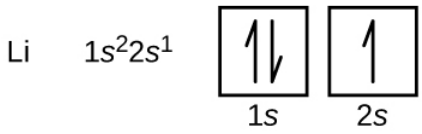
Following hydrogen is the noble gas helium, which has an atomic number of 2. The helium atom contains two protons and two electrons. The first electron has the same four quantum numbers as the hydrogen atom electron (n = 1, l = 0, m_l = 0, $m_s = +\frac{1}{2}$). The second electron also goes into the 1*s* orbital and fills that orbital. The second electron has the same n, l, and m_l quantum numbers, but must have the opposite spin quantum number, $m_s = -\frac{1}{2}$. This is in accord with the Pauli exclusion principle: No two electrons in the same atom can have the same set of four quantum numbers. For orbital diagrams, this means two arrows go in each box

(representing two electrons in each orbital) and the arrows must point in opposite directions (representing paired spins). The electron configuration and orbital diagram of helium are:

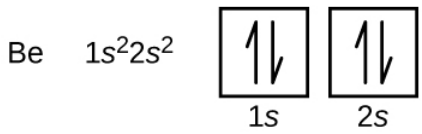


The n = 1 shell is completely filled in a helium atom.

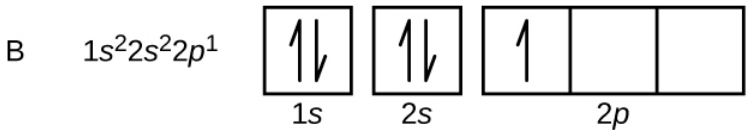
The next atom is the alkali metal lithium with an atomic number of 3. The first two electrons in lithium fill the 1*s* orbital and have the same sets of four quantum numbers as the two electrons in helium. The remaining electron must occupy the orbital of next lowest energy, the 2*s* orbital (Figure **2.1.3** or **2.1.4**). Thus, the electron configuration and orbital diagram of lithium are:



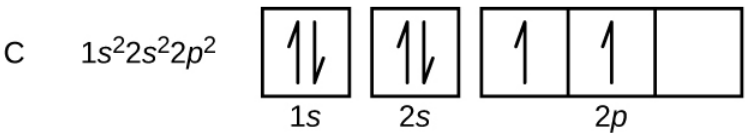
An atom of the alkaline earth metal beryllium, with an atomic number of 4, contains four protons in the nucleus and four electrons surrounding the nucleus. The fourth electron fills the remaining space in the 2*s* orbital.



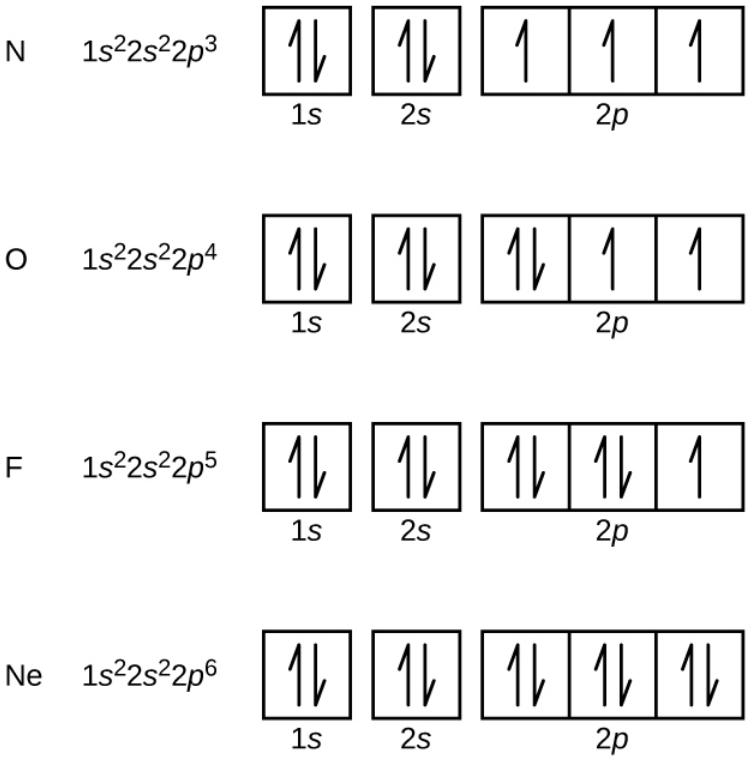
An atom of boron (atomic number 5) contains five electrons. The n = 1 shell is filled with two electrons and three electrons will occupy the n = 2 shell. Because any *s* subshell can contain only two electrons, the fifth electron must occupy the next energy level, which will be a 2*p* orbital. There are three degenerate 2*p* orbitals (m_l = −1, 0, +1) and the electron can occupy any one of these *p* orbitals. When drawing orbital diagrams, we include empty boxes to depict any empty orbitals in the same subshell that we are filling.



Carbon (atomic number 6) has six electrons. Four of them fill the 1*s* and 2*s* orbitals. The remaining two electrons occupy the 2*p* subshell. We now have a choice of filling one of the 2*p* orbitals and pairing the electrons or of leaving the electrons unpaired in two different, but degenerate, *p* orbitals. The orbitals are filled as described by Hund's rule: the lowest-energy configuration for an atom with electrons within a set of degenerate orbitals is that having the maximum number of unpaired electrons. Thus, the two electrons in the carbon 2*p* orbitals have identical n, l, and m_s quantum numbers and differ in their m_l quantum number (in accord with the Pauli exclusion principle). The electron configuration and orbital diagram for carbon are:



Nitrogen (atomic number 7) fills the 1*s* and 2*s* subshells and has one electron in each of the three 2*p* orbitals, in accordance with Hund's rule. These three electrons have unpaired spins. Oxygen (atomic number 8) has a pair of electrons in any one of the 2*p* orbitals (the electrons have opposite spins) and a single electron in each of the other two. Fluorine (atomic number 9) has only one 2*p* orbital containing an unpaired electron. All of the electrons in the noble gas neon (atomic number 10) are paired, and all of the orbitals in the n = 1 and the n = 2 shells are filled. The electron configurations and orbital diagrams of these four elements are:



The alkali metal sodium (atomic number 11) has one more electron than the neon atom. This electron must go into the lowest-energy subshell available, the 3*s* orbital, giving a $1s^2 2s^2 2p^6 3s^1$ configuration. The electrons occupying the outermost shell orbital(s) (highest value of *n*) are called valence electrons, and those occupying the inner shell orbitals are called core electrons (Figure **2.1.5**). Since the core electron shells correspond to noble gas electron configurations, we can abbreviate electron configurations by writing the noble gas that matches the core electron configuration, along with the valence electrons in a condensed format. For our sodium example, the symbol [Ne] represents core electrons, ($1s^2 2s^2 2p^6$) and our abbreviated or condensed configuration is $[Ne]3s^1$.

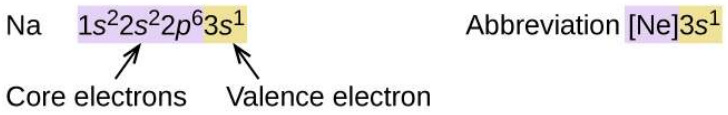


***Figure* 2.1.5**: *A core-abbreviated electron configuration (right) replaces the core electrons with the noble gas symbol whose configuration matches the core electron configuration of the other element.*

Similarly, the abbreviated configuration of lithium can be represented as $[He]2s^1$, where [He] represents the configuration of the helium atom, which is identical to that of the filled inner shell of lithium. Writing the configurations in this way emphasizes the similarity of the configurations of lithium and sodium. Both atoms, which are in the alkali metal family, have only one electron in a valence *s* subshell outside a filled set of inner shells.

$$\begin{aligned} \textbf{Li} &: [\textbf{He}]\, 2s^1 \\ \textbf{Na} &: [\textbf{Ne}]\, 3s^1 \end{aligned} \qquad (2.1.1)$$

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

The electron configurations of silicon (14 electrons), phosphorus (15 electrons), sulfur (16 electrons), chlorine (17 electrons), and argon (18 electrons) are analogous in the electron configurations of their outer shells to their corresponding family members carbon, nitrogen, oxygen, fluorine, and neon, respectively, except that the principal quantum number of the outer shell of the heavier elements has increased by one to $n = 3$. Figure **2.1.6** shows the lowest energy, or ground-state, electron configuration for these elements as well as that for atoms of each of the known elements.

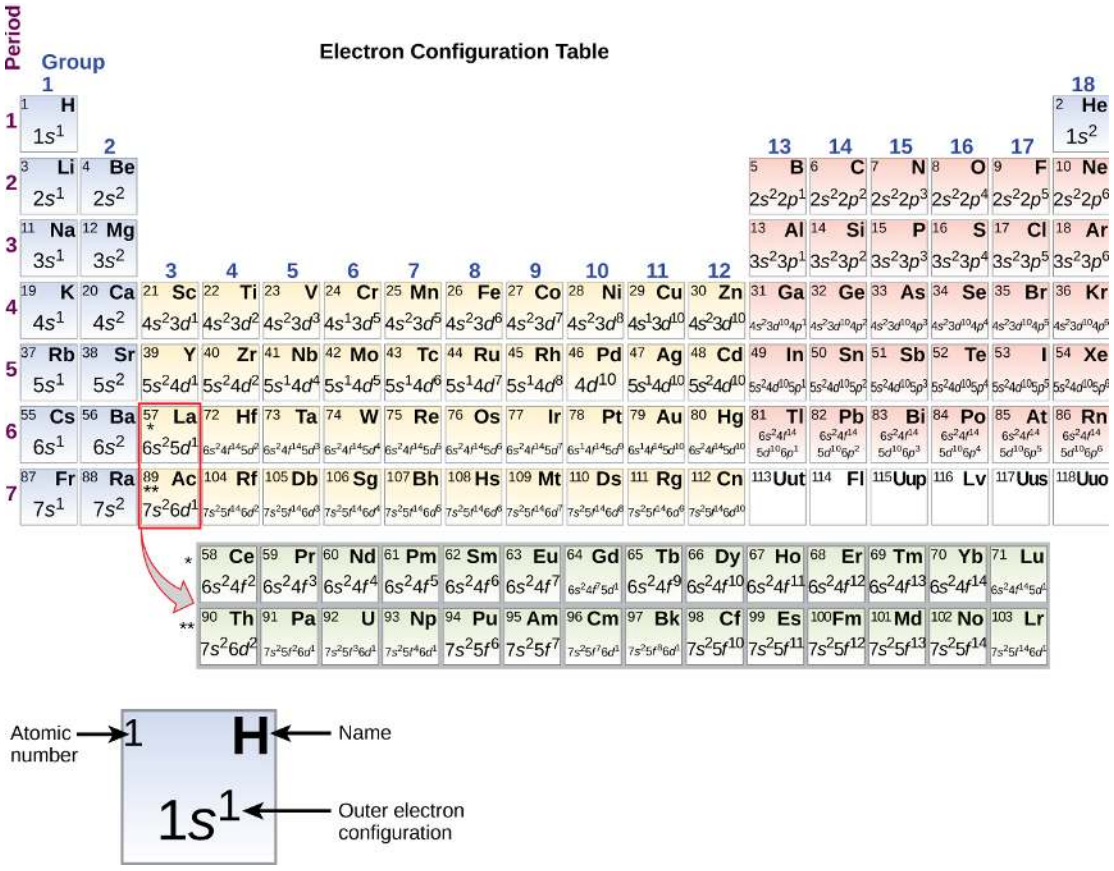


***Figure* 2.1.6**: *This version of the periodic table shows the outer-shell electron configuration of each element. Note that down each group, the configuration is often similar.*

When we come to the next element in the periodic table, the alkali metal potassium (atomic number 19), we might expect that we would begin to add electrons to the 3*d* subshell. However, all available chemical and physical evidence indicates that potassium is like lithium and sodium, and that the next electron is not added to the 3*d* level but is, instead, added to the 4*s* level (Figure **2.1.3** or **2.1.4**). As discussed previously, the 3*d* orbital with no radial nodes is higher in energy because it is less penetrating and more shielded from the nucleus than the 4*s*, which has three radial nodes. Thus, potassium has an electron configuration of $[Ar]4s^1$. Hence, potassium corresponds to Li and Na in its valence shell configuration. The next electron is added to complete the 4*s* subshell and calcium has an electron configuration of $[Ar]4s^2$. This gives calcium an outer-shell electron configuration corresponding to that of beryllium and magnesium.

Beginning with the transition metal scandium (atomic number 21), additional electrons are added successively to the 3*d* subshell. This subshell is filled to its capacity with 10 electrons (remember that for $l = 2$ [*d* orbitals], there are $2l + 1 = 5$ values of m_l, meaning that there are five *d* orbitals that have a combined capacity of 10 electrons). The 4*p* subshell fills next. Note that for three series of elements, scandium (Sc) through copper (Cu), yttrium (Y) through silver (Ag), and lutetium (Lu) through gold (Au), a total of 10 *d* electrons are successively added to the $(n - 1)$ shell next to the *n* shell to bring that $(n - 1)$ shell from 8 to 18 electrons. For two series, lanthanum (La) through lutetium (Lu) and actinium (Ac) through lawrencium (Lr), 14 *f* electrons ($l = 3$, $2l + 1 = 7$ m_l values; thus, seven orbitals with a combined capacity of 14 electrons) are successively added to the $(n - 2)$ shell to bring that shell from 18 electrons to a total of 32 electrons.

Example 2.1.1: Quantum Numbers and Electron Configurations

What is the electron configuration and orbital diagram for a phosphorus atom? What are the four quantum numbers for the last electron added?

Solution

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



The last electron added is a 3*p* electron. Therefore, $n = 3$ and, for a *p*-type orbital, $l = 1$. The m_l value could be –1, 0, or +1. The three *p* orbitals are degenerate, so any of these m_l values is correct. For unpaired electrons, convention assigns the value of $+\frac{1}{2}$ for the spin quantum number; thus, $m_s = +\frac{1}{2}$.

Exercise 2.1.1

Identify the atoms from the electron configurations given:

a. $[Ar]4s^2 3d^5$
b. $[Kr]5s^2 4d^{10} 5p^6$

Answer a

Mn

Answer b

Xe

The periodic table can be a powerful tool in predicting the electron configuration of an element. However, we do find exceptions to the order of filling of orbitals that are shown in Figure **2.1.3** or **2.1.4**. For instance, the electron configurations of the transition metals chromium (Cr; atomic number 24) and copper (Cu; atomic number 29), among others, are not those we would expect. In general, such exceptions involve subshells with very similar energy, and small effects can lead to changes in the order of filling.

In the case of Cr and Cu, we find that half-filled and completely filled subshells apparently represent conditions of preferred stability. This stability is such that an electron shifts from the 4*s* into the 3*d* orbital to gain the extra stability of a half-filled 3*d* subshell (in Cr) or a filled 3*d* subshell (in Cu). Other exceptions also occur. For example, niobium (Nb, atomic number 41) is predicted to have the electron configuration $[Kr]5s^2 4d^3$. Experimentally, we observe that its ground-state electron configuration is actually $[Kr]5s^1 4d^4$. We can rationalize this observation by saying that the electron–electron repulsions experienced by pairing the electrons in the 5*s* orbital are larger than the gap in energy between the 5*s* and 4*d* orbitals. There is no simple method to predict the exceptions for atoms where the magnitude of the repulsions between electrons is greater than the small differences in energy between subshells.

Electron Configurations and the Periodic Table



***Video* 2.1.1**: *A trick for writing electron configurations based on the organization of the periodic table.*

As described earlier, the periodic table arranges atoms based on increasing atomic number so that elements with the same chemical properties recur periodically. When their electron configurations are added to the table (Figure **2.1.6**), we also see a periodic recurrence of similar electron configurations in the outer shells of these elements. Because they are in the outer shells of an atom, valence electrons play the most important role in chemical reactions. The outer electrons have the highest energy of the electrons in an atom and are more easily lost or shared than the core electrons. Valence electrons are also the determining factor in some physical properties of the elements.

Elements in any one group (or column) have the same number of valence electrons; the alkali metals lithium and sodium each have only one valence electron, the alkaline earth metals beryllium and magnesium each have two, and the halogens fluorine and chlorine each have seven valence electrons. The similarity in chemical properties among elements of the same group occurs because they have the same number of valence electrons. It is the loss, gain, or sharing of valence electrons that defines how elements react.

It is important to remember that the periodic table was developed on the basis of the chemical behavior of the elements, well before any idea of their atomic structure was available. Now we can understand why the periodic table has the arrangement it has—the arrangement puts elements whose atoms have the same number of valence electrons in the same group. This arrangement is emphasized in Figure **2.1.6**, which shows in periodic-table form the electron configuration of the last subshell to be filled by the Aufbau principle. The colored sections of Figure **2.1.6** show the three categories of elements classified by the orbitals being filled: main group, transition, and inner transition elements. These classifications determine which orbitals are counted in the valence shell, or highest energy level orbitals of an atom.

1. **Main group elements** (sometimes called **representative elements**) are those in which the last electron added enters an *s* or a *p* orbital in the outermost shell, shown in blue and red in Figure **2.1.6**. This category includes all the nonmetallic elements, as well as many metals and the intermediate semimetallic elements. The valence electrons for main group elements are those with the highest *n* level. For example, gallium (Ga, atomic number 31) has the electron configuration [Ar]$\underline{4s^2}3d^{10}\underline{4p^1}$, which contains three valence electrons (underlined). The completely filled *d* orbitals count as core, not valence, electrons.
2. **Transition elements or transition metals**. These are metallic elements in which the last electron added enters a *d* orbital. The valence electrons (those added after the last noble gas configuration) in these elements include the *ns* and $(n - 1)$ *d* electrons. The official IUPAC definition of transition elements specifies those with partially filled *d* orbitals. Thus, the elements with completely filled orbitals (Zn, Cd, Hg, as well as Cu, Ag, and Au in Figure **2.1.6**) are not technically transition elements. However, the term is frequently used to refer to the entire *d* block (colored yellow in Figure **2.1.6**), and we will adopt this usage in this textbook.
3. **Inner transition elements** are metallic elements in which the last electron added occupies an *f* orbital. They are shown in green in Figure **2.1.6**. The valence shells of the inner transition elements consist of the $(n - 2)f$, the $(n - 1)d$, and the *ns* subshells. There are two inner transition series:
    1. The lanthanide series: lanthanide (La) through lutetium (Lu)
    2. The actinide series: actinide (Ac) through lawrencium (Lr)

Lanthanum and actinium, because of their similarities to the other members of the series, are included and used to name the series, even though they are transition metals with no *f* electrons.

Electron Configurations of Ions

We have seen that ions are formed when atoms gain or lose electrons. A cation (positively charged ion) forms when one or more electrons are removed from a parent atom. For main group elements, the electrons that were added last are the first electrons removed. For transition metals and inner transition metals, however, electrons in the *s* orbital are easier to remove than the *d* or *f* electrons, and so the highest *ns* electrons are lost, and then the $(n - 1)d$ or $(n - 2)f$ electrons are removed. An anion (negatively charged ion) forms when one or more electrons are added to a parent atom. The added electrons fill in the order predicted by the Aufbau principle.

Example 2.1.2: Predicting Electron Configurations of Ions

What is the electron configuration and orbital diagram of:

a. Na^+

b. P^{3-}
c. Al^{2+}
d. Fe^{2+}
e. Sm^{3+}

Solution

First, write out the electron configuration for each parent atom. We have chosen to show the full, unabbreviated configurations to provide more practice for students who want it, but listing the core-abbreviated electron configurations is also acceptable.

Next, determine whether an electron is gained or lost. Remember electrons are negatively charged, so ions with a positive charge have *lost* an electron. For main group elements, the last orbital gains or loses the electron. For transition metals, the last *s* orbital loses an electron before the *d* orbitals.

a. Na: $1s^2 2s^2 2p^6 3s^1$. Sodium cation loses one electron, so Na^+: $1s^2 2s^2 2p^6 3s^1 = Na^+$: $1s^2 2s^2 2p^6$.
b. P: $1s^2 2s^2 2p^6 3s^2 3p^3$. Phosphorus trianion gains three electrons, so P^{3-}: $1s^2 2s^2 2p^6 3s^2 3p^6$.
c. Al: $1s^2 2s^2 2p^6 3s^2 3p^1$. Aluminum dication loses two electrons Al^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^1 = Al^{2+}$: $1s^2 2s^2 2p^6 3s^1$.
d. Fe: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$. Iron(II) loses two electrons and, since it is a transition metal, they are removed from the 4*s* orbital Fe^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6 = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$.
e. Sm: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^6$. Samarium trication loses three electrons. The first two will be lost from the 6*s* orbital, and the final one is removed from the 4*f* orbital. Sm^{3+}: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^6 = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 4f^5$.

Exercise 2.1.2

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

Answer a

Tc^{2+}

Answer b

Ru^{3+}

Electronic Structures of Cations

When forming a cation, an atom of a main group element tends to lose all of its valence electrons, thus assuming the electronic structure of the noble gas that precedes it in the periodic table. For groups 1 (the alkali metals) and 2 (the alkaline earth metals), the group numbers are equal to the numbers of valence shell electrons and, consequently, to the charges of the cations formed from atoms of these elements when all valence shell electrons are removed. For example, calcium is a group 2 element whose neutral atoms have 20 electrons and a ground state electron configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$. When a Ca atom loses both of its valence electrons, the result is a cation with 18 electrons, a 2+ charge, and an electron configuration of $1s^2 2s^2 2p^6 3s^2 3p^6$. The Ca^{2+} ion is therefore isoelectronic with the noble gas Ar.

For groups 12–17, the group numbers exceed the number of valence electrons by 10 (accounting for the possibility of full *d* subshells in atoms of elements in the fourth and greater periods). Thus, the charge of a cation formed by the loss of all valence electrons is equal to the group number minus 10. For example, aluminum (in group 13) forms 3+ ions (Al^{3+}).

Exceptions to the expected behavior involve elements toward the bottom of the groups. In addition to the expected ions Tl^{3+}, Sn^{4+}, Pb^{4+}, and Bi^{5+}, a partial loss of these atoms' valence shell electrons can also lead to the formation of Tl^+, Sn^{2+}, Pb^{2+}, and Bi^{3+} ions. The formation of these 1+, 2+, and 3+ cations is ascribed to the inert pair effect, which reflects the relatively low energy of the valence *s*-electron pair for atoms of the heavy elements of groups 13, 14, and 15. Mercury (group 12) also exhibits an unexpected behavior: it forms a diatomic ion, Hg_2^{2+} (an ion formed from two mercury atoms, with an Hg-Hg bond), in addition to the expected monatomic ion Hg^{2+} (formed from only one mercury atom).

Transition and inner transition metal elements behave differently than main group elements. Most transition metal cations have 2+ or 3+ charges that result from the loss of their outermost *s* electron(s) first, sometimes followed by the loss of one or two *d* electrons from the next-to-outermost shell. For example, iron ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$) forms the ion Fe^{2+} ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$) by the loss of the 4*s* electrons and the ion Fe^{3+} ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$) by the loss of the 4*s* electrons and one of the 3*d* electrons. Although the *d* orbitals of the transition elements are—according to the Aufbau principle—the last to fill when building up electron configurations, the outermost *s* electrons are the first to be lost when these atoms ionize. When the inner transition metals form ions, they usually have a 3+ charge, resulting from the loss of their outermost *s* electrons and a *d* or *f* electron.

Example 2.1.3: Determining the Electronic Structures of Cations

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

Solution

First, write the electron configuration for the neutral atoms:

- Zn: $[Ar]3d^{10}4s^2$
- Cr: $[Ar]3d^5 4s^1$

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

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

Exercise 2.1.3

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

Answer

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

Electronic Structures of Anions

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

Example 2.1.4: Determining the Electronic Structure of Anions

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

Solution

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

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

Exercise 2.1.4

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

Answer

P: [Ne]$3s^2 3p^3$

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

In ionic compounds, electrons are transferred between atoms of different elements to form ions. But this is not the only way that compounds can be formed. Atoms can also make chemical bonds by sharing electrons between each other. Such bonds are called covalent bonds. Covalent bonds are formed between two atoms when both have similar tendencies to attract electrons to themselves (i.e., when both atoms have identical or fairly similar ionization energies and electron affinities). For example, two hydrogen atoms bond covalently to form an H_2 molecule; each hydrogen atom in the H_2 molecule has two electrons stabilizing it, giving each atom the same number of valence electrons as the noble gas He.

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

Summary



***Video* 2.1.2**: *An overview of the role of orbitals in electron configurations and how to write electron configurations.*

The relative energy of the subshells determine the order in which atomic orbitals are filled (1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, and so on). Electron configurations and orbital diagrams can be determined by applying the Pauli exclusion principle (no two electrons can have the same set of four quantum numbers) and Hund's rule (whenever possible, electrons retain unpaired spins in degenerate orbitals).

Electrons in the outermost orbitals, called valence electrons, are responsible for most of the chemical behavior of elements. In the periodic table, elements with analogous valence electron configurations usually occur within the same group. There are some exceptions to the predicted filling order, particularly when half-filled or completely filled orbitals can be formed. The periodic table can be divided into three categories based on the orbital in which the last electron to be added is placed: main group elements (*s* and *p* orbitals), transition elements (*d* orbitals), and inner transition elements (*f* orbitals).

Glossary

Aufbau principle

procedure in which the electron configuration of the elements is determined by "building" them in order of atomic numbers, adding one proton to the nucleus and one electron to the proper subshell at a time

core electron

electron in an atom that occupies the orbitals of the inner shells

electron configuration

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

Hund's rule

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

orbital diagram

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

valence electrons

electrons in the outermost or valence shell (highest value of *n*) of a ground-state atom; determine how an element reacts

valence shell

outermost shell of electrons in a ground-state atom; for main group elements, the orbitals with the highest *n* level (*s* and *p* subshells) are in the valence shell, while for transition metals, the highest energy *s* and *d* subshells make up the valence shell and for inner transition elements, the highest *s*, *d*, and *f* subshells are included

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2.1.1: Electron Configurations (Problems)

PROBLEM 2.1.1.1

Using complete subshell notation (no abbreviations), predict the electron configuration of each of the following atoms:

a. C
b. P
c. V
d. Sb
e. Sm

Answer a

$1s^2 2s^2 2p^2$

Answer b

$1s^2 2s^2 2p^6 3s^2 3p^3$

Answer c

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

Answer d

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

Answer e

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

PROBLEM 2.1.1.2

Using complete subshell notation, predict the electron configuration of each of the following atoms:

a. N
b. Si
c. Fe
d. Te
e. Tb

Answer a

$1s^2 2s^2 2p^3$

Answer b

$1s^2 2s^2 2p^6 3s^2 3p^2$

Answer c

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

Answer d

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

Answer e

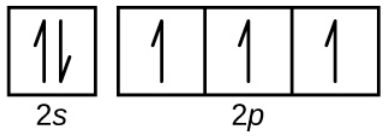
$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^9$

PROBLEM 2.1.1.3

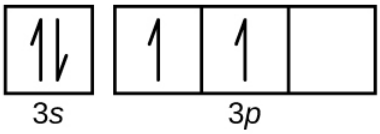
Use an orbital diagram to describe the electron configuration of the valence shell of each of the following atoms:

a. N
b. Si
c. Fe
d. Te
e. Mo

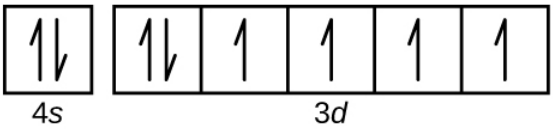
Answer a



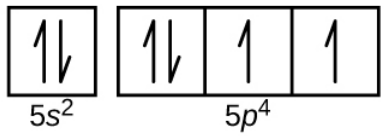
Answer b



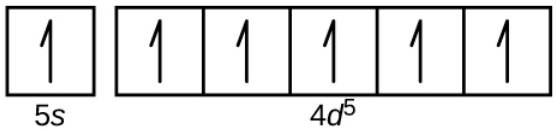
Answer c



Answer d



Answer e



PROBLEM 2.1.1.4

Using complete subshell notation ($1s^2 2s^2 2p^6$, and so forth), predict the electron configurations of the following ions.

a. N^{3-}
b. Ca^{2+}
c. S^{-}
d. Cs^{2+}
e. Cr^{2+}
f. Gd^{3+}

Answer a

$1s^2 2s^2 2p^6$

Answer b

$1s^2 2s^2 2p^6 3s^2 3p^6$

Answer c

$1s^2 2s^2 2p^6 3s^2 3p^5$

Answer d

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

Answer e

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

Answer f

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

Click here to see a video of the solution



PROBLEM 2.1.1.5

Which atom has the electron configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^2$?

Answer

Zr

PROBLEM 2.1.1.6

Which atom has the electron configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$?

Answer

Co

PROBLEM 2.1.1.7

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

b. Which ion with a –2 charge has this configuration?

Answer a

Rb^+

Answer b

Se^{2-}

PROBLEM 2.1.1.8

Which of the following atoms contains only three valence electrons: Li, B, N, F, Ne?

Answer

B

PROBLEM 2.1.1.9

Which of the following has two unpaired electrons?

a. Mg
b. Si
c. S
d. Both Mg and S
e. Both Si and S.

Answer

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

PROBLEM 2.1.1.10

Which atom would be expected to have a half-filled 6*p* subshell?

Answer

Bi

PROBLEM 2.1.1.11

Which atom would be expected to have a half-filled 4*s* subshell?

Answer

K

PROBLEM 2.1.1.12

In one area of Australia, the cattle did not thrive despite the presence of suitable forage. An investigation showed the cause to be the absence of sufficient cobalt in the soil. Cobalt forms cations in two oxidation states, Co^{2+} and Co^{3+}. Write the electron structure of the two cations.

Answer

Co^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$

Co^{3+}: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4$

Click here to see a video of the solution



PROBLEM 2.1.1.13

Thallium was used as a poison in the Agatha Christie mystery story “The Pale Horse.” Thallium has two possible cationic forms, +1 and +3. The +1 compounds are the more stable. Write the electron structure of the +1 cation of thallium.

Answer

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

PROBLEM 2.1.1.14

Write the electron configurations for the following atoms or ions:

a. B^{3+}
b. O^{-}
c. Cl^{3+}
d. Ca^{2+}
e. Ti

Answer a

$1s^2$

Answer b

$1s^2 2s^2 2p^5$

Answer c

$1s^2 2s^2 2p^6 3s^2 3p^2$

Answer d

$1s^2 2s^2 2p^6 3s^2 3p^6$

Answer e

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

PROBLEM 2.1.1.15

Cobalt–60 and iodine–131 are radioactive isotopes commonly used in nuclear medicine. How many protons, neutrons, and electrons are in atoms of these isotopes? Write the complete electron configuration for each isotope.

Answer

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

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

PROBLEM 2.1.1.16

Atoms of which group in the periodic table have a valence shell electron configuration of ns^2np^3?

Answer

15 (5A)

PROBLEM 2.1.1.17

Atoms of which group in the periodic table have a valence shell electron configuration of ns^2?

Answer

2 (2A)

PROBLEM 2.1.1.18

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

Answer

The protons in the nucleus do not change during normal chemical reactions. Only the outer electrons move. Positive charges form when electrons are lost.

PROBLEM 2.1.1.19

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

Answer

Two cations with a +3 charge give a total of +6 charge, while three anions of -2 charge give a total of -6 charge. +6-6=0, so when these ions bond, the charges will cancel, leaving the resulting compound uncharged.

PROBLEM 2.1.1.20

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

Answer

P, I, Cl, and O would form anions because they are nonmetals. Mg, In, Cs, Pb, and Co would form cations because they are metals.

PROBLEM 2.1.1.21

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

Answer

Anions: Br, N, F, S,

Cations: Ca, Na, Al, Sn (because it's a metal), Cd (because it is a metal)

PROBLEM 2.1.1.22

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

a. P
b. Mg

c. Al
d. O
e. Cl
f. Cs

Answer a

P^{3-}

Answer b

Mg^{2+}

Answer c

Al^{3+}

Answer d

O^{2-}

Answer e

Cl^{-}

Answer f

Cs^{+}

PROBLEM 2.1.1.23

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

a. I
b. Sr
c. K
d. N
e. S
f. In

Answer a

I^{-}

Answer b

Sr^{2+}

Answer c

K^{+}

Answer d

N^{3-}

Answer e

S^{2-}

Answer f

In^{3+}

PROBLEM 2.1.1.24

Write the noble gas electron configuration for each of the following ions:

a. As^{3-}
b. I^{-}
c. Be^{2+}
d. Cd^{2+}
e. O^{2-}
f. Ga^{3+}
g. Li^{+}
h. N^{3-}
i. Sn^{2+}
j. Co^{2+}
k. Fe^{2+}
l. As^{3+}

Answer a

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

Answer b

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

Answer c

$1s^2$

Answer d

$[Kr]4d^{10}$

Answer e

$[He]2s^2 2p^6$

Answer f

$[Ar]3d^{10}$

Answer g

$1s^2$

Answer h

$[He]2s^2 2p^6$

Answer i

$[Kr]4d^{10} 5s^2$

Answer j

$[Ar]3d^7$

Answer k

$[Ar]3d^6$

Answer l

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

PROBLEM 2.1.1.25

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

a. Al
b. Br
c. Sr
d. Li
e. As
f. S

Answer a

Al: $1s^2 2s^2 2p^6 3s^2 3p^1$

Al^{3+}: $1s^2 2s^2 2p^6$

Answer b

Br: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$

Br^-: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$

Answer c

Sr: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$

Sr^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$

Answer d

Li: $1s^2 2s^1$

Li^+: $1s^2$

Answer e

As: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$

As^{3-}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$

Answer f

S: $1s^2 2s^2 2p^6 3s^2 3p^4$

S^{2-}: $1s^2 2s^2 2p^6 3s^2 3p^6$

Contributors

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2.2: Trends in Size

Skills to Develop

- Describe and explain the observed trends in atomic size of the elements

The elements in groups (vertical columns) of the periodic table exhibit similar chemical behavior. This similarity occurs because the members of a group have the same number and distribution of electrons in their valence shells. However, there are also other patterns in chemical properties on the periodic table. For example, as we move down a group, the metallic character of the atoms increases. Oxygen, at the top of Group 16 (6A), is a colorless gas; in the middle of the group, selenium is a semiconducting solid; and, toward the bottom, polonium is a silver-grey solid that conducts electricity.

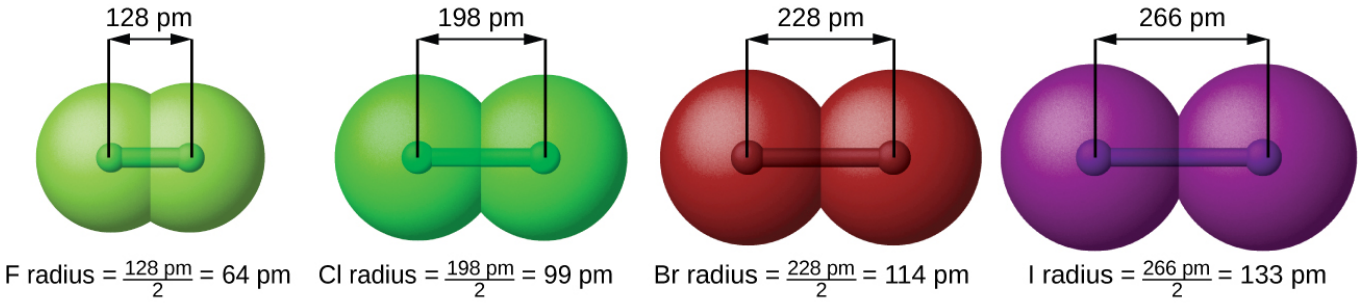
As we go across a period from left to right, we add a proton to the nucleus and an electron to the valence shell with each successive element. As we go down the elements in a group, the number of electrons in the valence shell remains constant, but the principal quantum number increases by one each time. An understanding of the electronic structure of the elements allows us to examine some of the properties that govern their chemical behavior. These properties vary periodically as the electronic structure of the elements changes. They are (1) size (radius) of atoms and ions, (2) ionization energies, and (3) electron affinities.

Visualizing periodic trends

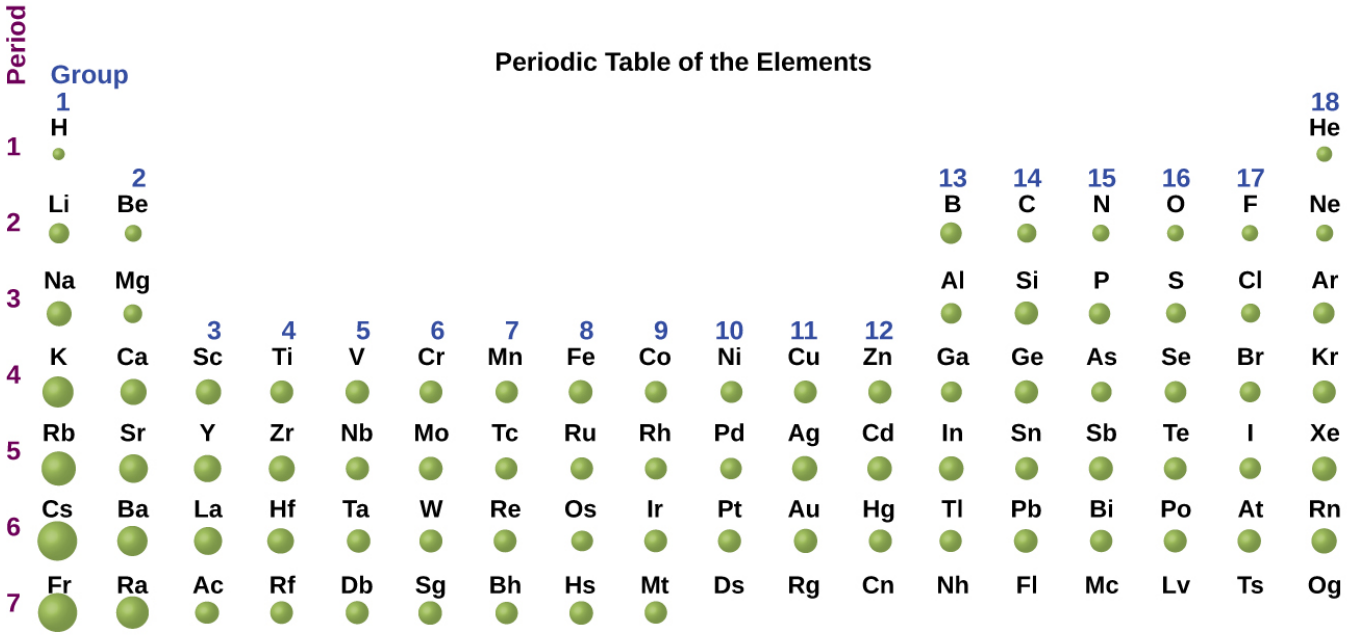
Explore visualizations of the periodic trends discussed in this section (and many more trends). With just a few clicks, you can create three-dimensional versions of the periodic table showing atomic size or graphs of ionization energies from all measured elements.

Variation in Covalent Radius

The quantum mechanical picture makes it difficult to establish a definite size of an atom. However, there are several practical ways to define the radius of atoms and, thus, to determine their relative sizes that give roughly similar values. We will use the covalent radius (Figure 2.2.1), which is defined as one-half the distance between the nuclei of two identical atoms when they are joined by a covalent bond (this measurement is possible because atoms within molecules still retain much of their atomic identity).



(a)



(b)

***Figure* 2.2.1**: *(a) The radius of an atom is defined as one-half the distance between the nuclei in a molecule consisting of two identical atoms joined by a covalent bond. The atomic radius for the halogens increases down the group as n increases. (b) Covalent radii of the elements are shown to scale. The general trend is that radii increase down a group and decrease across a period.*

We know that as we scan down a group, the principal quantum number, *n*, increases by one for each element. Thus, the electrons are being added to a region of space that is increasingly distant from the nucleus. Consequently, the size of the atom (and its covalent radius) must increase as we increase the distance of the outermost electrons from the nucleus. This trend is illustrated for the covalent radii of the halogens in Table **2.2.1** and Figure **2.2.1**. The trends for the entire periodic table can be seen in Figure **2.2.2**.

***Table* 2.2.1:** Covalent Radii of the Halogen Group Elements

Atom	Covalent radius (pm)	Nuclear charge
F	64	+9
Cl	99	+17
Br	114	+35
I	133	+53
At	148	+85

As shown in Figure **2.2.2**, as we move across a period from left to right, we generally find that each element has a smaller covalent radius than the element preceding it. This might seem counterintuitive because it implies that atoms with more electrons have a smaller atomic radius. This can be explained with the concept of effective nuclear charge, Z_{eff}. This is the pull exerted on a specific electron by the nucleus, taking into account any electron–electron repulsions. For hydrogen, there is only one electron and so the nuclear charge (Z) and the effective nuclear charge (Z_{eff}) are equal. For all other atoms, the inner electrons partially *shield* the outer electrons from the pull of the nucleus, and thus:

$$Z_{\text{eff}} = Z - shielding \tag{2.2.1}$$

Shielding is determined by the probability of another electron being between the electron of interest and the nucleus, as well as by the electron–electron repulsions the electron of interest encounters. Core electrons are adept at shielding, while electrons in the same valence shell do not block the nuclear attraction experienced by each other as efficiently. Thus, each time we move from one element to the next across a period, Z increases by one, but the shielding increases only slightly. Thus, Z_{eff} increases as we move from left to right across a period. The stronger pull (higher effective nuclear charge) experienced by electrons on the right side of the periodic table draws them closer to the nucleus, making the covalent radii smaller.

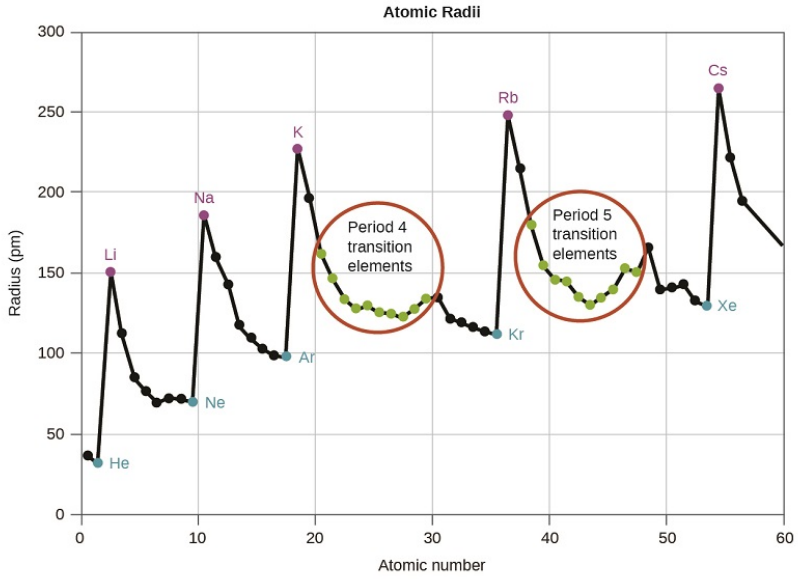


***Figure* 2.2.2**: *Within each period, the trend in atomic radius decreases as Z increases; for example, from K to Kr. Within each group (e.g., the alkali metals shown in purple), the trend is that atomic radius increases as Z increases.*



***Video* 2.2.1**: *Learn more about shielding.*

Thus, as we would expect, the outermost or valence electrons are easiest to remove because they have the highest energies, are shielded more, and are farthest from the nucleus. As a general rule, when the representative elements form cations, they do so by the loss of the *ns* or *np* electrons that were added last in the Aufbau process. The transition elements, on the other hand, lose the *ns* electrons before they begin to lose the $(n - 1)d$ electrons, even though the *ns* electrons are added first, according to the Aufbau principle.

Example 2.2.1: Sorting Atomic Radii

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

Solution

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

Exercise 2.2.1

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

Answer

Ne or He

Variation in Ionic Radii

Ionic radius is the measure used to describe the size of an ion. A cation always has fewer electrons and the same number of protons as the parent atom; it is smaller than the atom from which it is derived (Figure **2.2.3**). For example, the covalent radius of an aluminum atom ($1s^2 2s^2 2p^6 3s^2 3p^1$) is 118 pm, whereas the ionic radius of an Al^{3+} ($1s^2 2s^2 2p^6$) is 68 pm. As electrons are removed from the outer valence shell, the remaining core electrons occupying smaller shells experience a greater effective nuclear charge Z_{eff} (as discussed) and are drawn even closer to the nucleus.



***Figure* 2.2.3**: *The radius for a cation is smaller than the parent atom (Al), due to the lost electrons; the radius for an anion is larger than the parent (S), due to the gained electrons.*

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

An anion (negative ion) is formed by the addition of one or more electrons to the valence shell of an atom. This results in a greater repulsion among the electrons and a decrease in Z_{eff} per electron. Both effects (the increased number of electrons and the decreased Z_{eff}) cause the radius of an anion to be larger than that of the parent atom (Figure **2.2.3**). For example, a sulfur atom ($[Ne]3s^2 3p^4$) has a covalent radius of 104 pm, whereas the ionic radius of the sulfide anion ($[Ne]3s^2 3p^6$) is 170 pm. For consecutive elements proceeding down any group, anions have larger principal quantum numbers and, thus, larger radii.

Atoms and ions that have the same electron configuration are said to be isoelectronic. Examples of isoelectronic species are N^{3-}, O^{2-}, F^-, Ne, Na^+, Mg^{2+}, and Al^{3+} ($1s^2 2s^2 2p^6$). Another isoelectronic series is P^{3-}, S^{2-}, Cl^-, Ar, K^+, Ca^{2+}, and Sc^{3+} ($[Ne]3s^2 3p^6$). For atoms or ions that are isoelectronic, the number of protons determines the size. The greater the nuclear charge, the smaller the radius in a series of isoelectronic ions and atoms.

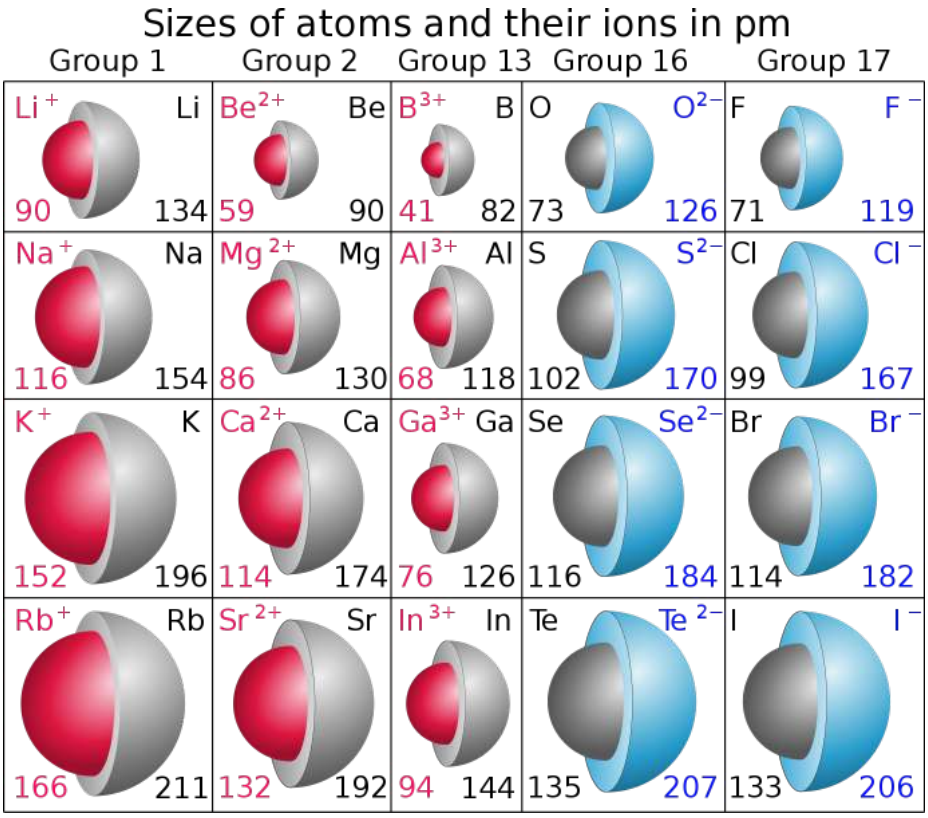


***Figure* 2.2.4**: *Comparison of Ionic and Atomic Radius. Image Credit: By Popnose [CC BY-SA 3.0 (http://creativecommons.org/licenses/by-sa/3.0) or GFDL (http://www.gnu.org/copyleft/fdl.html)], via Wikimedia Commons*

Summary



***Video* 2.2.2**: *A summary on atomic radius.*

Electron configurations allow us to understand many periodic trends. Covalent radius increases as we move down a group because the *n* level (orbital size) increases. Covalent radius mostly decreases as we move left to right across a period because the effective nuclear charge experienced by the electrons increases, and the electrons are pulled in tighter to the nucleus. Anionic radii are larger than the parent atom, while cationic radii are smaller, because the number of valence electrons has changed while the nuclear charge has remained constant.

Glossary

covalent radius

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

effective nuclear charge

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

isoelectronic

group of ions or atoms that have identical electron configurations

Contributors

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2.2.1: Trends in Size (Problems)

PROBLEM 2.2.1.1

Based on their positions in the periodic table, predict which has the smallest atomic radius: Mg, Sr, Si, Cl, I.

Answer

Cl

PROBLEM 2.2.1.2

Based on their positions in the periodic table, predict which has the largest atomic radius: Li, Rb, N, F, I.

Answer

Rb

PROBLEM 2.2.1.3

Based on their positions in the periodic table, list the following atoms in order of increasing radius: Cs, Ca, Rb, Mg

Answer

Mg < Ca < Rb < Cs

PROBLEM 2.2.1.4

Based on their positions in the periodic table, list the following atoms in order of increasing radius: Sr, Cl, Ca, Si.

Answer

Cl < Si < Ca < Sr

Click here to see a video of the solution



PROBLEM 2.2.1.5

Based on their positions in the periodic table, list the following ions in order of increasing radius: K^+, Ca^{2+}, Al^{3+}, Si^{4+}.

Answer

$Si^{4+} < Al^{3+} < Ca^{2+} < K^+$

PROBLEM 2.2.1.6

List the following ions in order of increasing radius: Br^-, Li^+, Te^{2-}, Mg^{2+}.

Answer

Answer

$Li^{+} < Mg^{2+} < Br^{-} < Te^{2-}$

Click here to see a video of the solution



PROBLEM 2.2.1.7

Which atom and/or ion is (are) isoelectronic with Br^{+}: Se^{2+}, Se, As^{-}, Kr, Ga^{3+}, Cl^{-}?

Answer

Se, As^{-}

PROBLEM 2.2.1.8

Which of the following atoms and ions is (are) isoelectronic with S^{2+}: Si^{4+}, Cl^{3+}, Ar, As^{3+}, Si, Al^{3+}?

Answer

Si, Cl^{3+}

Click here to see a video of the solution



PROBLEM 2.2.1.9

Compare both the numbers of protons and electrons present in each to rank the following ions in order of increasing radius: As^{3-}, Br^{-}, K^{+}, Mg^{2+}.

Answer

$Mg^{2+} < K^{+} < Br^{-} < As^{3-}$

PROBLEM 2.2.1.10

The ionic radii of the ions S^{2-}, Cl^{-}, and K^{+} are 184, 181, 138 pm respectively. Explain why these ions have different sizes even though they contain the same number of electrons.

Answer

They have different numbers of protons, which determines their size.

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2.3: Trends in Ionization Energy

Skills to Develop

- Describe and explain the observed trends in ionization energy of the elements



***Video* 2.3.1**: *A brief overview of ionization energy.*

Variation in Ionization Energies

The amount of energy required to remove the most loosely bound electron from a gaseous atom in its ground state is called its first ionization energy (IE_1). The first ionization energy for an element, X, is the energy required to form a cation with +1 charge:

$$\mathrm{X}(g) \longrightarrow \mathrm{X}^{+}(g) + \mathrm{e}^{-} \quad \mathrm{IE}_1 \tag{2.3.1}$$

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

$$\mathrm{X}^{+}(g) \longrightarrow \mathrm{X}^{2+}(g) + \mathrm{e}^{-} \quad \mathrm{IE}_2 \tag{2.3.2}$$

The energy required to remove the third electron is the third ionization energy, and so on. Energy is always required to remove electrons from atoms or ions, so ionization processes are endothermic and IE values are always positive. For larger atoms, the most loosely bound electron is located farther from the nucleus and so is easier to remove. Thus, as size (atomic radius) increases, the ionization energy should decrease. Relating this logic to what we have just learned about radii, we would expect first ionization energies to decrease down a group and to increase across a period.

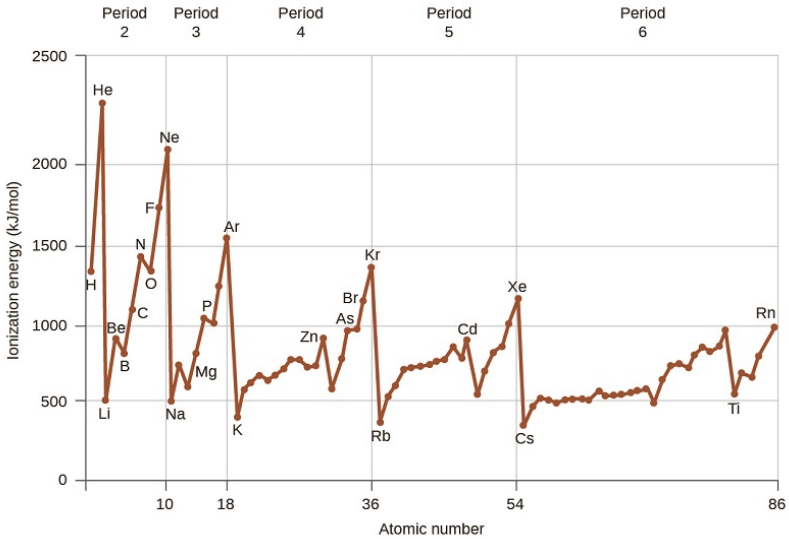


***Figure* 2.3.1**: *The first ionization energy of the elements in the first five periods are plotted against their atomic number.*

Figure **2.3.1** graphs the relationship between the first ionization energy and the atomic number of several elements. Within a period, the values of first ionization energy for the elements (IE_1) generally increases with increasing *Z*. Down a group, the IE_1 value generally decreases with increasing *Z*. There are some systematic deviations from this trend, however. Note that the ionization energy of boron (atomic number 5) is less than that of beryllium (atomic number 4) even though the nuclear charge of boron is greater by one proton. This can be explained because the energy of the subshells increases as *l* increases, due to penetration and shielding (as discussed previously in this chapter). Within any one shell, the *s* electrons are lower in energy than the *p* electrons. This means that an *s* electron is harder to remove from an atom than a *p* electron in the same shell. The electron removed during the ionization of beryllium ($[He]2s^2$) is an *s* electron, whereas the electron removed during the ionization of boron ($[He]2s^22p^1$) is a *p* electron; this results in a lower first ionization energy for boron, even though its nuclear charge is greater by one proton. Thus, we see a small deviation from the predicted trend occurring each time a new subshell begins.

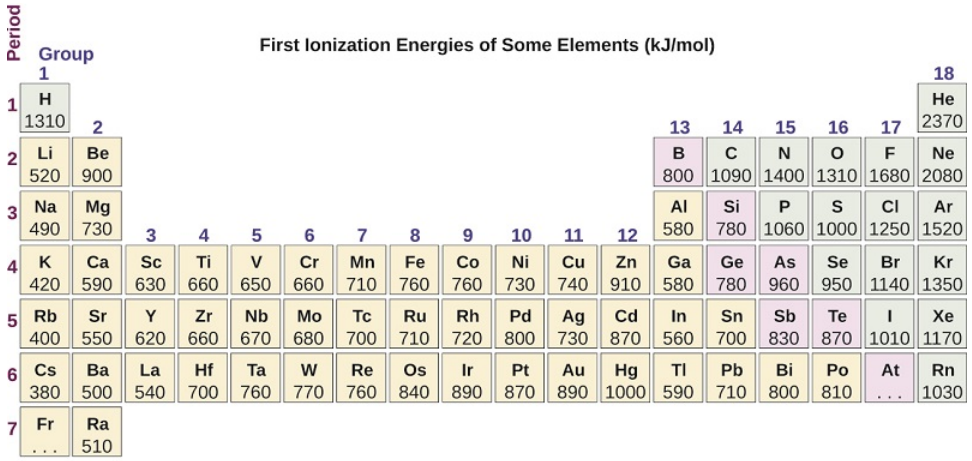
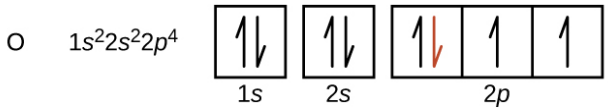


***Figure* 2.3.2**: *This version of the periodic table shows the first ionization energy of (IE: $_1$), in kJ/mol, of selected elements.*

Another deviation occurs as orbitals become more than one-half filled. The first ionization energy for oxygen is slightly less than that for nitrogen, despite the trend in increasing IE_1 values across a period. Looking at the orbital diagram of oxygen, we can see that removing one electron will eliminate the electron–electron repulsion caused by pairing the electrons in the 2*p* orbital and will result in a half-filled orbital (which is energetically favorable). Analogous changes occur in succeeding periods (note the dip for sulfur after phosphorus in Figure **2.3.2**.



Removing an electron from a cation is more difficult than removing an electron from a neutral atom because of the greater electrostatic attraction to the cation. Likewise, removing an electron from a cation with a higher positive charge is more difficult than removing an electron from an ion with a lower charge. Thus, successive ionization energies for one element always increase. As seen in Table **2.3.1**, there is a large increase in the ionization energies (color change) for each element. This jump corresponds to removal of the core electrons, which are harder to remove than the valence electrons. For example, Sc and Ga both have three valence electrons, so the rapid increase in ionization energy occurs after the third ionization.

***Table* 2.3.1**: *Successive Ionization Energies for Selected Elements (kJ/mol)*

Element	IE_1	IE_2	IE_3	IE_4	IE_5	IE_6	IE_7
K	418.8	3051.8	4419.6	5876.9	7975.5	9590.6	11343
Ca	589.8	1145.4	4912.4	6490.6	8153.0	10495.7	12272.9
Sc	633.1	1235.0	2388.7	7090.6	8842.9	10679.0	13315.0
Ga	578.8	1979.4	2964.6	6180	8298.7	10873.9	13594.8
Ge	762.2	1537.5	3302.1	4410.6	9021.4	Not available	Not available
As	944.5	1793.6	2735.5	4836.8	6042.9	12311.5	Not available

Example 2.3.1: Ranking Ionization Energies

Predict the order of increasing energy for the following processes: IE_1 for Al, IE_1 for Tl, IE_2 for Na, IE_3 for Al.

Solution

Removing the $6p^1$ electron from Tl is easier than removing the $3p^1$ electron from Al because the higher n orbital is farther from the nucleus, so $IE_1(Tl) < IE_1(Al)$. Ionizing the third electron from

$$\mathrm{Al} \quad (\mathrm{Al}^{2+} \longrightarrow \mathrm{Al}^{3+} + \mathrm{e}^-)$$

requires more energy because the cation Al^{2+} exerts a stronger pull on the electron than the neutral Al atom, so $IE_1(Al) < IE_3(Al)$. The second ionization energy for sodium removes a core electron, which is a much higher energy process than removing valence electrons. Putting this all together, we obtain:

$$IE_1(Tl) < IE_1(Al) < IE_3(Al) < IE_2(Na).$$

Exercise 2.3.1

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

Answer

Ba

Summary



***Video* 2.3.2**: *A brief review of ionization energy.*

Ionization energy (the energy associated with forming a cation) decreases down a group and mostly increases across a period because it is easier to remove an electron from a larger, higher energy orbital.

Glossary

ionization energy

energy required to remove an electron from a gaseous atom or ion. The associated number (e.g., second ionization energy) corresponds to the charge of the ion produced (X^{2+})

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2.3.1: Trends in Ionization Energy (Problems)

PROBLEM 2.3.1.1

Based on their positions in the periodic table, predict which has the largest first ionization energy: Mg, Ba, B, O, Te.

Answer

O

PROBLEM 2.3.1.2

Based on their positions in the periodic table, predict which has the smallest first ionization energy: Li, Cs, N, F, I.

Answer

Cs

PROBLEM 2.3.1.3

Based on their positions in the periodic table, rank the following atoms in order of increasing first ionization energy: F, Li, N, Rb.

Answer

Rb < Li < N < F

PROBLEM 2.3.1.4

Based on their positions in the periodic table, rank the following atoms or compounds in order of increasing first ionization energy: Mg, O, S, Si

Answer

Mg< Si < S < O

PROBLEM 2.3.1.5

Which main group atom would be expected to have the lowest second ionization energy?

Answer

Ra

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2.4: Trends in Electron Affinity and Metallic Character

Skills to Develop

- Describe and explain the observed trends in electron affinity and metallic character of the elements
- To recognize the inverse relationship of ionization energies and electron affinities

Variation in Electron Affinities



***Video* 2.4.1**: *A brief overview of electron affinity.*

The electron affinity [EA] is the energy change for the process of adding an electron to a gaseous atom to form an anion (negative ion).

$$\mathrm{X}(g) + \mathrm{e}^- \longrightarrow \mathrm{X}^-(g) \quad \mathrm{EA}_1 \tag{2.4.1}$$

This process can be either endothermic or exothermic, depending on the element. The EA of some of the elements is given in Figure **2.4.6**. You can see that many of these elements have negative values of EA, which means that energy is released when the gaseous atom accepts an electron. However, for some elements, energy is required for the atom to become negatively charged and the value of their EA is positive. Just as with ionization energy, subsequent EA values are associated with forming ions with more charge. The second EA is the energy associated with adding an electron to an anion to form a –2 ion, and so on.

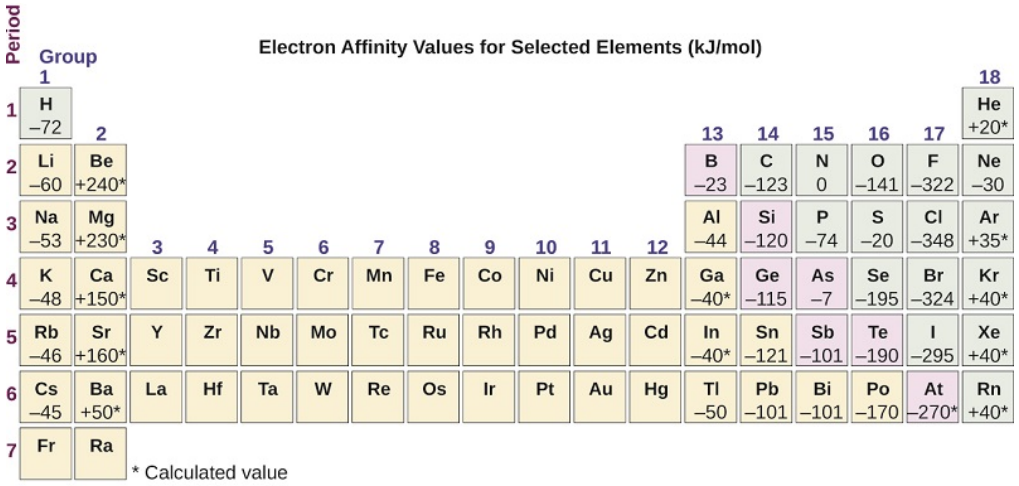


Figure* 2.4.1*: This version of the periodic table displays the electron affinity values (in kJ/mol) for selected elements.:

As we might predict, it becomes easier to add an electron across a series of atoms as the effective nuclear charge of the atoms increases. We find, as we go from left to right across a period, EAs tend to become more negative. The exceptions found among the elements of group 2 (2A), group 15 (5A), and group 18 (8A) can be understood based on the electronic structure of these groups.

The noble gases, group 18 (8A), have a completely filled shell and the incoming electron must be added to a higher *n* level, which is more difficult to do. Group 2 (2A) has a filled *ns* subshell, and so the next electron added goes into the higher energy *np*, so, again, the observed EA value is not as the trend would predict. Finally, group 15 (5A) has a half-filled *np* subshell and the next electron must be paired with an existing *np* electron. In all of these cases, the initial relative stability of the electron configuration disrupts the trend in EA.

We also might expect the atom at the top of each group to have the largest EA; their first ionization potentials suggest that these atoms have the largest effective nuclear charges. However, as we move down a group, we see that the second element in the group most often has the greatest EA. The reduction of the EA of the first member can be attributed to the small size of the $n = 2$ shell and the resulting large electron–electron repulsions. For example, chlorine, with an EA value of –348 kJ/mol, has the highest value of any element in the periodic table. The EA of fluorine is –322 kJ/mol. When we add an electron to a fluorine atom to form a fluoride anion (F^-), we add an electron to the $n = 2$ shell. The electron is attracted to the nucleus, but there is also significant repulsion from the other electrons already present in this small valence shell. The chlorine atom has the same electron configuration in the valence shell, but because the entering electron is going into the $n = 3$ shell, it occupies a considerably larger region of space and the electron–electron repulsions are reduced. The entering electron does not experience as much repulsion and the chlorine atom accepts an additional electron more readily.

The properties discussed in this unit (size of atoms and ions, effective nuclear charge, ionization energies, and electron affinities) are central to understanding chemical reactivity. For example, because fluorine has an energetically favorable EA and a large energy barrier to ionization (IE), it is much easier to form fluorine anions than cations.



***Video* 2.4.2**: *An overview of electron effinity.*

Trends in Metallic and Nonmetallic Character

In this course thusfar (and in the previous course), we have seen that metals are on the left side of the periodic table while nonmetals are generally on the right (exception: Hydrogen). We can classify the metallic character of all the elements with trends similar to those we've previous examined in this unit. Metallic character has the opposite trend of ionization energy and electronegativity, but is similar to the trend we saw for atomic radius: it INCREASES as you move from right to left across rows of the periodic table and INCREASES as you move down columns. This trend does not necessarily apply to transition metals. Figure **2.4.2** shows this trend as well as the others we've discussed in Unit 3.

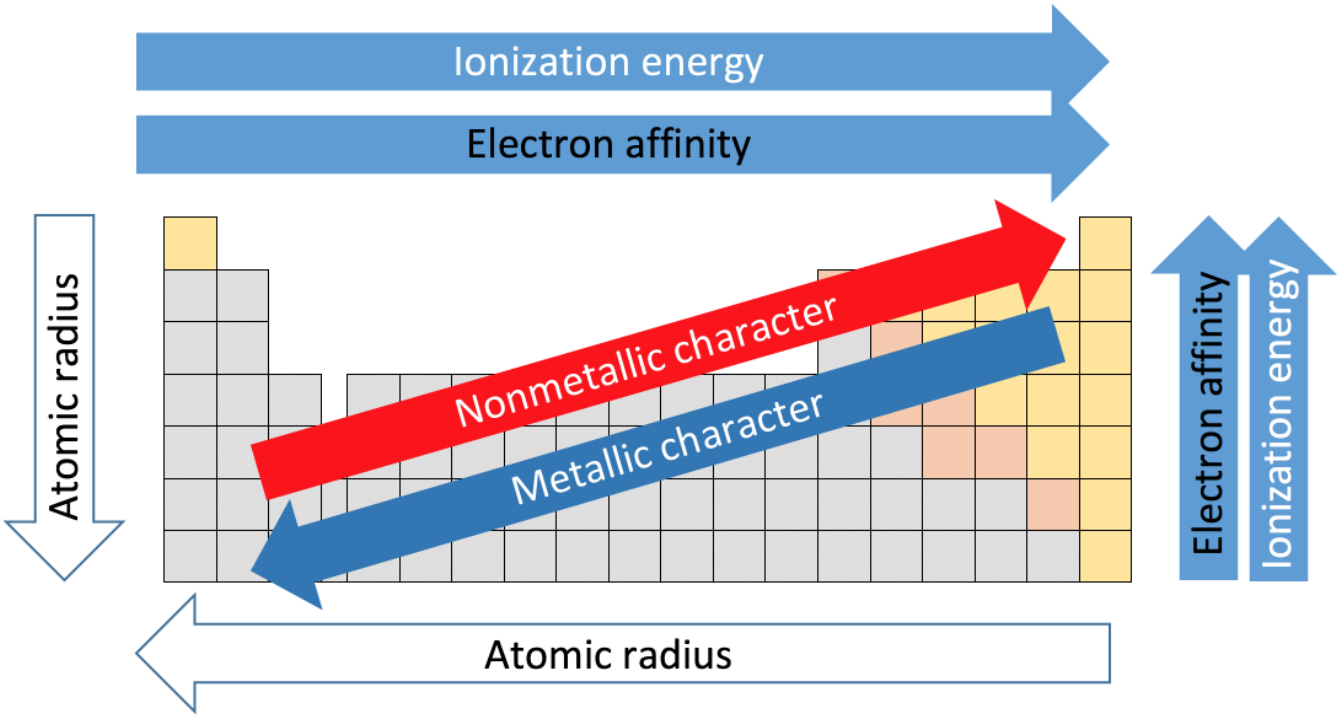


***Figure* 2.4.2:** *Metallic character increases as you go from right to left on periods and move down groups on the periodic table. The gray squares represent metals, the orange squares are "metalloids" and the yellow squares are nonmetals.*

Credit: "Various Periodic Trends" by Sandbh is licensed under CC BY-SA 4.0

Metallic properties including conductivity and malleability (the ability to be formed into sheets) depend on having electrons that can be removed easily. Thus, metallic character increases as we move down a group and decreases across a period in the same trend observed for atomic size because it is easier to remove an electron that is farther away from the nucleus.

Summary

Electron affinity (the energy associated with forming an anion) is more favorable (exothermic) when electrons are placed into lower energy orbitals, closer to the nucleus. Therefore, electron affinity becomes increasingly negative as we move left to right across the periodic table and decreases as we move down a group. For both IE and electron affinity data, there are exceptions to the trends when dealing with completely filled or half-filled subshells. Metallic character increases from right to left across periods on the periodic table and down columns.

Glossary

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

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2.4.1: Trends in Electron Affinity and Metallic Character (Problems)

PROBLEM 2.4.1.1

Based on their positions in the periodic table, predict which has the largest electron affinity: Mg, Ba, B, O, Te.

Answer

O

PROBLEM 2.4.1.2

Based on their positions in the periodic table, predict which has the smallest electron affinity: Li, Cs, N, F, I.

Answer

Cs

PROBLEM 2.4.1.3

Based on their positions in the periodic table, rank the following atoms in order of increasing electron affinity: F, Li, N, Rb.

Answer

Rb < Li < N < F

PROBLEM 2.4.1.4

Based on their positions in the periodic table, rank the following atoms or compounds in order of increasing electron affnity: Mg, O, S, Si

Answer

S < Si < Mg < O

PROBLEM 2.4.1.5

Based on their positions in the periodic table, rank the following atoms in order of increasing metallic character: F, Li, N, Rb.

Answer

F < N < Li < Rb

PROBLEM 2.4.1.6

Based on their positions in the periodic table, predict which is the most metallic element: Mg, Ba, B, O, Te.

Answer

Ba

PROBLEM 2.4.1.7

Based on their positions in the periodic table, predict which is the most nonmetallic element: Li, Cs, N, F, I.

Answer

F

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CHAPTER OVERVIEW

3: Lewis Structures

Unit Objectives

- Explain the formation of cations, anions, and ionic compounds
- Predict the charge of common metallic and nonmetallic elements, and write their electron configurations
- Describe the formation of covalent bonds
- Define electronegativity and assess the polarity of covalent bonds
- Write Lewis symbols for neutral atoms and ions
- Draw Lewis structures depicting the bonding in simple molecules
- Compute formal charges for atoms in any Lewis structure
- Use formal charges to identify the most reasonable Lewis structure for a given molecule
- Identify the oxidation states of atoms in Lewis structures

3.1: Bond Types

3.1.1: Bond Types (Problems)

3.2: Lewis Dot Diagrams

3.2.1: Lewis Dot Diagrams (Problems)

3.3: Lewis Structures

3.3.1: Lewis Structures (Problems)

3.4: Formal Charge

3.4.1: Formal Charge and Oxidation State (Problems)

3.5: Electronegativity and Polarity

3.5.1: Electronegativity and Polarity (Problems)

3.6: Bond Strength

3.6.1: Bond Strength (Problems)

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3.1: Bond Types

5.1: Bond Types

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3.1.1: Bond Types (Problems)

4.1: Bond Types (Problems)

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3.2: Lewis Dot Diagrams

Skills to Develop

- Write Lewis symbols for neutral atoms and ions

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 3.2.1 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 3.2.1**: 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 3.2.2 demonstrates the use of Lewis symbols to show the transfer of electrons during the formation of ionic compounds.

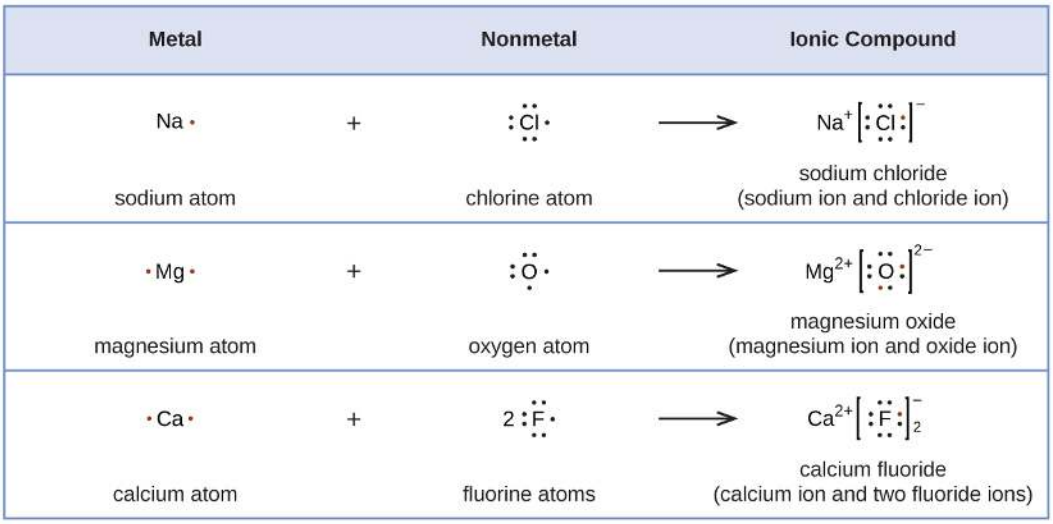


***Figure* 3.2.2**: *Cations are formed when atoms lose electrons, represented by fewer Lewis dots, whereas anions are formed by atoms gaining electrons. The total number of electrons does not change.*

Summary

Valence electronic structures can be visualized by drawing Lewis symbols (for atoms and monatomic ions) . Lone pairs, unpaired electrons, and single, double, or triple bonds are used to indicate where the valence electrons are located around the atom.

Glossary

Lewis symbol

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

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3.2.1: Lewis Dot Diagrams (Problems)

PROBLEM 3.2.1.1

Write the Lewis symbols for each of the following ions:

a. As^{3-}
b. I^{-}
c. Be^{2+}
d. O^{2-}
e. Ga^{3+}
f. Li^{+}
g. N^{3-}

Answer a

eight electrons:



Answer b

eight electrons:



Answer c

no electrons

Be^{2+}

Answer d

eight electrons:



Answer e

no electrons

Ga^{3+}

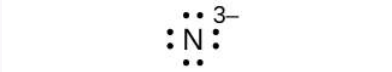
Answer f

no electrons

Li^{+}

Answer g

eight electrons:



PROBLEM 3.2.1.2

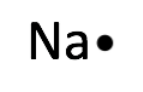
Write the Lewis symbols for the following elements:

a. Cl
b. Na
c. Mg
d. Ca
e. K
f. Br
g. Sr
h. F

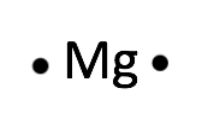
Answer a



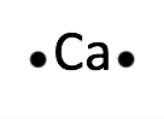
Answer b



Answer c



Answer d



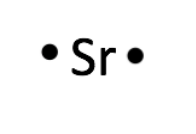
Answer e



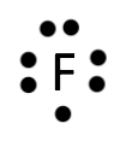
Answer f



Answer g



Answer h

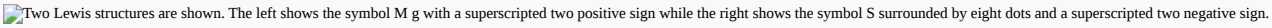


PROBLEM 3.2.1.3

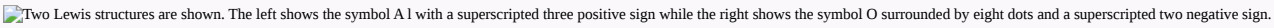
Write the Lewis symbols of the ions in each of the following ionic compounds and the Lewis symbols of the atom from which they are formed:

a. MgS
b. Al_2O_3
c. $GaCl_3$
d. K_2O
e. Li_3N
f. KF

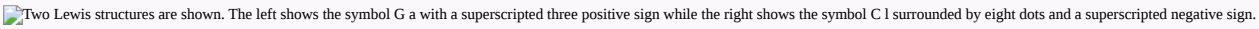
Answer a



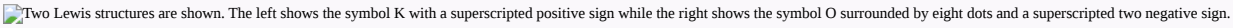
Answer b



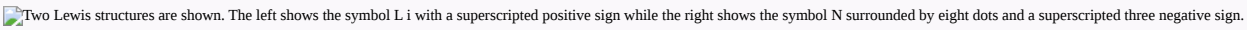
Answer c



Answer d



Answer e



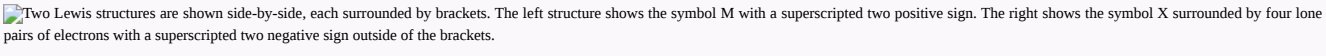
Answer f



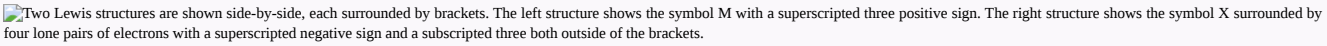
PROBLEM 3.2.1.4

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

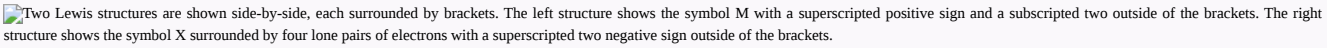
(a)



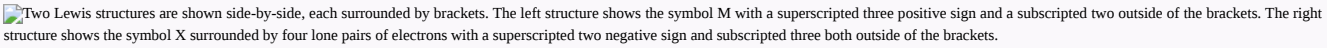
(b)



(c)



(d)



Answer a

MgS

Answer b

$AlCl_3$

Answer c

Na_2S

Answer d

Al_2S_3

PROBLEM 3.2.1.5

Identify the atoms that correspond to each of the following electron configurations.

a. $1s^2 2s^2 2p^5$
b. $1s^2 2s^2 2p^6 3s^2$
c. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^4$
d. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^1$

Answer a

F

Answer b

Mg

Answer c

Se

Answer d

Ga

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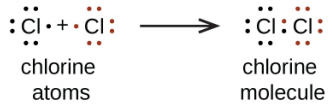
3.3: Lewis Structures

Skills to Develop

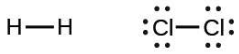
- Draw Lewis structures depicting the bonding in simple molecules

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:

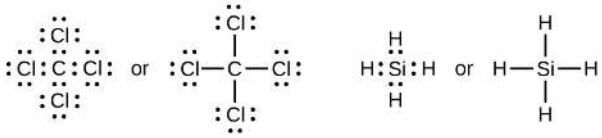


In the Lewis model, a single shared pair of electrons is a single bond. Each Cl atom interacts with eight valence electrons total: the six in the lone pairs and the two in the single bond.

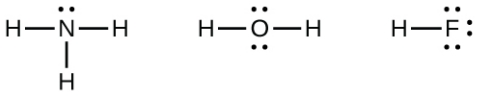
The Octet Rule

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. 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.

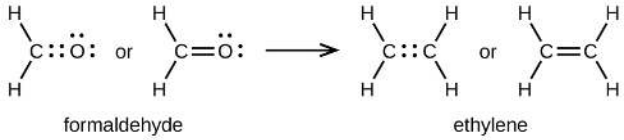


Group 15 elements such as nitrogen have five valence electrons in the atomic Lewis symbol: one lone pair and three unpaired electrons. To obtain an octet, these atoms form three covalent bonds, as in NH_3 (ammonia). Oxygen and other atoms in group 16 obtain an octet by forming two covalent bonds:



Double and Triple Bonds

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

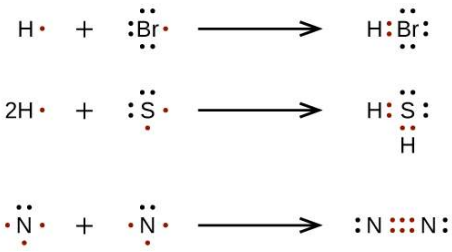


A triple bond forms when three electron pairs are shared by a pair of atoms, as in carbon monoxide (CO) and the cyanide ion (CN^-):



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).
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:

$$\mathrm{SiH_4} \tag{3.3.1}$$
$$\mathrm{Si:\ 4\ valence\ electrons/atom \times 1\ atom = 4} \tag{3.3.2}$$
$$\mathrm{+H:\ 1\ valence\ electron/atom \times 4\ atoms = 4} \tag{3.3.3}$$
$$\mathrm{= 8\ valence\ electrons} \tag{3.3.4}$$

   - 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):

$$\mathbf{CHO_2^-}$$

$$\begin{aligned}\mathbf{C:\ 4\ valence\ electrons/atom \times 1\ atom} &= \mathbf{4}\\ \mathbf{H:\ 1\ valence\ electron/atom \times 1\ atom} &= \mathbf{1}\\ \mathbf{O:\ 6\ valence\ electrons/atom \times 2\ atoms} &= \mathbf{12}\\ \mathbf{+\quad 1\ additional\ electron} &= \mathbf{1}\\ &= \mathbf{18\ valence\ electrons}\end{aligned}$$

- 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:

$$\mathbf{NO^+}$$

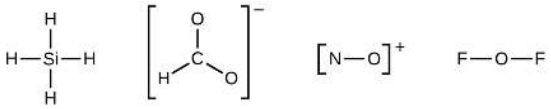
$$\begin{aligned}\mathbf{N:\ 5\ valence\ electrons/atom \times 1\ atom} &= \mathbf{5}\\ \mathbf{O:\ 6\ valence\ electron/atom \times 1\ atom} &= \mathbf{6}\\ \mathbf{+\ -1\ electron\ (positive\ charge)} &= \mathbf{-1}\\ &= \mathbf{10\ valence\ electrons}\end{aligned}$$

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

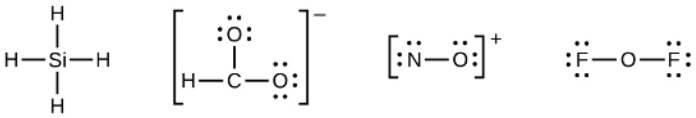
$$\mathbf{OF_2}$$

$$\begin{aligned}\mathbf{O:\ 6\ valence\ electrons/atom \times 1\ atom} &= \mathbf{6}\\ \mathbf{+\ F:\ 7\ valence\ electrons/atom \times 2\ atoms} &= \mathbf{14}\\ &= \mathbf{20\ valence\ electrons}\end{aligned}$$

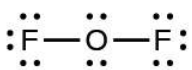
2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom and connecting each atom to the central atom with a single (one electron pair) bond. (Note that we denote ions with brackets around the structure, indicating the charge outside the brackets:)



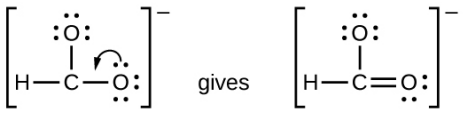
3. When several arrangements of atoms are possible, as for $\mathbf{CHO_2^-}$, we must use experimental evidence to choose the correct one. In general, the less electronegative elements are more likely to be central atoms. In $\mathbf{CHO_2^-}$, the less electronegative carbon atom occupies the central position with the oxygen and hydrogen atoms surrounding it. Other examples include P in $POCl_3$, S in SO_2, and Cl in $\mathbf{ClO_4^-}$. An exception is that hydrogen is almost never a central atom. As the most electronegative element, fluorine also cannot be a central atom.
4. 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:



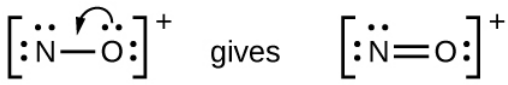
5. Place all remaining electrons on the central atom.
   - For SiH_4, $\mathbf{CHO_2^-}$, and NO^+, there are no remaining electrons; we already placed all of the electrons determined in Step 1.
   - For OF_2, we had 16 electrons remaining in Step 3, and we placed 12, leaving 4 to be placed on the central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



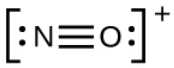
6. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.
   - SiH_4: Si already has an octet, so nothing needs to be done.
   - $\mathbf{CHO_2^-}$: We have distributed the valence electrons as lone pairs on the oxygen atoms, 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 3.3.1: Writing Lewis Structures

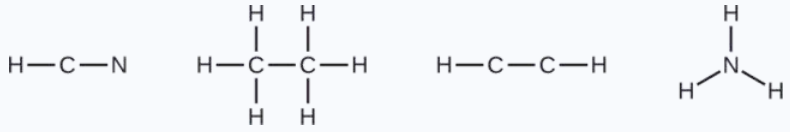
NASA's Cassini-Huygens mission detected a large cloud of toxic hydrogen cyanide (HCN) on Titan, one of Saturn's moons. Titan also contains ethane (H_3CCH_3), acetylene (HCCH), and ammonia (NH_3). What are the Lewis structures of these molecules?

Solution

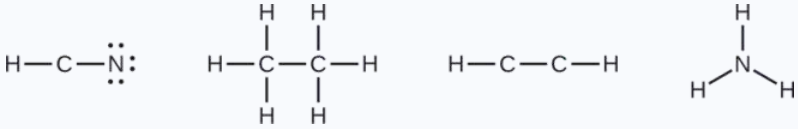
Calculate the number of valence electrons.

- 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:

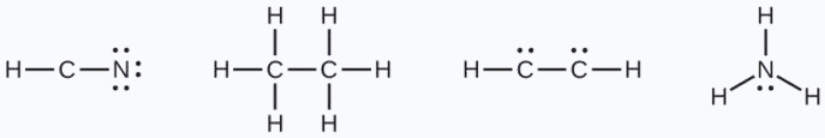


Where needed, distribute electrons to the terminal atoms:



- 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:

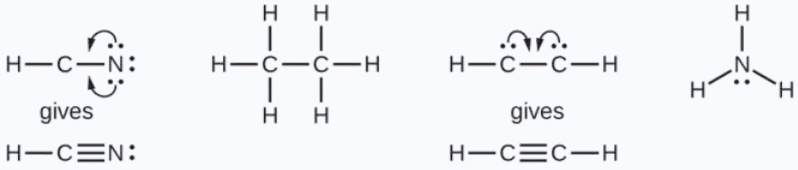


- HCN: no electrons remain

- 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 3.3.1

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.

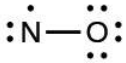
Odd-electron Molecules

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.

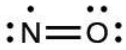
To draw the Lewis structure for an odd-electron molecule like NO, we follow the same five steps we would for other molecules, but with a few minor changes:

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:

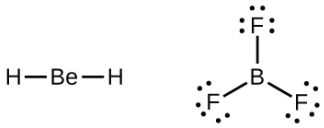


4. *Place all remaining electrons on the central atom*. Since there are no remaining electrons, this step does not apply.
5. *Rearrange the electrons to make multiple bonds with the central atom in order to obtain octets wherever possible.* We know that an odd-electron molecule cannot have an octet for 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:)

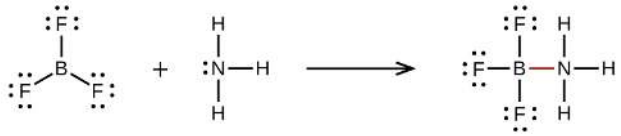


Electron-deficient Molecules

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 because they have only four valence orbitals (one 2*s* and three 2*p* orbitals). Elements in the third and higher periods ($n \geq 3$) have more than four valence orbitals and can share more than four pairs of electrons with other atoms because they have empty *d* orbitals in the same shell. Molecules formed from these elements are sometimes called hypervalent molecules.Table **3.3.5** shows the Lewis structures for two hypervalent molecules, PCl_5 and SF_6.

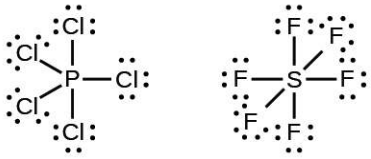
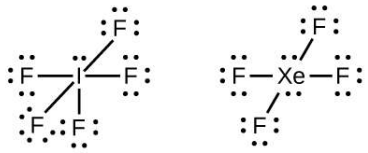


Table* 3.3.5*: *In PCl_5, the central atom phosphorus shares five pairs of electrons. In SF_6, sulfur shares six pairs of electrons.*

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



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

Example 3.3.2: Octet Rule Violations

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

Solution

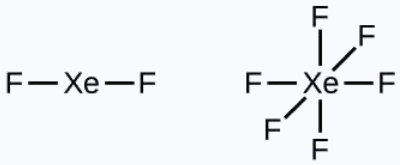
We can draw the Lewis structure of any covalent molecule by following the six steps discussed earlier. In this case, we can condense the last few steps, since not all of them apply.

Step 1: Calculate the number of valence electrons:

$\mathbf{XeF_2}$: $8 + (2 \times 7) = 22$

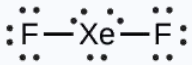
$\mathbf{XeF_6}$: $8 + (6 \times 7) = 50$

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

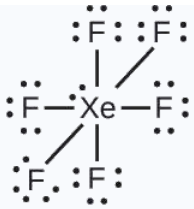


Step 3: Distribute the remaining electrons.

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:



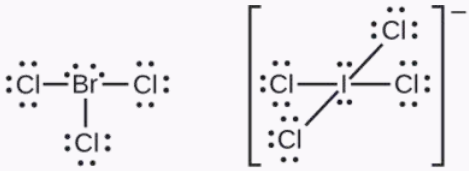
XeF_6: We place three lone pairs of electrons around each F atom, accounting for 36 electrons. Two electrons remain, and this lone pair is placed on the Xe atom:



Exercise 3.3.2: interhalogens

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

Answer



Summary



Video* 3.3.1: Need more help with Lewis Structures? This video provides a great explanation!*

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.

Glossary

double bond

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

free radical

molecule that contains an odd number of electrons

hypervalent molecule

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

Lewis structure

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

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

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

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

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

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

Contributors

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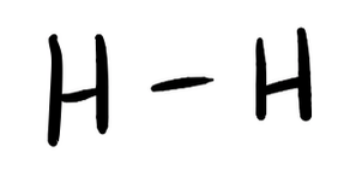
3.3.1: Lewis Structures (Problems)

PROBLEM 3.3.1.1

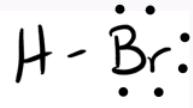
Write Lewis structures for the following: (please note, none of the solutions are using the expanded octet rule or formal charges)

a. H_2
b. HBr
c. PCl_3
d. SF_2
e. H_2CCH_2
f. HNNH
g. H_2CNH
h. NO^-
i. N_2
j. CO
k. CN^-

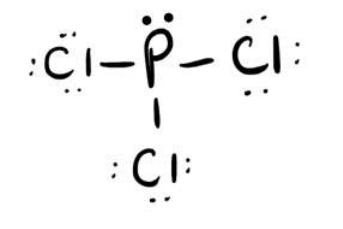
Answer a



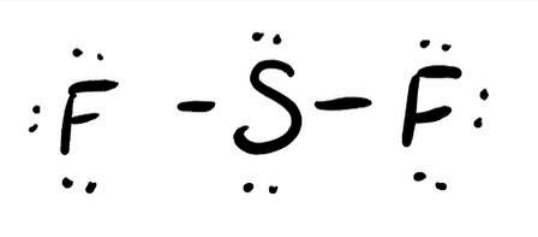
Answer b



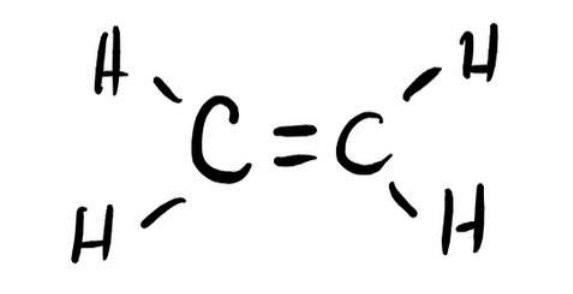
Answer c



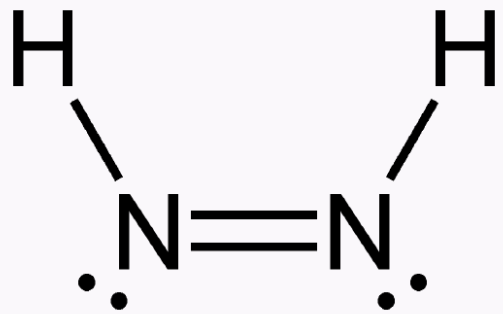
Answer d



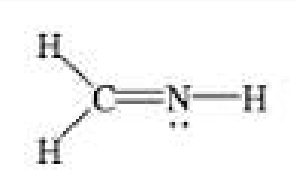
Answer e



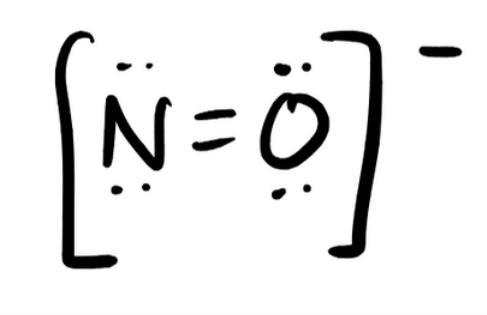
Answer f



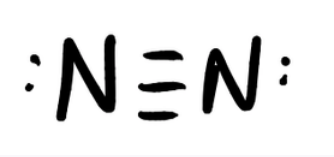
Answer g



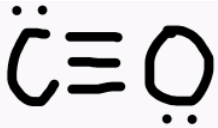
Answer h



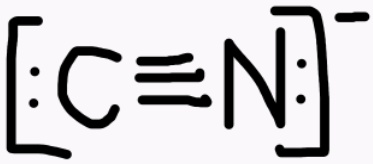
Answer i



Answer j



Answer k



PROBLEM 3.3.1.2

Write Lewis structures for the following: (please note, none of the solutions are using the expanded octet rule or formal charges)

a. O_2
b. H_2CO
c. ClNO
d. $SiCl_4$
e. H_3O^+
f. $\mathbf{NH_4^+}$
g. $\mathbf{BF_4^-}$
h. HCCH
i. ClCN
j. $\mathbf{C_2^{2+}}$

Answer a

A Lewis structure shows two oxygen atoms double bonded together, and each has two lone pairs of electrons.

Answer b

A Lewis structure shows a carbon atom that is single bonded to two hydrogen atoms and double bonded to an oxygen atom. The oxygen atom has two lone pairs of electrons.

Answer c

A Lewis structure shows a nitrogen atom with a lone pair of electrons single bonded to a chlorine atom that has three lone pairs of electrons. The nitrogen is also double bonded to an oxygen which has two lone pairs of electrons.

Answer d

A Lewis structure shows a silicon atom that is single bonded to four chlorine atoms. Each chlorine atom has three lone pairs of electrons.

Answer e

A Lewis structure shows an oxygen atom with a lone pair of electrons single bonded to three hydrogen atoms. The structure is surrounded by brackets with a superscripted positive sign.

Answer f

A Lewis structure shows a nitrogen atom single bonded to four hydrogen atoms. The structure is surrounded by brackets with a superscripted positive sign.

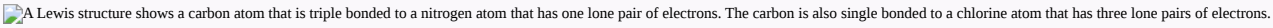
Answer g

A Lewis structure shows a boron atom single bonded to four fluorine atoms. Each fluorine atom has three lone pairs of electrons. The structure is surrounded by brackets with a superscripted negative sign.

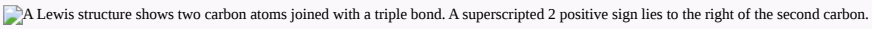
Answer h

A Lewis structure shows two carbon atoms that are triple bonded together. Each carbon is also single bonded to a hydrogen atom.

Answer i



Answer j

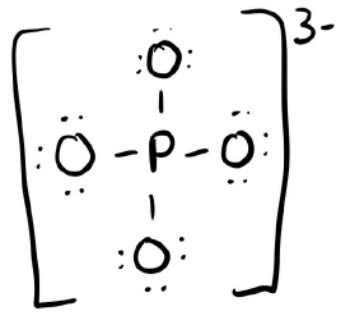


PROBLEM 3.3.1.3

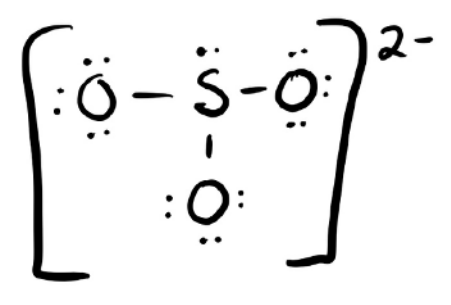
Write Lewis structures for: (please note, none of the solutions are using the expanded octet rule or formal charges)

a. PO_4^{3-}
c. SO_3^{2-}
d. HONO

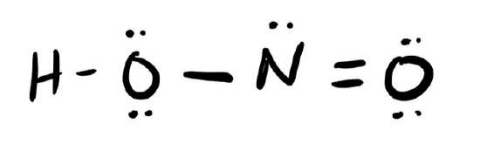
Answer a



Answer b



Answer c



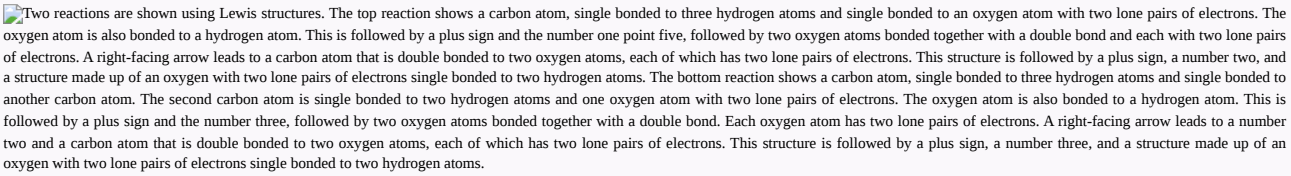
Click here to see a video of the solution



PROBLEM 3.3.1.4

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

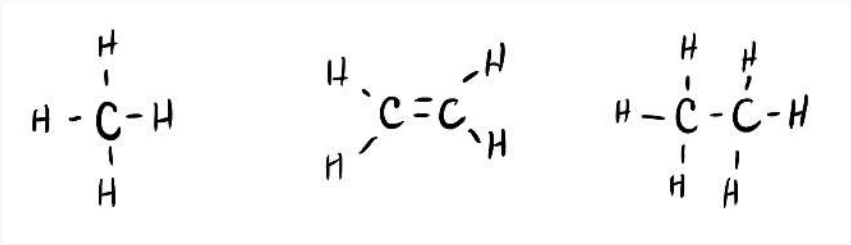
Answer

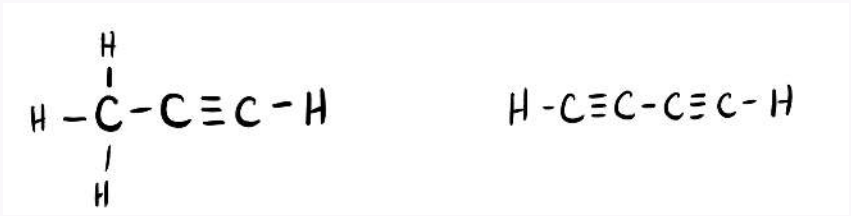

Two reactions are shown using Lewis structures. The top reaction shows a carbon atom, single bonded to three hydrogen atoms and single bonded to an oxygen atom with two lone pairs of electrons. The oxygen atom is also bonded to a hydrogen atom. This is followed by a plus sign and the number one point five, followed by two oxygen atoms bonded together with a double bond and each with two lone pairs of electrons. A right-facing arrow leads to a carbon atom that is double bonded to two oxygen atoms, each of which has two lone pairs of electrons. This structure is followed by a plus sign, a number two, and a structure made up of an oxygen with two lone pairs of electrons single bonded to two hydrogen atoms. The bottom reaction shows a carbon atom, single bonded to three hydrogen atoms and single bonded to another carbon atom. The second carbon atom is single bonded to two hydrogen atoms and one oxygen atom with two lone pairs of electrons. The oxygen atom is also bonded to a hydrogen atom. This is followed by a plus sign and the number three, followed by two oxygen atoms bonded together with a double bond. Each oxygen atom has two lone pairs of electrons. A right-facing arrow leads to a number two and a carbon atom that is double bonded to two oxygen atoms, each of which has two lone pairs of electrons. This structure is followed by a plus sign, a number three, and a structure made up of an oxygen with two lone pairs of electrons single bonded to two hydrogen atoms.

PROBLEM 3.3.1.5

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

Answer





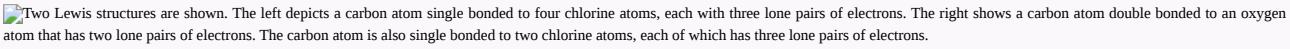
Click here to see a video of the solution



PROBLEM 3.3.1.6

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

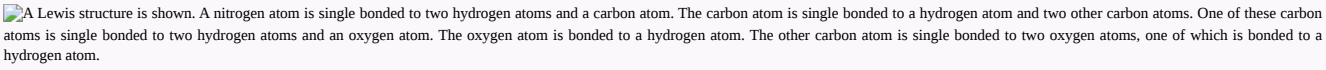
Answer


Two Lewis structures are shown. The left depicts a carbon atom single bonded to four chlorine atoms, each with three lone pairs of electrons. The right shows a carbon atom double bonded to an oxygen atom that has two lone pairs of electrons. The carbon atom is also single bonded to two chlorine atoms, each of which has three lone pairs of electrons.

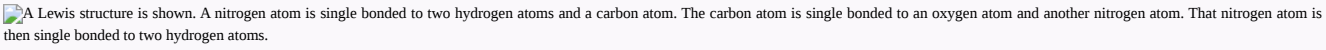
PROBLEM 3.3.1.7

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

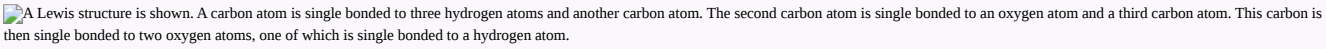
a. the amino acid serine:


A Lewis structure is shown. A nitrogen atom is single bonded to two hydrogen atoms and a carbon atom. The carbon atom is single bonded to a hydrogen atom and two other carbon atoms. One of these carbon atoms is single bonded to two hydrogen atoms and an oxygen atom. The oxygen atom is bonded to a hydrogen atom. The other carbon atom is single bonded to two oxygen atoms, one of which is bonded to a hydrogen atom.

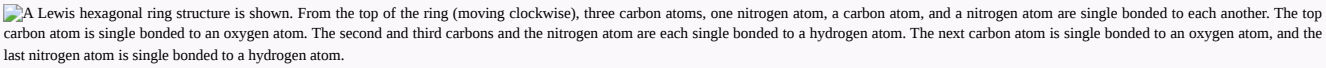
b. urea:


A Lewis structure is shown. A nitrogen atom is single bonded to two hydrogen atoms and a carbon atom. The carbon atom is single bonded to an oxygen atom and another nitrogen atom. That nitrogen atom is then single bonded to two hydrogen atoms.

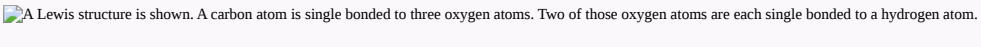
c. pyruvic acid:


A Lewis structure is shown. A carbon atom is single bonded to three hydrogen atoms and another carbon atom. The second carbon atom is single bonded to an oxygen atom and a third carbon atom. This carbon is then single bonded to two oxygen atoms, one of which is single bonded to a hydrogen atom.

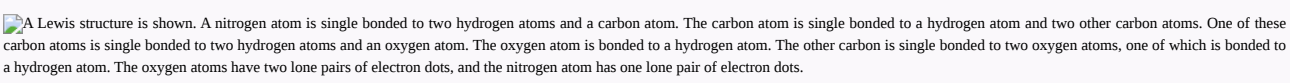
d. uracil:


A Lewis hexagonal ring structure is shown. From the top of the ring (moving clockwise), three carbon atoms, one nitrogen atom, a carbon atom, and a nitrogen atom are single bonded to each another. The top carbon atom is single bonded to an oxygen atom. The second and third carbons and the nitrogen atom are each single bonded to a hydrogen atom. The next carbon atom is single bonded to an oxygen atom, and the last nitrogen atom is single bonded to a hydrogen atom.

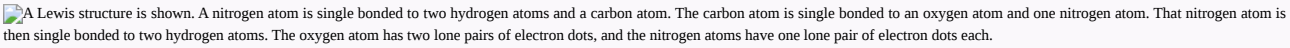
e. carbonic acid:


A Lewis structure is shown. A carbon atom is single bonded to three oxygen atoms. Two of those oxygen atoms are each single bonded to a hydrogen atom.

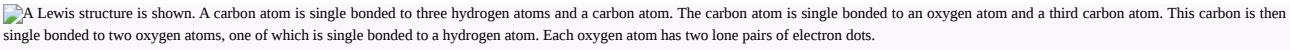
Answer a


A Lewis structure is shown. A nitrogen atom is single bonded to two hydrogen atoms and a carbon atom. The carbon atom is single bonded to a hydrogen atom and two other carbon atoms. One of these carbon atoms is single bonded to two hydrogen atoms and an oxygen atom. The oxygen atom is bonded to a hydrogen atom. The other carbon is single bonded to two oxygen atoms, one of which is bonded to a hydrogen atom. The oxygen atoms have two lone pairs of electron dots, and the nitrogen atom has one lone pair of electron dots.

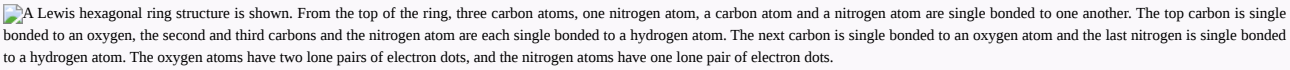
Answer b


A Lewis structure is shown. A nitrogen atom is single bonded to two hydrogen atoms and a carbon atom. The carbon atom is single bonded to an oxygen atom and one nitrogen atom. That nitrogen atom is then single bonded to two hydrogen atoms. The oxygen atom has two lone pairs of electron dots, and the nitrogen atoms have one lone pair of electron dots each.

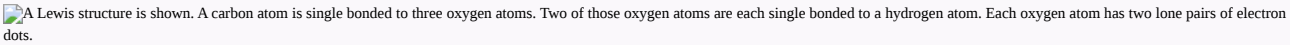
Answer c



Answer d



Answer e



PROBLEM 3.3.1.8

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

Answer

Each bond includes a sharing of electrons between atoms. Two electrons are shared in a single bond; four electrons are shared in a double bond; and six electrons are shared in a triple bond.

Contributors

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- Adelaide Clark, Oregon Institute of Technology

Feedback

Think one of the answers above is wrong? Let us know here.

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3.4: Formal Charge

Skills to Develop

- Compute formal charges for atoms in any Lewis structure
- Use formal charges to identify the most reasonable Lewis structure for a given molecule
- Identify the oxidation states of atoms in Lewis structures

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. But first, let's introduce a concept we will refer back to frequently for the rest of this term: **electronegativity.**

Electronegativity

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

Figure 3.4.1 shows the electronegativity values of the elements as proposed by one of the most famous chemists of the twentieth century: Linus Pauling. In general, electronegativity increases from left to right across a period in the periodic table and decreases down a group. Thus, the nonmetals, which lie in the upper right, tend to have the highest electronegativities, with fluorine the most electronegative element of all (EN = 4.0). Metals tend to be less electronegative elements, and the group 1 metals have the lowest electronegativities. Note that noble gases are excluded from this figure because these atoms usually do not share electrons with others atoms since they have a full valence shell. (While noble gas compounds such as XeO_2 do exist, they can only be formed under extreme conditions, and thus they do not fit neatly into the general model of electronegativity.)

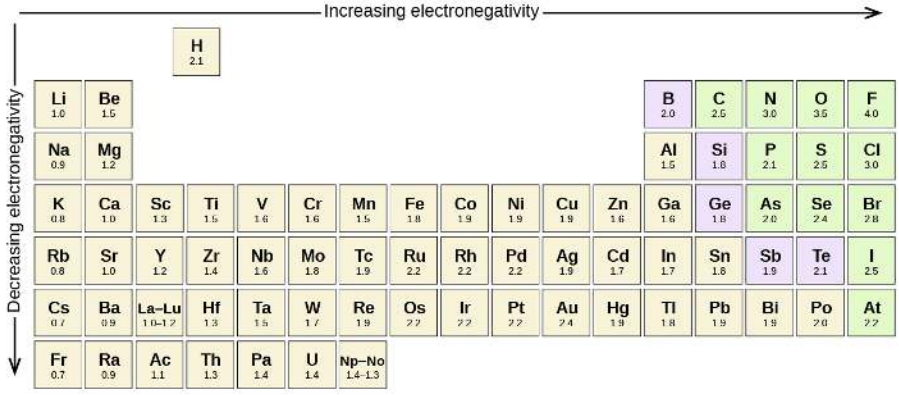


Figure* 3.4.1*: *The electronegativity values derived by Pauling follow predictable periodic trends with the higher electronegativities toward the upper right of the periodic table.*

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:

Misplaced '#'

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

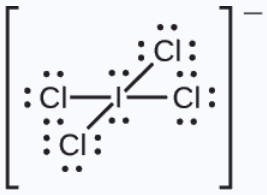
We must remember that the formal charge calculated for an atom is not the *actual* charge of the atom in the molecule. Formal charge is only a useful bookkeeping procedure; it does not indicate the presence of actual charges.

Example 3.4.1: 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 3.4.1

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



Answer

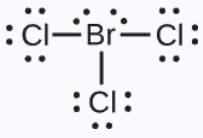
C −1, O +1

Example 3.4.2: 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

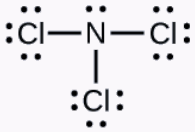
All atoms in $BrCl_3$ have a formal charge of zero, and the sum of the formal charges totals zero, as it must in a neutral molecule.

Exercise 3.4.2

Determine the formal charge for each atom in NCl_3.

Answer

N: 0; all three Cl atoms: 0





Video* 3.4.1*: *A video overview on calculating formal charges.*

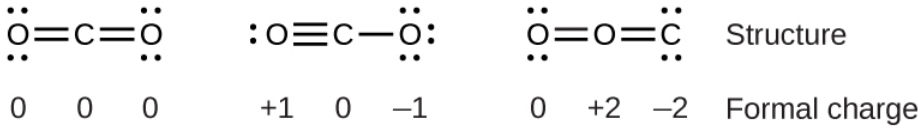
Using Formal Charge to Predict Molecular Structure

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

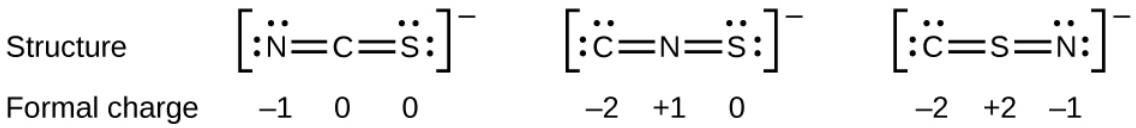
1. A molecular structure in which all formal charges are zero is preferable to one in which some formal charges are not zero.
2. If the Lewis structure must have nonzero formal charges, the arrangement with the smallest nonzero formal charges is preferable.
3. Lewis structures are preferable when adjacent 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:



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).

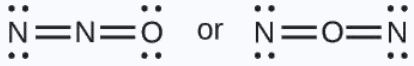
As another example, the thiocyanate ion, an ion formed from a carbon atom, a nitrogen atom, and a sulfur atom, could have three different molecular structures: CNS^-, NCS^-, or CSN^-. The formal charges present in each of these molecular structures can help us pick the most likely arrangement of atoms.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



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 3.4.3: Using Formal Charge to Determine Molecular Structure

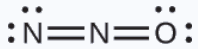
Nitrous oxide, N_2O, commonly known as laughing gas, is used as an anesthetic in minor surgeries, such as the routine extraction of wisdom teeth. Which is the likely structure for nitrous oxide?



Solution Determining formal charge yields the following:



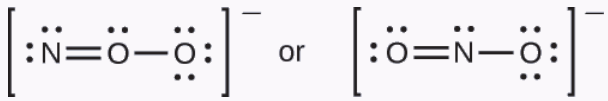
The structure with a terminal oxygen atom best satisfies the criteria for the most stable distribution of formal charge:



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 3.4.3

Which is the most likely molecular structure for the nitrite (NO_2^-) ion?



Answer

ONO^-

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.

Key Equations

- Misplaced '#'

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

Contributors

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- Ed Vitz (Kutztown University), John W. Moore (UW-Madison), Justin Shorb (Hope College), Xavier Prat-Resina (University of Minnesota Rochester), Tim Wendorff, and Adam Hahn.
- Adelaide Clark, Oregon Institute of Technology
- Wayne Breslyn (video 1)

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3.4.1: Formal Charge and Oxidation State (Problems)

PROBLEM 3.4.1.1

Determine the formal charge and oxidation state of each element in the following:

a. HCl
b. CF_4
c. PCl_3

Answer a

FC: H: 0, Cl: 0

OX: H: +1, Cl: -1

Answer b

FC: C: 0, F: 0

OX: C: +4, F: -1

Answer c

FC: P: 0, Cl: 0

OX: P: +3, Cl: -1

PROBLEM 3.4.1.2

Determine the formal charge and oxidation state of each element in the following:

a. H_3O^+
b. SO_4^{2-}
c. NH_3
d. O_2^{2-}
e. H_2O_2

Answer a

FC: H: 0, O: +1

OX: H: +1, O: -2

Answer b

FC: S: +2, O: -1

OX: S: +6, O: -2

Answer c

FC: N: 0, H: 0

OX: N: -3, H: +1

Answer d

FC: -1

OX: -1

Answer e

FC: O: 0, H: 0

OX: O: -1, H: +1

Click here to see a video of the solution



PROBLEM 3.4.1.3

Calculate the formal charge and oxidation state of chlorine in the molecules Cl_2 and CCl4.

Answer

FC: Cl in Cl_2: 0; Cl in CCl_4: 0

OX: Cl in Cl_2: 0; Cl in CCl_4: -1

PROBLEM 3.4.1.4

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

a. F_2CO
b. NO^-
c. $\mathbf{BF_4^-}$
d. $\mathbf{SnCl_3^-}$
e. H_2CCH_2
f. $\mathbf{PO_4^{3-}}$

Answer a

FC: C: 0, F :0, O: 0

OX: C: +4, F: -1, O: -2

Answer b

FC: N: -1, O: 0

OX: N: +1, O: -2

Answer c

FC: B: -1, F: 0

OX: B: +3, F: -1

Answer d

FC: Sn: -1; Cl: 0

OX: Sn: +2, Cl: -1

Answer e

FC: C: 0, H: 0

OX: C: -2, H: +1

Answer f

FC: P: +1, O: -1

OX: P: +5, O: -2

PROBLEM 3.4.1.5

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

Answer

ClNO

Click here to see a video of the solution



PROBLEM 3.4.1.6

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

Answer

HOCl

PROBLEM 3.4.1.7

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

Answer

OSO

Click here to see a video of the solution

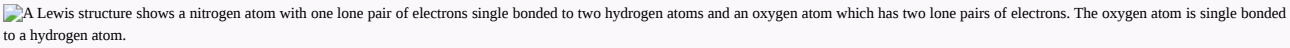


PROBLEM 3.4.1.8

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

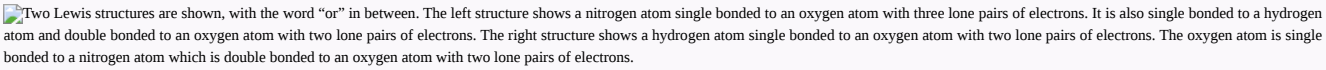
Answer

The structure that gives zero formal charges is consistent with the actual structure:



PROBLEM 3.4.1.9

Which of the following structures would we expect for nitrous acid? Determine the formal charges:



Answer

The first structure is the best structure. the formal charges are closest to 0 (and also the second structure does not give a complete octet on N)

Contributors

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3.5: Electronegativity and Polarity

Skills to Develop

- Define electronegativity and assess the polarity of covalent bonds



Video* 3.5.1*: *A preview of electronegativity's role in molecular polarity.*

Electronegativity Review

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

Figure **3.5.1** shows the electronegativity values of the elements as proposed by one of the most famous chemists of the twentieth century: Linus Pauling. In general, electronegativity increases from left to right across a period in the periodic table and decreases down a group. Thus, the nonmetals, which lie in the upper right, tend to have the highest electronegativities, with fluorine the most electronegative element of all (EN = 4.0). Metals tend to be less electronegative elements, and the group 1 metals have the lowest electronegativities. Note that noble gases are excluded from this figure because these atoms usually do not share electrons with others atoms since they have a full valence shell. (While noble gas compounds such as XeO_2 do exist, they can only be formed under extreme conditions, and thus they do not fit neatly into the general model of electronegativity.)

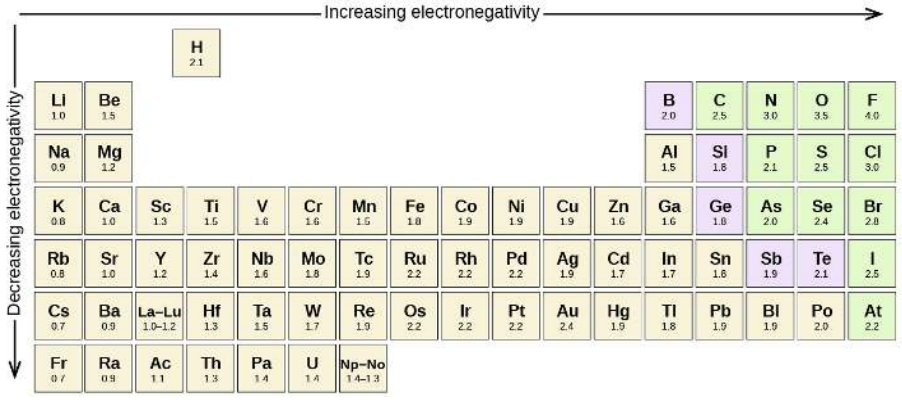


Figure* 3.5.1*: *The electronegativity values derived by Pauling follow predictable periodic trends with the higher electronegativities toward the upper right of the periodic table.*

Linus Pauling

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

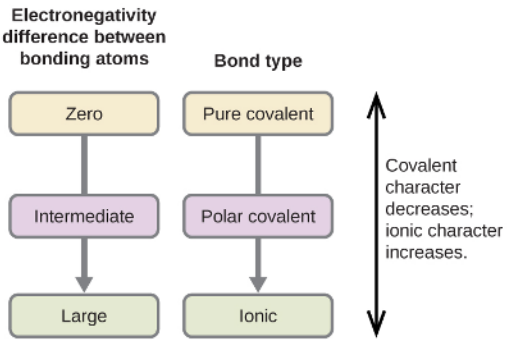
Pauling also contributed to many other fields besides chemistry. His research on sickle cell anemia revealed the cause of the disease—the presence of a genetically inherited abnormal protein in the blood—and paved the way for the field of molecular genetics. His work was also pivotal in curbing the testing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

Electronegativity versus Electron Affinity

We must be careful not to confuse electronegativity and electron affinity. The electron affinity of an element is a measurable physical quantity, namely, the energy released or absorbed when an isolated gas-phase atom acquires an electron, measured in kJ/mol. Electronegativity, on the other hand, describes how tightly an atom attracts electrons in a bond. It is a dimensionless quantity that is calculated, not measured. Pauling derived the first electronegativity values by comparing the amounts of energy required to break different types of bonds. He chose an arbitrary relative scale ranging from 0 to 4.

Electronegativity and Bond Type

The absolute value of the difference in electronegativity (ΔEN) of two bonded atoms provides a rough measure of the polarity to be expected in the bond and, thus, the bond type. When the difference is very small or zero, the bond is covalent and nonpolar. When it is large, the bond is polar covalent or ionic. The absolute values of the electronegativity differences between the atoms in the bonds H–H, H–Cl, and Na–Cl are 0 (nonpolar), 0.9 (polar covalent), and 2.1 (ionic), respectively. The degree to which electrons are shared between atoms varies from completely equal (pure covalent bonding) to not at all (ionic bonding). Figure **3.5.2** shows the relationship between electronegativity difference and bond type.



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

***Figure* 3.5.2:** *As the electronegativity difference increases between two atoms, the bond becomes more ionic.*

A rough approximation of the electronegativity differences associated with covalent, polar covalent, and ionic bonds is shown in Figure **3.5.4**. This table is just a general guide, however, with many exceptions. For example, the H and F atoms in HF have an electronegativity difference of 1.9, and the N and H atoms in NH_3 a difference of 0.9, yet both of these compounds form bonds that

are considered polar covalent. Likewise, the Na and Cl atoms in NaCl have an electronegativity difference of 2.1, and the Mn and I atoms in MnI_2 have a difference of 1.0, yet both of these substances form ionic compounds.

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

Some compounds contain both covalent and ionic bonds. The atoms in polyatomic ions, such as OH^-, $\mathbf{NO_3^-}$, and $\mathbf{NH_4^+}$, are held together by polar covalent bonds. However, these polyatomic ions form ionic compounds by combining with ions of opposite charge. For example, potassium nitrate, KNO_3, contains the K^+ cation and the polyatomic $\mathbf{NO_3^-}$ anion. Thus, bonding in potassium nitrate is ionic, resulting from the electrostatic attraction between the ions K^+ and $\mathbf{NO_3^-}$, as well as covalent between the nitrogen and oxygen atoms in $\mathbf{NO_3^-}$.

Example 3.5.1: Electronegativity and Bond Polarity

Bond polarities play an important role in determining the structure of proteins. Using the electronegativity values in ***Figure* 3.5.1**, arrange the following covalent bonds—all commonly found in amino acids—in order of increasing polarity. Then designate the positive and negative atoms using the symbols δ+ and δ–:

C–H, C–N, C–O, N–H, O–H, S–H

Solution

The polarity of these bonds increases as the absolute value of the electronegativity difference increases. The atom with the δ– designation is the more electronegative of the two. Table **3.5.1** shows these bonds in order of increasing polarity.

***Table* 3.5.1:** Bond Polarity and Electronegativity Difference

Bond	ΔEN	Polarity
C–H	0.4	$\overset{\delta-}{\mathbf{C}}-\overset{\delta+}{\mathbf{H}}$
S–H	0.4	$\overset{\delta-}{\mathbf{S}}-\overset{\delta+}{\mathbf{H}}$
C–N	0.5	$\overset{\delta+}{\mathbf{C}}-\overset{\delta-}{\mathbf{N}}$
N–H	0.9	$\overset{\delta-}{\mathbf{N}}-\overset{\delta+}{\mathbf{H}}$
C–O	1.0	$\overset{\delta+}{\mathbf{C}}-\overset{\delta-}{\mathbf{O}}$
O–H	1.4	$\overset{\delta-}{\mathbf{O}}-\overset{\delta+}{\mathbf{H}}$

Exercise 3.5.1

Silicones are polymeric compounds containing, among others, the following types of covalent bonds: Si–O, Si–C, C–H, and C–C. Using the electronegativity values in Figure **3.5.3**, arrange the bonds in order of increasing polarity and designate the positive and negative atoms using the symbols δ+ and δ–.

Answer

Bond	Electronegativity Difference	Polarity
C–C	0.0	nonpolar
C–H	0.4	$\overset{\delta-}{\mathbf{C}}-\overset{\delta+}{\mathbf{H}}$
Si–C	0.7	$\overset{\delta+}{\mathbf{Si}}-\overset{\delta-}{\mathbf{C}}$
Si–O	1.7	$\overset{\delta+}{\mathbf{Si}}-\overset{\delta-}{\mathbf{O}}$

Learn More



Video* 3.5.2*: *Water is a unique polar molecule.*

Summary



Video* 3.5.3*: *A review of electronegativity.*

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

Glossary

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

covalent bond
: bond formed when electrons are shared between atoms

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

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

pure covalent bond

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

Contributors

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3.5.1: Electronegativity and Polarity (Problems)

PROBLEM 3.5.1.1

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

a. Cl_2CO
b. MnO
c. NCl_3
d. $CoBr_2$
e. K_2S
f. CO
g. CaF_2
h. HI
i. CaO
j. IBr
k. CO_2

Answer a

covalent

Answer b

ionic

Answer c

covalent

Answer d

ionic

Answer e

ionic

Answer f

covalent

Answer g

ionic

Answer h

covalent

Answer i

ionic

Answer j

covalent

Answer k

covalent

PROBLEM 3.5.1.2

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

Answer

nonpolar covalent: electronegativity difference is less than 0.4 (nonmetal+nonmetal close together on the periodic table)

polar covalent: electronegativity difference in between 0.4 and 2.0 (nonmetal + nonmental further apart on the periodic table)

ionic: electronegativity difference is above 2.0 (metal + nonmetal)

PROBLEM 3.5.1.3

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

a. Br or Cl
b. N or O
c. S or O
d. P or S
e. Si or N
f. Ba or P
g. N or K

Answer a

Cl

Answer b

O

Answer c

O

Answer d

S

Answer e

N

Answer f

P

Answer g

N

PROBLEM 3.5.1.4

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

a. N or P
b. N or Ge
c. S or F
d. Cl or S
e. H or C
f. Se or P
g. C or Si

Answer a

N

Answer b

N

Answer c

F

Answer d

Cl

Answer e

C

Answer f

P

Answer g

C

PROBLEM 3.5.1.5

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

a. C, F, H, N, O
b. Br, Cl, F, H, I
c. F, H, O, P, S
d. Al, H, Na, O, P
e. Ba, H, N, O, As

Answer a

H, C, N, O, F

Answer b

H, I, Br, Cl, F

Answer c

H, P, S, O, F

Answer d

Na, Al, H, P, O

Answer e

Ba, H, As, N, O

PROBLEM 3.5.1.6

Which is the most polar bond?

C–C; C–H; N–H; O–H; Se–H

Answer

O–H

PROBLEM 3.5.1.7

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

a. HF or HCl
b. NO or CO
c. SH or OH
d. PCl or SCl
e. CH or NH
f. SO or PO
g. CN or NN

Answer a

HF

Answer b

CO

Answer c

OH

Answer d

PCl

Answer e

NH

Answer f

PO

Answer g

CN

PROBLEM 3.5.1.8

Which of the following molecules or ions contain polar bonds?

a. O_3
b. $\mathbf{O_2^{2-}}$
c. $\mathbf{NO_3^-}$
d. CO_2
e. H_2S
f. $\mathbf{BH_4^-}$
g. S_8

Answer

c, d, e, f

Contributors

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3.6: Bond Strength

Skills to Develop

- Describe the formation of covalent bonds
- Describe the energetics of covalent bond formation and breakage

Formation of Covalent Bonds



Video* 3.6.1*: *What are covalent bonds?*

Nonmetal atoms frequently form covalent bonds with other nonmetal atoms. For example, the hydrogen molecule, H_2, contains a covalent bond between its two hydrogen atoms. Figure **3.6.1** illustrates why this bond is formed. Starting on the far right, we have two separate hydrogen atoms with a particular potential energy, indicated by the red line. Along the *x*-axis is the distance between the two atoms. As the two atoms approach each other (moving left along the *x*-axis), their valence orbitals (1*s*) begin to overlap. The single electrons on each hydrogen atom then interact with both atomic nuclei, occupying the space around both atoms. The strong attraction of each shared electron to both nuclei stabilizes the system, and the potential energy decreases as the bond distance decreases. If the atoms continue to approach each other, the positive charges in the two nuclei begin to repel each other, and the potential energy increases. The bond length is determined by the distance at which the lowest potential energy is achieved.

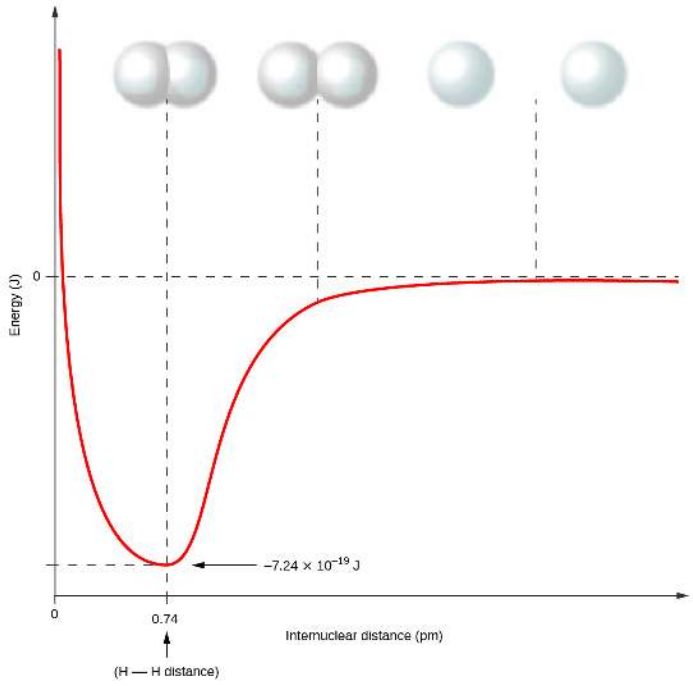


Figure* 3.6.1*: *The potential energy of two separate hydrogen atoms (right) decreases as they approach each other, and the single electrons on each atom are shared to form a covalent bond. The bond length is the internuclear distance at which the lowest potential energy is achieved.*

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

$$\mathrm{H_2}(g) \longrightarrow 2\,\mathrm{H}(g) \quad \Delta H = 436\ \mathrm{kJ} \tag{3.6.1}$$

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

$$2\,\mathrm{H}(g) \longrightarrow \mathrm{H_2}(g) \quad \Delta H = -436\ \mathrm{kJ} \tag{3.6.2}$$

Pure vs. Polar Covalent Bonds

If the atoms that form a covalent bond are identical, as in H_2, Cl_2, and other diatomic molecules, then the electrons in the bond must be shared equally. We refer to this as a pure covalent bond. Electrons shared in pure covalent bonds have an equal probability of being near each nucleus. In the case of Cl_2, each atom starts off with seven valence electrons, and each Cl shares one electron with the other, forming one covalent bond:

$$\mathrm{Cl} + \mathrm{Cl} \longrightarrow \mathrm{Cl_2} \tag{3.6.3}$$

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

When the atoms linked by a covalent bond are different, the bonding electrons are shared, but no longer equally. Instead, the bonding electrons are more attracted to one atom than the other, giving rise to a shift of electron density toward that atom. This unequal distribution of electrons is known as a polar covalent bond, characterized by a partial positive charge on one atom and a partial negative charge on the other. The atom that attracts the electrons more strongly acquires the partial negative charge and vice versa. For example, the electrons in the H–Cl bond of a hydrogen chloride molecule spend more time near the chlorine atom than near the hydrogen atom. Thus, in an HCl molecule, the chlorine atom carries a partial negative charge and the hydrogen atom has a partial positive charge. Figure **3.6.2** shows the distribution of electrons in the H–Cl bond. Note that the shaded area around Cl is much larger than it is around H. Compare this to Figure **3.6.1**, which shows the even distribution of electrons in the H_2 nonpolar bond.

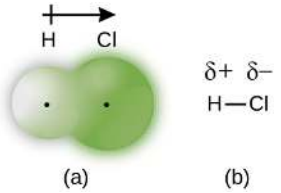


Figure* 3.6.2: (a) The distribution of electron density in the HCl molecule is uneven. The electron density is greater around the chlorine nucleus. The small, black dots indicate the location of the hydrogen and chlorine nuclei in the molecule. (b) Symbols δ+ and δ– indicate the polarity of the H–Cl bond.*

We sometimes designate the positive and negative atoms in a polar covalent bond using a lowercase Greek letter "delta," δ, with a plus sign or minus sign to indicate whether the atom has a partial positive charge (δ+) or a partial negative charge (δ–). This symbolism is shown for the H–Cl molecule in Figure **3.6.2***b*.

A bond's strength describes how strongly each atom is joined to another atom, and therefore how much energy is required to break the bond between the two atoms. In this section, you will learn about the bond strength of covalent bonds. Later in this course, we will compare that to the strength of ionic bonds, which is related to the lattice energy of a compound.

Bond Strength: Covalent Bonds

Stable molecules exist because covalent bonds hold the atoms together. We measure the strength of a covalent bond by the energy required to break it, that is, the energy necessary to separate the bonded atoms. Separating any pair of bonded atoms requires energy; *the stronger a bond, the greater the energy required to break it.* The energy required to break a specific covalent bond in one mole of gaseous molecules is called the bond energy or the bond dissociation energy. The bond energy for a diatomic molecule, D_{X-Y}, is defined as the standard enthalpy change for the endothermic reaction:

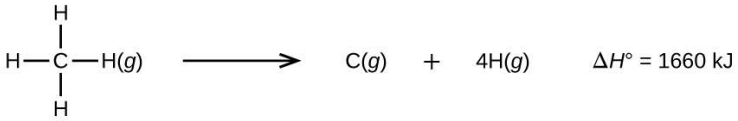
$$XY_{(g)} \longrightarrow X_{(g)} + Y_{(g)} \quad D_{X-Y} = \Delta H° \tag{3.6.4}$$

For example, the bond energy of the pure covalent H–H bond, Δ_{H-H}, is 436 kJ per mole of H–H bonds broken:

$$H_{2(g)} \longrightarrow 2H_{(g)} \quad D_{H-H} = \Delta H° = 436kJ \tag{3.6.5}$$

> *Breaking a bond **always** require energy to be added to the molecule. Correspondingly, making a bond **always** releases energy.*

Molecules with three or more atoms have two or more bonds. The sum of all bond energies in such a molecule is equal to the standard enthalpy change for the endothermic reaction that breaks all the bonds in the molecule. For example, the sum of the four C–H bond energies in CH_4, 1660 kJ, is equal to the standard enthalpy change of the reaction:



The average C–H bond energy, D_{C-H}, is 1660/4 = 415 kJ/mol because there are four moles of C–H bonds broken per mole of the reaction. Although the four C–H bonds are equivalent in the original molecule, they do not each require the same energy to break; once the first bond is broken (which requires 439 kJ/mol), the remaining bonds are easier to break. The 415 kJ/mol value is the average, not the exact value required to break any one bond.

The strength of a bond between two atoms increases as the number of electron pairs in the bond increases. Generally, as the bond strength increases, the bond length decreases. Thus, we find that triple bonds are stronger and shorter than double bonds between the same two atoms; likewise, double bonds are stronger and shorter than single bonds between the same two atoms. Average bond energies for some common bonds appear in Table **3.6.2**, and a comparison of bond lengths and bond strengths for some common bonds appears in Table **3.6.2**. When one atom bonds to various atoms in a group, the bond strength typically decreases as we move down the group. For example, C–F is 439 kJ/mol, C–Cl is 330 kJ/mol, and C–Br is 275 kJ/mol.

Table* 3.6.1*: *Bond Energies (kJ/mol)*

Bond	Bond Energy	Bond	Bond Energy	Bond	Bond Energy
H–H	436	C–S	260	F–Cl	255
H–C	415	C–Cl	330	F–Br	235
H–N	390	C–Br	275	Si–Si	230
H–O	464	C–I	240	Si–P	215
H–F	569	N–N	160	Si–S	225
H–Si	395	N = N	418	Si–Cl	359
H–P	320	N ≡ N	946	Si–Br	290
H–S	340	N–O	200	Si–I	215
H–Cl	432	N–F	270	P–P	215
H–Br	370	N–P	210	P–S	230
H–I	295	N–Cl	200	P–Cl	330
C–C	345	N–Br	245	P–Br	270
C = C	611	O–O	140	P–I	215
C ≡ C	837	O = O	498	S–S	215
C–N	290	O–F	160	S–Cl	250
C = N	615	O–Si	370	S–Br	215
C ≡ N	891	O–P	350	Cl–Cl	243
C–O	350	O–Cl	205	Cl–Br	220
C = O	741	O–I	200	Cl–I	210
C ≡ O	1080	F–F	160	Br–Br	190
C–F	439	F–Si	540	Br–I	180
C–Si	360	F–P	489	I–I	150
C–P	265	F–S	285		

Table 3.6.2: *Average Bond Lengths and Bond Energies for Some Common Bonds*

Bond	Bond Length (Å)	Bond Energy (kJ/mol)
C–C	1.54	345
C = C	1.34	611
C ≡ C	1.20	837
C–N	1.43	290
C = N	1.38	615
C ≡ N	1.16	891
C–O	1.43	350
C = O	1.23	741
C ≡ O	1.13	1080

We can use bond energies to calculate approximate enthalpy changes for reactions where enthalpies of formation are not available. Calculations of this type will also tell us whether a reaction is exothermic or endothermic.

- An **exothermic reaction** (ΔH negative, heat produced) results when the bonds in the products are stronger than the bonds in the reactants.
- An **endothermic reaction** (ΔH positive, heat absorbed) results when the bonds in the products are weaker than those in the reactants.

The enthalpy change, ΔH, for a chemical reaction is approximately equal to the sum of the energy required to break all bonds in the reactants (energy "in", positive sign) plus the energy released when all bonds are formed in the products (energy "out," negative sign). This can be expressed mathematically in the following way:

$$\Delta H = \sum D_{\text{bonds broken}} - \sum D_{\text{bonds formed}} \tag{3.6.6}$$

In this expression, the symbol Σ means "the sum of" and D represents the bond energy in kilojoules per mole, which is always a positive number. The bond energy is obtained from a table and will depend on whether the particular bond is a single, double, or triple bond. Thus, in calculating enthalpies in this manner, it is important that we consider the bonding in all reactants and products. Because D values are typically averages for one type of bond in many different molecules, this calculation provides a rough estimate, not an exact value, for the enthalpy of reaction.

Consider the following reaction:

$$\mathrm{H_{2(g)} + Cl_{2(g)} \longrightarrow 2\,HCl_{(g)}} \tag{3.6.7}$$

or

$$\mathrm{H{-}H_{(g)} + Cl{-}Cl_{(g)} \longrightarrow 2\,H{-}Cl_{(g)}} \tag{3.6.8}$$

To form two moles of HCl, one mole of H–H bonds and one mole of Cl–Cl bonds must be broken. The energy required to break these bonds is the sum of the bond energy of the H–H bond (436 kJ/mol) and the Cl–Cl bond (243 kJ/mol). During the reaction, two moles of H–Cl bonds are formed (bond energy = 432 kJ/mol), releasing 2 × 432 kJ; or 864 kJ. Because the bonds in the products are stronger than those in the reactants, the reaction releases more energy than it consumes:

$$\begin{aligned}\Delta H &= \sum \mathrm{D_{bonds\ broken}} - \sum \mathrm{D_{bonds\ formed}} \\ \Delta H &= [\mathrm{D_{H-H}} + \mathrm{D_{Cl-Cl}}] - 2\mathrm{D_{H-Cl}} \\ &= [436 + 243] - 2(432) = -185\ \mathrm{kJ}\end{aligned}$$

This excess energy is released as heat, so the reaction is exothermic. Table T2 gives a value for the standard molar enthalpy of formation of HCl(g), ΔH_f°, of –92.307 kJ/mol. Twice that value is –184.6 kJ, which agrees well with the answer obtained earlier for the formation of two moles of HCl.

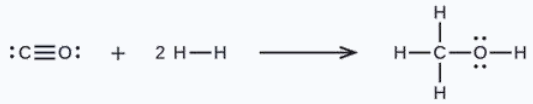
Example 3.6.1: Using Bond Energies to Approximate Enthalpy Changes

Methanol, CH_3OH, may be an excellent alternative fuel. The high-temperature reaction of steam and carbon produces a mixture of the gases carbon monoxide, CO, and hydrogen, H_2, from which methanol can be produced. Using the bond energies in Table **3.6.2**, calculate the approximate enthalpy change, ΔH, for the reaction here:

$$CO_{(g)} + 2H2_{(g)} \longrightarrow CH_3OH_{(g)} \tag{3.6.9}$$

Solution

First, we need to write the Lewis structures of the reactants and the products:



From this, we see that ΔH for this reaction involves the energy required to break a C–O triple bond and two H–H single bonds, as well as the energy produced by the formation of three C–H single bonds, a C–O single bond, and an O–H single bond. We can express this as follows (via Equation 3.6.6):

$$\Delta H = \sum D_{bonds\ broken} - \sum D_{bonds\ formed}$$
$$\Delta H = [D_{C\equiv O} + 2(D_{H-H})] - [3(D_{C-H}) + D_{C-O} + D_{O-H}]$$

Using the bond energy values in Table **3.6.2**, we obtain:

$$\begin{aligned}\Delta H &= [1080 + 2(436)] - [3(415) + 350 + 464] \\ &= -107\ kJ\end{aligned}$$

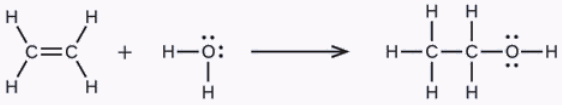
We can compare this value to the value calculated based on ΔH_f° data from Appendix G:

$$\begin{aligned}\Delta H &= [\Delta H_f^\circ CH_3OH(g)] - [\Delta H_f^\circ CO(g) + 2 \times \Delta H_f^\circ H_2] \\ &= [-201.0] - [-110.52 + 2 \times 0] \\ &= -90.5\ kJ\end{aligned}$$

Note that there is a fairly significant gap between the values calculated using the two different methods. This occurs because D values are the *average* of different bond strengths; therefore, they often give only rough agreement with other data.

Exercise 3.6.1

Ethyl alcohol, CH_3CH_2OH, was one of the first organic chemicals deliberately synthesized by humans. It has many uses in industry, and it is the alcohol contained in alcoholic beverages. It can be obtained by the fermentation of sugar or synthesized by the hydration of ethylene in the following reaction:



Using the bond energies in Table **3.6.2**, calculate an approximate enthalpy change, ΔH, for this reaction.

Answer

–35 kJ

Summary



***Video* 3.6.2:** *A review of atomic bonding.*

Covalent bonds form when electrons are shared between atoms and are attracted by the nuclei of both atoms. In pure covalent bonds, the electrons are shared equally. In polar covalent bonds, the electrons are shared unequally, as one atom exerts a stronger force of attraction on the electrons than the other.

The strength of a covalent bond is measured by its bond dissociation energy, that is, the amount of energy required to break that particular bond in a mole of molecules. Multiple bonds are stronger than single bonds between the same atoms. The enthalpy of a reaction can be estimated based on the energy input required to break bonds and the energy released when new bonds are formed.

Key Equations

- Bond energy for a diatomic molecule: $\mathrm{XY}(g) \longrightarrow \mathrm{X}(g) + \mathrm{Y}(g) \quad \mathrm{D_{X-Y}} = \Delta H°$
- Enthalpy change: $\Delta H = \Sigma \mathrm{D_{bonds\ broken}} - \Sigma \mathrm{D_{bonds\ formed}}$

Footnotes

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

Glossary

bond energy

(also, bond dissociation energy) energy required to break a covalent bond in a gaseous substance

Contributors

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3.6.1: Bond Strength (Problems)

PROBLEM 3.6.1.1

Which bond in each of the following pairs of bonds is the strongest?

a. C–C or $\mathbf{C=C}$
b. C–N or $\mathbf{C\equiv N}$
c. $\mathbf{C\equiv O}$ or $\mathbf{C=O}$
d. H–F or H–Cl
e. C–H or O–H
f. C–N or C–O

Answer a

$\mathbf{C=C}$

Answer b

$\mathbf{C\equiv N}$

Answer c

$\mathbf{C\equiv O}$

Answer d

H–F

Answer e

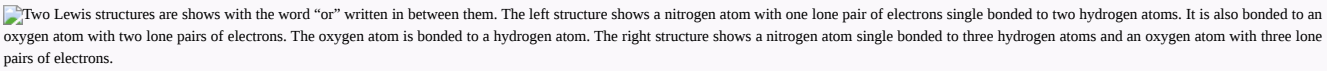
O–H

Answer f

C–O

PROBLEM 3.6.1.2

When a molecule can form two different structures, the structure with the stronger bonds is usually the more stable form. Use bond energies to predict the correct structure of the hydroxylamine molecule:



Answer

The greater bond energy is in the figure on the left. It is the more stable form.

PROBLEM 3.6.1.3

Use principles of atomic structure to answer each of the following:[1]

a. The radius of the Ca atom is 197 pm; the radius of the Ca^{2+} ion is 99 pm. Account for the difference.
b. Given these ionization values, explain the difference between Ca and K with regard to their first and second ionization energies.

Element	First Ionization Energy (kJ/mol)	Second Ionization Energy (kJ/mol)
K	419	3050
Ca	590	1140

c. The first ionization energy of Mg is 738 kJ/mol and that of Al is 578 kJ/mol. Account for this difference.

Answer a

When two electrons are removed from the valence shell, the Ca radius loses the outermost energy level and reverts to the lower $n = 3$ level, which is much smaller in radius.

Answer b

Removal of the 4*s* electron in Ca requires more energy than removal of the 4*s* electron in K because of the stronger attraction of the nucleus and the extra energy required to break the pairing of the electrons. The second ionization energy for K requires that an electron be removed from a lower energy level, where the attraction is much stronger from the nucleus for the electron. In addition, energy is required to unpair two electrons in a full orbital. For Ca, the second ionization potential requires removing only a lone electron in the exposed outer energy level.

Answer c

In Al, the removed electron is relatively unprotected and unpaired in a *p* orbital. The higher energy for Mg mainly reflects the unpairing of the 2*s* electron

Contributors

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- Adelaide Clark, Oregon Institute of Technology

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CHAPTER OVERVIEW

4: Molecular Shape

Unit Objectives

- Describe the energetics of covalent bond formation and breakage
- Predict the structures of small molecules using valence shell electron pair repulsion (VSEPR) theory
- Describe the formation of covalent bonds in terms of atomic orbital overlap
- Define and give examples of σ and π bonds
- Explain the concept of atomic orbital hybridization
- Determine the hybrid orbitals associated with various molecular geometries

4.1: Molecular Shape

4.1.1: Molecular Shape (Problems)

4.2: Molecular Shape and Polarity

4.2.1: Molecular Shape and Polarity (Problems)

4.3: Valence Bond Theory and Hybrid Orbitals

4.3.1: Valence Bond Theory and Hybrid Orbitals (Problems)

4.4: Bond Types and Molecular Orbital Theory

4.4.1: Bond Types and Molecular Orbital Theory (Problems)

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4.1: Molecular Shape

Skills to Develop

- Predict the structures of small molecules using valence shell electron pair repulsion (VSEPR) theory

Thus far, we have used two-dimensional Lewis structures to represent molecules. However, molecular structure is actually three-dimensional, and it is important to be able to describe molecular bonds in terms of their distances, angles, and relative arrangements in space (Figure 4.1.1). 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).

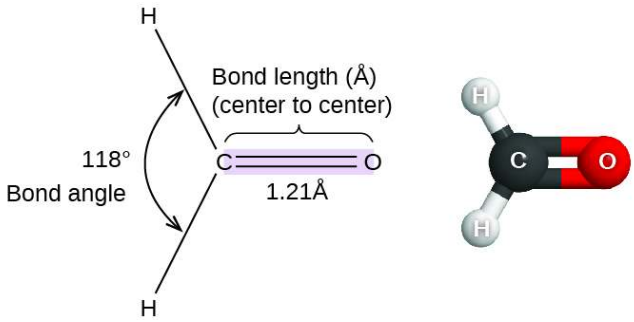


Figure* 4.1.1*: *Bond distances (lengths) and angles are shown for the formaldehyde molecule, H_2CO.*

VSEPR Theory

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

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

As a simple example of VSEPR theory, let us predict the structure of a gaseous BeF_2 molecule. The Lewis structure of BeF_2 (Figure 4.1.2) shows only two electron pairs around the central beryllium atom. With two bonds and no lone pairs of electrons on the central atom, the bonds are as far apart as possible, and the electrostatic repulsion between these regions of high electron density is reduced to a minimum when they are on opposite sides of the central atom. The bond angle is 180° (Figure 4.1.2).

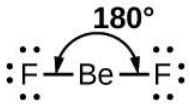


Figure* 4.1.2*: *The BeF_2 molecule adopts a linear structure in which the two bonds are as far apart as possible, on opposite sides of the Be atom.*

Figure 4.1.3 illustrates this and other electron-pair geometries that minimize the repulsions among regions of high electron density (bonds and/or lone pairs). Two regions of electron density around a central atom in a molecule form a linear geometry; three regions form a trigonal planar geometry; four regions form a tetrahedral geometry; five regions form a trigonal bipyramidal geometry; and six regions form an octahedral geometry.

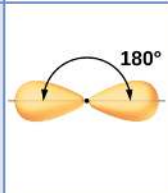
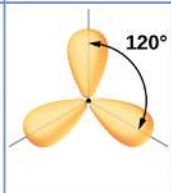
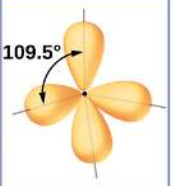
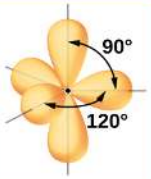
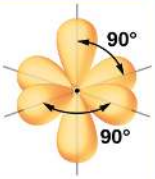
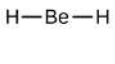
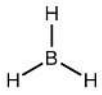
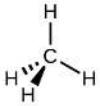
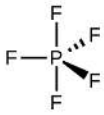
Number of regions	Two regions of high electron density (bonds and/or unshared pairs)	Three regions of high electron density (bonds and/or unshared pairs)	Four regions of high electron density (bonds and/or unshared pairs)	Five regions of high electron density (bonds and/or unshared pairs)	Six regions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

***Figure* 4.1.3:** *The basic electron-pair geometries predicted by VSEPR theory maximize the space around any region of electron density (bonds or lone pairs).*

Electron-pair Geometry versus Molecular Structure

It is important to note that electron-pair geometry around a central atom is *not* the same thing as its molecular structure. The electron-pair geometries shown in Figure **4.1.3** describe all regions where electrons are located, bonds as well as lone pairs. Molecular structure describes the location of the *atoms*, not the electrons.

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

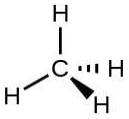


***Figure* 4.1.4:** *The molecular structure of the methane molecule, CH_4, is shown with a tetrahedral arrangement of the hydrogen atoms. VSEPR structures like this one are often drawn using the wedge and dash notation, in which solid lines represent bonds in the plane of the page, solid wedges represent bonds coming up out of the plane, and dashed lines represent bonds going down into the plane.*

For example, the methane molecule, CH_4, which is the major component of natural gas, has four bonding pairs of electrons around the central carbon atom; the electron-pair geometry is tetrahedral, as is the molecular structure (Figure **4.1.4**). On the other hand, the

ammonia molecule, NH_3, also has four electron pairs associated with the nitrogen atom, and thus has a tetrahedral electron-pair geometry. One of these regions, however, is a lone pair, which is not included in the molecular structure, and this lone pair influences the shape of the molecule (Figure **4.1.5**).

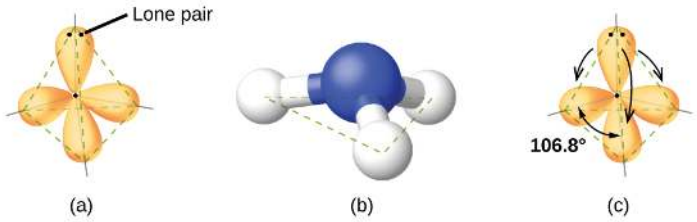


Figure* 4.1.5*: *(a) The electron-pair geometry for the ammonia molecule is tetrahedral with one lone pair and three single bonds. (b) The trigonal pyramidal molecular structure is determined from the electron-pair geometry. (c) The actual bond angles deviate slightly from the idealized angles because the lone pair takes up a larger region of space than do the single bonds, causing the HNH angle to be slightly smaller than 109.5°.*

Small distortions from the ideal angles in Figure **4.1.5** can result from differences in repulsion between various regions of electron density. VSEPR theory predicts these distortions by establishing an order of repulsions and an order of the amount of space occupied by different kinds of electron pairs. The order of electron-pair repulsions from greatest to least repulsion is:

lone pair-lone pair > lone pair-bonding pair > bonding pair-bonding pair

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

lone pair > triple bond > double bond > single bond

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

In the ammonia molecule, the three hydrogen atoms attached to the central nitrogen are not arranged in a flat, trigonal planar molecular structure, but rather in a three-dimensional trigonal pyramid (Figure **4.1.6**) with the nitrogen atom at the apex and the three hydrogen atoms forming the base. The ideal bond angles in a trigonal pyramid are based on the tetrahedral electron pair geometry. Again, there are slight deviations from the ideal because lone pairs occupy larger regions of space than do bonding electrons. The H–N–H bond angles in NH_3 are slightly smaller than the 109.5° angle in a regular tetrahedron (Figure **4.1.6**) because the lone pair-bonding pair repulsion is greater than the bonding pair-bonding pair repulsion. The ideal molecular structures are predicted based on the electron-pair geometries for various combinations of lone pairs and bonding pairs.

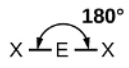
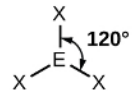
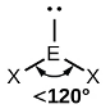
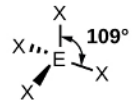
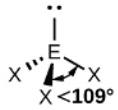
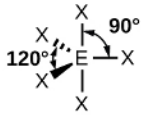
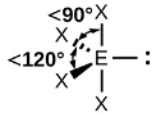
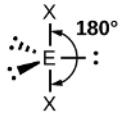
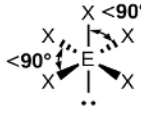
Number of electron pairs	Electron pair geometries: 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	 Linear				
3	 Trigonal planar	 Bent or angular			
4	 Tetrahedral	 Trigonal pyramid	 Bent or angular		
5	 Trigonal bipyramid	 Sawhorse or seesaw	 T-shape	 Linear	
6	 Octahedral	 Square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

***Figure* 4.1.6:** *The molecular structures are identical to the electron-pair geometries when there are no lone pairs present (first column). For a particular number of electron pairs (row), the molecular structures for one or more lone pairs are determined based on modifications of the corresponding electron-pair geometry.*

According to VSEPR theory, the terminal atom locations (Xs in Figure **4.1.7**) are equivalent within the linear, trigonal planar, and tetrahedral electron-pair geometries (the first three rows of the table). It does not matter which X is replaced with a lone pair because the molecules can be rotated to convert positions. For trigonal bipyramidal electron-pair geometries, however, there are two distinct X positions (Figure **4.1.7**a): an axial position (if we hold a model of a trigonal bipyramid by the two axial positions, we have an axis around which we can rotate the model) and an equatorial position (three positions form an equator around the middle of the molecule). The axial position is surrounded by bond angles of 90°, whereas the equatorial position has more space available because of the 120° bond angles. In a trigonal bipyramidal electron-pair geometry, lone pairs always occupy equatorial positions because these more spacious positions can more easily accommodate the larger lone pairs.

Theoretically, we can come up with three possible arrangements for the three bonds and two lone pairs for the ClF_3 molecule (Figure **4.1.7**). The stable structure is the one that puts the lone pairs in equatorial locations, giving a T-shaped molecular structure.

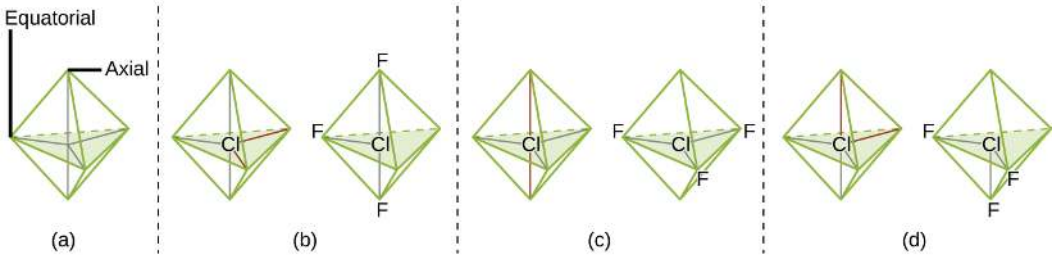


***Figure* 4.1.7:** *(a) In a trigonal bipyramid, the two axial positions are located directly across from one another, whereas the three equatorial positions are located in a triangular arrangement. (b–d) The two lone pairs (red lines) in ClF_3 have several possible*

arrangements, but the T-shaped molecular structure (b) is the one actually observed, consistent with the larger lone pairs both occupying equatorial positions.

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

Predicting Electron Pair Geometry and Molecular Structure

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

1. Write the Lewis structure of the molecule or polyatomic ion.
2. Count the number of regions of electron density (lone pairs and bonds) around the central atom. A single, double, or triple bond counts as one region of electron density.
3. Identify the electron-pair geometry based on the number of regions of electron density: linear, trigonal planar, tetrahedral, trigonal bipyramidal, or octahedral (Figure **4.1.7**, first column).
4. Use the number of lone pairs to determine the molecular structure (Figure **4.1.7**). If more than one arrangement of lone pairs and chemical bonds is possible, choose the one that will minimize repulsions, remembering that lone pairs occupy more space than multiple bonds, which occupy more space than single bonds. In trigonal bipyramidal arrangements, repulsion is minimized when every lone pair is in an equatorial position. In an octahedral arrangement with two lone pairs, repulsion is minimized when the lone pairs are on opposite sides of the central atom.

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

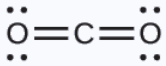
Example 4.1.1: Predicting Electron-pair Geometry and Molecular Structure

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

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

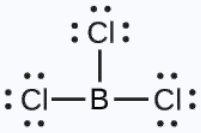
Solution

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

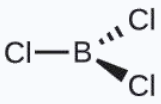


This shows us two regions of high electron density around the carbon atom—each double bond counts as one region, and there are no lone pairs on the carbon atom. Using VSEPR theory, we predict that the two regions of electron density arrange themselves on opposite sides of the central atom with a bond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

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



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



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

Exercise 4.1.1

Carbonate, CO_3^{2-}, is a common polyatomic ion found in various materials from eggshells to antacids. What are the electron-pair geometry and molecular structure of this polyatomic ion?

Answer

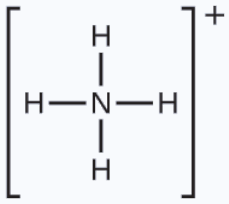
The electron-pair geometry is trigonal planar and the molecular structure is trigonal planar. Due to resonance, all three C–O bonds are identical. Whether they are single, double, or an average of the two, each bond counts as one region of electron density.

Example 4.1.2: Predicting Electron-pair Geometry and Molecular Structure

Two of the top 50 chemicals produced in the United States, ammonium nitrate and ammonium sulfate, both used as fertilizers, contain the ammonium ion. Predict the electron-pair geometry and molecular structure of the NH_4^+ cation.

Solution

We write the Lewis structure of NH_4^+ as:



We can see that NH_4^+ contains four bonds from the nitrogen atom to hydrogen atoms and no lone pairs. We expect the four regions of high electron density to arrange themselves so that they point to the corners of a tetrahedron with the central nitrogen atom in the middle (Figure 4.1.7). Therefore, the electron pair geometry of NH_4^+ is tetrahedral, and the molecular structure is also tetrahedral (Figure 4.1.7).

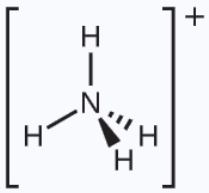


Figure 4.1.8: *The ammonium ion displays a tetrahedral electron-pair geometry as well as a tetrahedral molecular structure.*

Exercise 4.1.2

Identify a molecule with trigonal bipyramidal molecular structure.

Answer

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

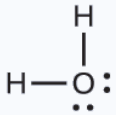
The next several examples illustrate the effect of lone pairs of electrons on molecular structure.

Example 4.1.3: Lone Pairs on the Central Atom

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

Solution

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



We predict that these four regions are arranged in a tetrahedral fashion (Figure **4.1.6**), as indicated in Figure **4.1.9**. Thus, the electron-pair geometry is tetrahedral and the molecular structure is bent with an angle slightly less than 109.5°. In fact, the bond angle is 104.5°.

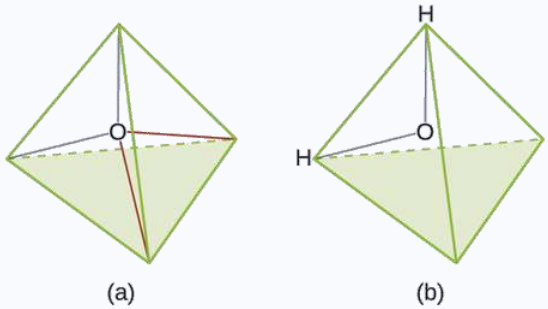


Figure* 4.1.9*: *(a) H_2O has four regions of electron density around the central atom, so it has a tetrahedral electron-pair geometry. (b) Two of the electron regions are lone pairs, so the molecular structure is bent.*

Exercise 4.1.3

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

Answer

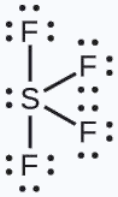
electron pair geometry: tetrahedral; molecular structure: trigonal pyramidal

Example 4.1.4: SF_4 Sulfur tetrafluoride,

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

Solution

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



We expect these five regions to adopt a trigonal bipyramidal electron-pair geometry. To minimize lone pair repulsions, the lone pair occupies one of the equatorial positions. The molecular structure (Figure **4.1.6**) is that of a seesaw (Figure **4.1.10**).

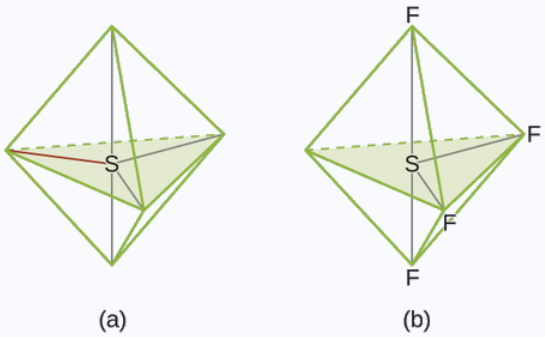


Figure* 4.1.10*: *(a) SF_4 has a trigonal bipyramidal arrangement of the five regions of electron density. (b) One of the regions is a lone pair, which results in a seesaw-shaped molecular structure.*

Exercise 4.1.4

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

Answer

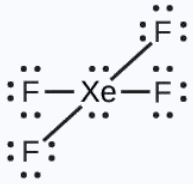
The electron-pair geometry is trigonal bipyramidal. The molecular structure is linear.

Example 4.1.4: XeF_4

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

Solution

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



These six regions adopt an octahedral arrangement (Figure **4.1.6**), which is the electron-pair geometry. To minimize repulsions, the lone pairs should be on opposite sides of the central atom (Figure **4.1.11**). The five atoms are all in the same plane and have a square planar molecular structure.

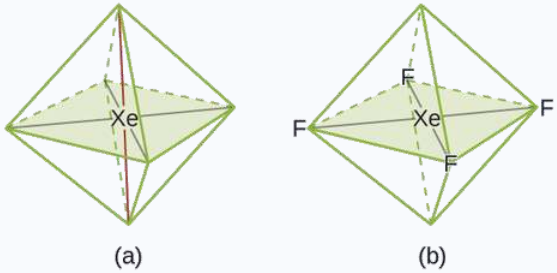


Figure* 4.1.11*: *(a) XeF_4 adopts an octahedral arrangement with two lone pairs (red lines) and four bonds in the electron-pair geometry. (b) The molecular structure is square planar with the lone pairs directly across from one another.*

Exercise 4.1.4

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

Answer

electron pair geometry: trigonal bipyramidal; molecular structure: linear



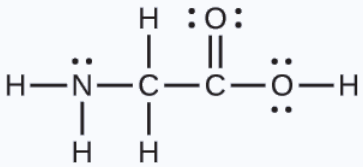
Video* 4.1.1*: *An overview of simple molecular shapes.*

Molecular Structure for Multicenter Molecules

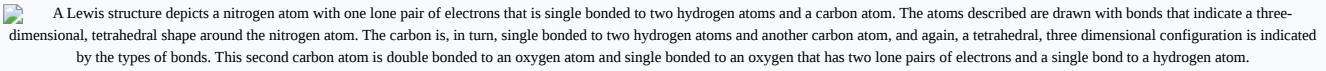
When a molecule or polyatomic ion has only one central atom, the molecular structure completely describes the shape of the molecule. Larger molecules do not have a single central atom, but are connected by a chain of interior atoms that each possess a "local" geometry. The way these local structures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

Example 4.1.5: Predicting Structure in Multicenter Molecules

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



Solution


A Lewis structure depicts a nitrogen atom with one lone pair of electrons that is single bonded to two hydrogen atoms and a carbon atom. The atoms described are drawn with bonds that indicate a three-dimensional, tetrahedral shape around the nitrogen atom. The carbon is, in turn, single bonded to two hydrogen atoms and another carbon atom, and again, a tetrahedral, three dimensional configuration is indicated by the types of bonds. This second carbon atom is double bonded to an oxygen atom and single bonded to an oxygen that has two lone pairs of electrons and a single bond to a hydrogen atom.

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

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

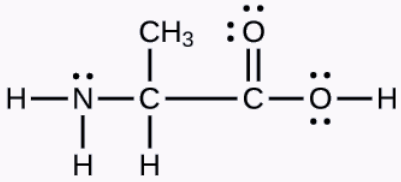
The local structures:

- nitrogen—three bonds, one lone pair; trigonal pyramidal

- carbon (CH_2)—four bonds, no lone pairs; tetrahedral
- carbon (CO_2)—three bonds (double bond counts as one bond), no lone pairs; trigonal planar
- oxygen (OH)—two bonds, two lone pairs; bent (109°)

Exercise 4.1.5

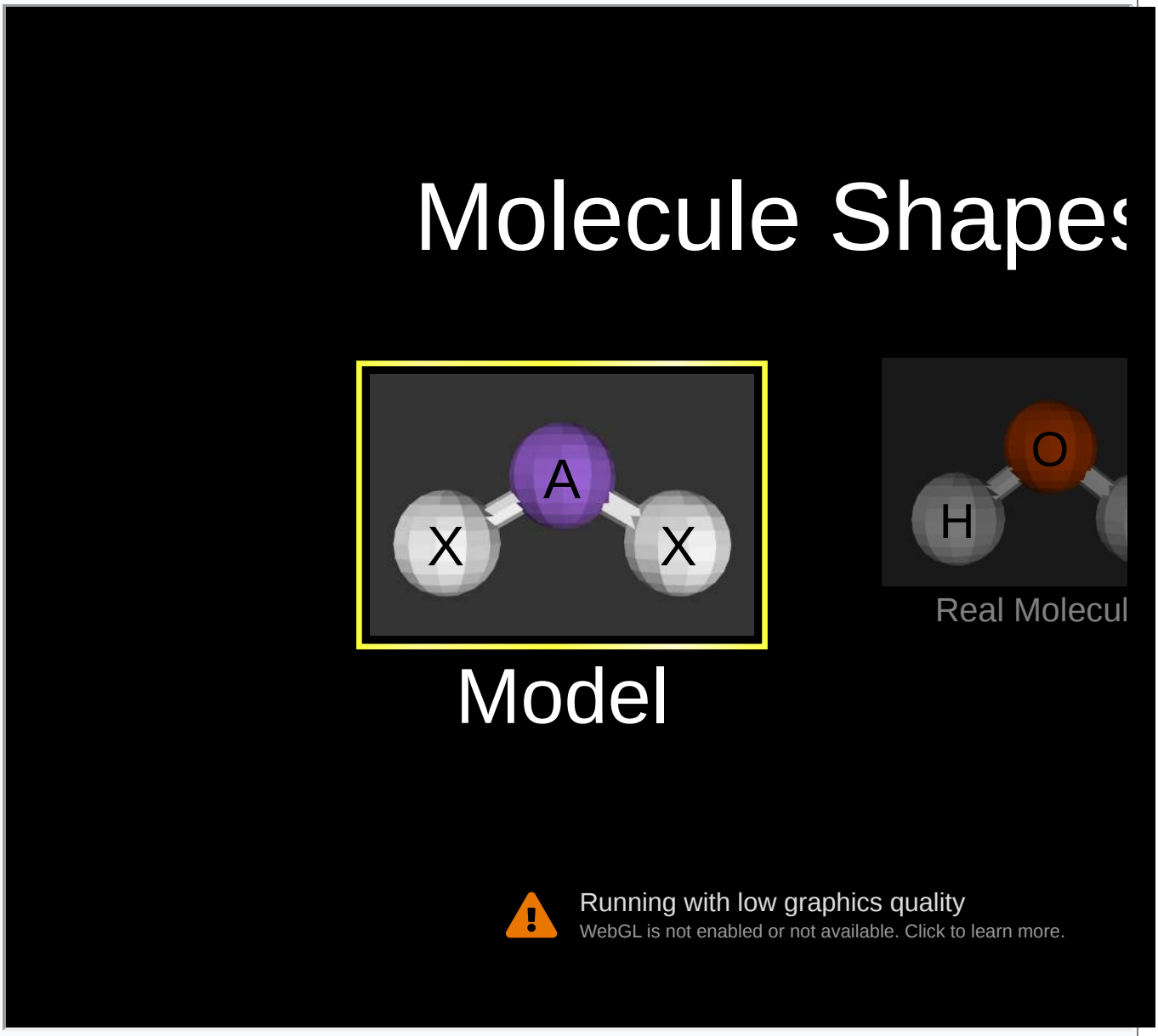
Another amino acid is alanine, which has the Lewis structure shown here. Predict the electron-pair geometry and local structure of the nitrogen atom, the three carbon atoms, and the oxygen atom with hydrogen attached:



Answer

electron-pair geometries: nitrogen—tetrahedral; carbon (CH)—tetrahedral; carbon (CH_3)—tetrahedral; carbon (CO_2)—trigonal planar; oxygen (OH)—tetrahedral; local structures: nitrogen—trigonal pyramidal; carbon (CH)—tetrahedral; carbon (CH_3)—tetrahedral; carbon (CO_2)—trigonal planar; oxygen (OH)—bent (109°)

Example 4.1.6: Molecular Simulation



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

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

$$\mathbf{H–C \equiv N}$$

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

Solution

The molecular structure is linear.

Exercise 4.1.6

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

Answer

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

Summary



Video* 4.1.2*: *What is the shape of a molecule?*

VSEPR theory predicts the three-dimensional arrangement of atoms in a molecule. It states that valence electrons will assume an electron-pair geometry that minimizes repulsions between areas of high electron density (bonds and/or lone pairs). Molecular structure, which refers only to the placement of atoms in a molecule and not the electrons, is equivalent to electron-pair geometry only when there are no lone electron pairs around the central atom.

Glossary

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

bond angle
angle between any two covalent bonds that share a common atom

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

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

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

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

equatorial position

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

linear

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

molecular structure

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

octahedral

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

polar molecule

(also, dipole) molecule with an overall dipole moment

tetrahedral

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

trigonal bipyramidal

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

trigonal planar

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

valence shell electron-pair repulsion theory (VSEPR)

theory used to predict the bond angles in a molecule based on positioning regions of high electron density as far apart as possible to minimize electrostatic repulsion

vector

quantity having magnitude and direction

Contributors

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4.1.1: Molecular Shape (Problems)

PROBLEM 4.1.1.1

Explain why the HOH molecule is bent, whereas the HBeH molecule is linear.

Answer

The placement of the two sets of unpaired electrons in water forces the bonds to assume a tetrahedral arrangement, and the resulting HOH molecule is bent. The HBeH molecule (in which Be has only two electrons to bond with the two electrons from the hydrogens) must have the electron pairs as far from one another as possible and is therefore linear.

PROBLEM 4.1.1.2

Explain the difference between electron-pair geometry and molecular structure.

Answer

Space must be provided for each pair of electrons whether they are in a bond or are present as lone pairs. Electron-pair geometry considers the placement of all electrons. Molecular structure considers only the bonding-pair geometry.

PROBLEM 4.1.1.3

Why is the H–N–H angle in NH_3 smaller than the H–C–H bond angle in CH_4? Why is the H–N–H angle in $\mathbf{NH_4^+}$ identical to the H–C–H bond angle in CH_4?

Answer

NH_3 has a lone pair of electrons, which forces the bonds closer together, lessening the bond angle compared to species with 4 bonds and no lone pairs.

PROBLEM 4.1.1.4

Predict the electron pair geometry and the molecular structure of each of the following molecules or ions:

a. BeH_2 (hint: Be does not have a complete octet)
b. $\mathbf{CH_3^+}$ (hint: C does ot have a complete octet)

Answer a

Both the electron geometry and the molecular structure are linear.

Answer b

Both the electron geometry and the molecular structure are trigonal planar.

Click here to see a video of the solution



PROBLEM 4.1.1.5

Identify the electron pair geometry and the molecular structure of each of the following molecules or ions:

a. CF_4
b. BF_3
c. $BeCl_2$

Answer a

Both the electron geometry and the molecular structure are tetrahedral.

Answer b

Both the electron geometry and the molecular structure are trigonal planar.

Answer c

Both the electron geometry and the molecular structure are linear.

PROBLEM 4.1.1.6

What are the electron-pair geometry and the molecular structure of each of the following molecules or ions?

a. $\mathbf{ClO_2^-}$
b. PCl_3
c. $\mathbf{PH_2^-}$

Answer a

electron-pair geometry: tetrahedral

molecular structure: bent

Answer b

electron-pair geometry: tetrahedral

molecular structure: trigonal pyramidal

Answer c

electron-pair geometry: tetrahedral

molecular structure: bent (109°)

Click here to see a video of the solution



PROBLEM 4.1.1.7

Identify the electron pair geometry and the molecular structure of each of the following molecules:

a. ClNO (N is the central atom)
b. CS_2
c. Cl_2CO (C is the central atom)
d. Cl_2SO (S is the central atom)
e. SO_2F_2 (S is the central atom)
f. (g) $ClOF_2^+$ (Cl is the central atom)

Answer a

electron-pair geometry: trigonal planar, molecular structure: bent (120°)

Answer b

electron-pair geometry: linear, molecular structure: linear

Answer c

electron-pair geometry: trigonal planar, molecular structure: trigonal planar

Answer d

electron-pair geometry: tetrahedral, molecular structure: trigonal pyramidal

Answer e

electron-pair geometry: tetrahedral, molecular structure: tetrahedral

Answer f

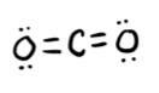
electron-pair geometry: tetrahedral, molecular structure: trigonal pyramidal

PROBLEM 4.1.1.8

Draw the Lewis structures and predict the shape of each compound or ion:

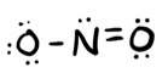
a. CO_2
b. NO_2^-
c. SO_3
d. SO_3^{2-}

Answer a



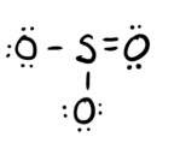
linear

Answer b



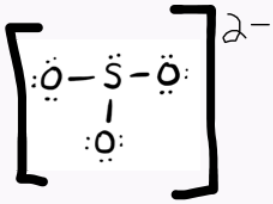
trigonal planar (bent 120)

Answer c



trigonal planar

Answer d



tetrahedral (trigonal pyramidal)

Click here to see a video of the solution



PROBLEM 4.1.1.9

A molecule with the formula AB_2, in which A and B represent different atoms, could have one of three different shapes. Sketch and name the three different shapes that this molecule might have. Give an example of a molecule or ion for each shape.

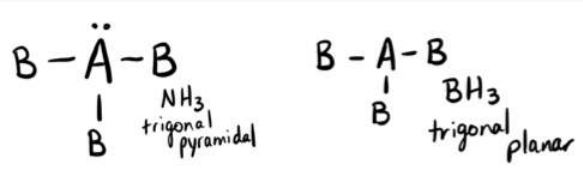
Answer

Three Lewis diagrams are shown. The first diagram shows the letter A single bonded to the left and right to the letter B. An example, “C O subscript 2,” and the term, “linear,” are written beside this diagram. The second diagram shows the letter A with two lone pairs of electrons, single bonded to the left and lower right to the letter B. An example, “H subscript 2 O,” and the term, “bent with an approximately 109 degree angle,” are written beside this diagram. The third diagram shows the letter A with one lone electron pair, single bonded to the left and lower right to the letter B. An example, “S O subscript 2,” and the term, “bent with an approximately 120 degree angle,” are written beside this diagram.

PROBLEM 4.1.1.10

A molecule with the formula AB_3, in which A and B represent different atoms, could have one of two different shapes. Sketch and name the three different shapes that this molecule might have. Give an example of a molecule or ion that has each shape.

Answer



Contributors

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4.2: Molecular Shape and 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

Molecular Polarity and Dipole Moment

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

$$\mu = Qr \tag{4.2.1}$$

where

- Q is the magnitude of the partial charges (determined by the electronegativity difference) and
- r is the distance between the charges:

This bond moment can be represented as a vector, a quantity having both direction and magnitude (Figure **4.2.1**). 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.

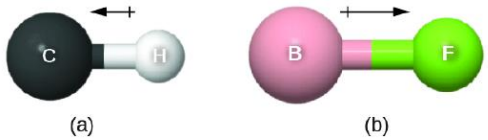


Figure* 4.2.1*: *(a) There is a small difference in electronegativity between C and H, represented as a short vector. (b) The electronegativity difference between B and F is much larger, so the vector representing the bond moment is much longer.*

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

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

When a molecule contains more than one bond, the geometry must be taken into account. If the bonds in a molecule are arranged such that their bond moments cancel (vector sum equals zero), then the molecule is nonpolar. This is the situation in CO_2 (Figure **4.2.2*A***). Each of the bonds is polar, but the molecule as a whole is nonpolar. From the Lewis structure, and using VSEPR theory, we determine that the CO_2 molecule is linear with polar C=O bonds on opposite sides of the carbon atom. The bond moments cancel because they are pointed in opposite directions. In the case of the water molecule (Figure **4.2.2*B***), the Lewis structure again shows that there are two bonds to a central atom, and the electronegativity difference again shows that each of these bonds has a nonzero bond moment. In this case, however, the molecular structure is bent because of the lone pairs on O, and the two bond moments do not cancel. Therefore, water does have a net dipole moment and is a polar molecule (dipole).

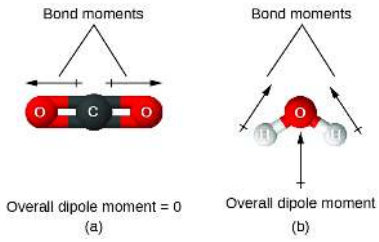
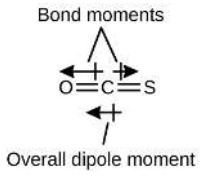


Figure* 4.2.2*: *The overall dipole moment of a molecule depends on the individual bond dipole moments and how they are arranged. (a) Each CO bond has a bond dipole moment, but they point in opposite directions so that the net CO_2 molecule is nonpolar. (b) In contrast, water is polar because the OH bond moments do not cancel out.*

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

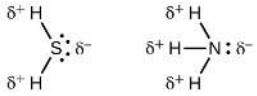


The C–O bond is considerably polar. Although C and S have very similar electronegativity values, S is slightly more electronegative than C, and so the C-S bond is just slightly polar. Because oxygen is more electronegative than sulfur, the oxygen end of the molecule is the negative end.

Chloromethane, CH_3Cl, is 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:



When we examine the highly symmetrical molecules BF_3 (trigonal planar), CH_4 (tetrahedral), PF_5 (trigonal bipyramidal), and SF_6 (octahedral), in which all the polar bonds are identical, the molecules are nonpolar. The bonds in these molecules are arranged such that their dipoles cancel. However, just because a molecule contains identical bonds does not mean that the dipoles will always cancel. Many molecules that have identical bonds and lone pairs on the central atoms have bond dipoles that do not cancel. Examples include H_2S and NH_3. A hydrogen atom is at the positive end and a nitrogen or sulfur atom is at the negative end of the polar bonds in these molecules:



To summarize, to be polar, a molecule must:

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

Properties of Polar Molecules

Polar molecules tend to align when placed in an electric field with the positive end of the molecule oriented toward the negative plate and the negative end toward the positive plate (Figure **4.2.3**). We can use an electrically charged object to attract polar molecules, but nonpolar molecules are not attracted. Also, polar solvents are better at dissolving polar substances, and nonpolar solvents are better at dissolving nonpolar substances.

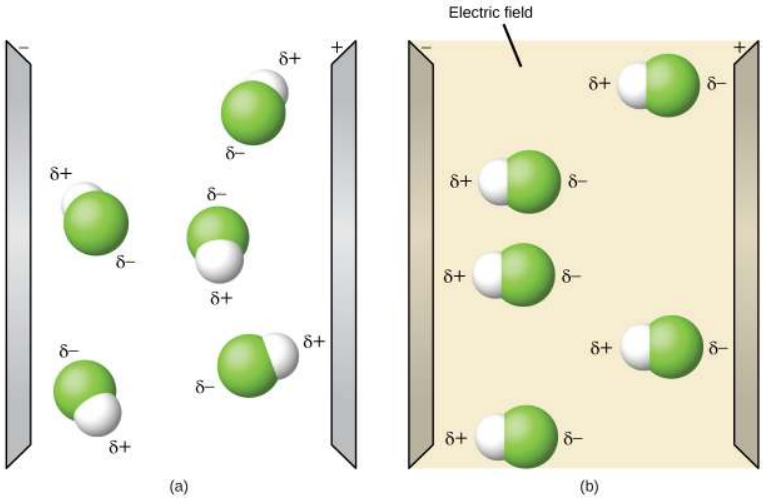
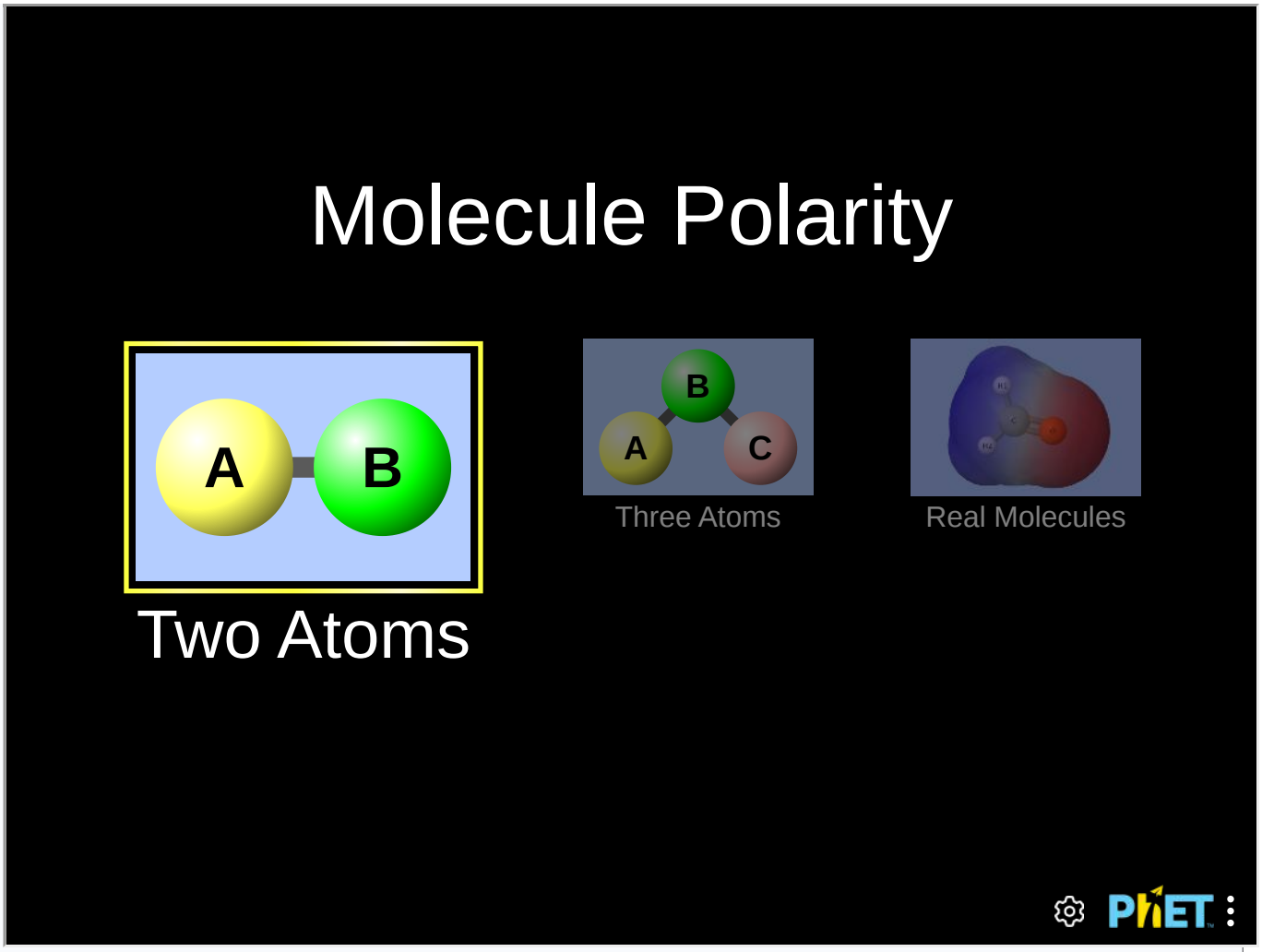


***Figure* 4.2.3**: *(a) Molecules are always randomly distributed in the liquid state in the absence of an electric field. (b) When an electric field is applied, polar molecules like HF will align to the dipoles with the field direction.*

Example 4.2.1: Polarity Simulations



Using the above simulator, 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 **4.2.14**.

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 4.2.1

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

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Video* 4.2.1*: *An overview of polarity and molecular shape.*

A dipole moment measures a separation of charge. For one bond, the bond dipole moment is determined by the difference in electronegativity between the two atoms. For a molecule, the overall dipole moment is determined by both the individual bond moments and how these dipoles are arranged in the molecular structure. Polar molecules (those with an appreciable dipole moment) interact with electric fields, whereas nonpolar molecules do not.

Glossary

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

bond angle
angle between any two covalent bonds that share a common atom

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

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

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

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

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

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

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

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

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

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

trigonal bipyramidal

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

trigonal planar

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

valence shell electron-pair repulsion theory (VSEPR)

theory used to predict the bond angles in a molecule based on positioning regions of high electron density as far apart as possible to minimize electrostatic repulsion

vector

quantity having magnitude and direction

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4.2.1: Molecular Shape and Polarity (Problems)

PROBLEM 4.2.1.1

Explain how a molecule that contains polar bonds can be nonpolar.

Answer

As long as the polar bonds are compensated (for example. two identical atoms are found directly across the central atom from one another), the molecule can be nonpolar.

PROBLEM 4.2.1.2

Which of the following molecules and ions contain polar bonds? Which of these molecules and ions have dipole moments?

a. ClF_5
b. $\mathbf{ClO_2^-}$
c. $\mathbf{TeCl_4^{2-}}$
d. PCl_3
e. SeF_4
f. $\mathbf{PH_2^-}$
g. XeF_2

Answer

All of these molecules and ions contain polar bonds. Only ClF_5, $\mathbf{ClO_2^-}$, PCl_3, SeF_4, and $\mathbf{PH_2^-}$ have dipole moments.

PROBLEM 4.2.1.3

Which of the following molecules have dipole moments?

a. CS_2
b. SeS_2
c. CCl_2F_2
d. PCl_3 (P is the central atom)
e. ClNO (N is the central atom)

Answer

SeS_2, CCl_2F_2, PCl_3, and ClNO all have dipole moments.

PROBLEM 4.2.1.4

The molecule XF_3 has a dipole moment. Is X boron or phosphorus?

Answer

P

PROBLEM 4.2.1.5

The molecule XCl_2 has a dipole moment. Is X beryllium or sulfur?

Answer

S

PROBLEM 4.2.1.6

Is the Cl_2BBCl_2 molecule polar or nonpolar?

Answer

nonpolar

Contributors

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4.3: Valence Bond Theory and Hybrid Orbitals

Skills to Develop

- Describe the formation of covalent bonds in terms of atomic orbital overlap
- Define and give examples of σ and π bonds
- Explain the concept of atomic orbital hybridization
- Determine the hybrid orbitals associated with various molecular geometries



Video* 4.3.1*: *A preview of how orbitals are involved in 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. One popular theory holds that a covalent bond forms when a pair of electrons is shared by two atoms and is simultaneously attracted by the nuclei of both atoms. In the following sections, we will discuss how such bonds are described by valence bond theory and hybridization.

Valence bond theory describes a covalent bond as the overlap of half-filled atomic orbitals (each containing a single electron) that yield a pair of electrons shared between the two bonded atoms. We say that orbitals on two different atoms overlap when a portion of one orbital and a portion of a second orbital occupy the same region of space. According to valence bond theory, a covalent bond results when two conditions are met:

1. an orbital on one atom overlaps an orbital on a second atom and
2. the single electrons in each orbital combine to form an electron pair.

The mutual attraction between this negatively charged electron pair and the two atoms' positively charged nuclei serves to physically link the two atoms through a force we define as a covalent bond. The strength of a covalent bond depends on the extent of overlap of the orbitals involved. Orbitals that overlap extensively form bonds that are stronger than those that have less overlap.

The energy of the system depends on how much the orbitals overlap. Figure **4.3.1** 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. (A bond begins to form.) As the atoms move closer together, the overlap increases, so the attraction of the nuclei for the electrons

continues to increase (as do the repulsions among electrons and between the nuclei). At some specific distance between the atoms, which varies depending on the atoms involved, the energy reaches its lowest (most stable) value. This optimum distance between the two bonded nuclei is the bond distance between the two atoms. The bond is stable because at this point, the attractive and repulsive forces combine to create the lowest possible energy configuration. If the distance between the nuclei were to decrease further, the repulsions between nuclei and the repulsions as electrons are confined in closer proximity to each other would become stronger than the attractive forces. The energy of the system would then rise (making the system destabilized), as shown at the far left of Figure 4.3.1.

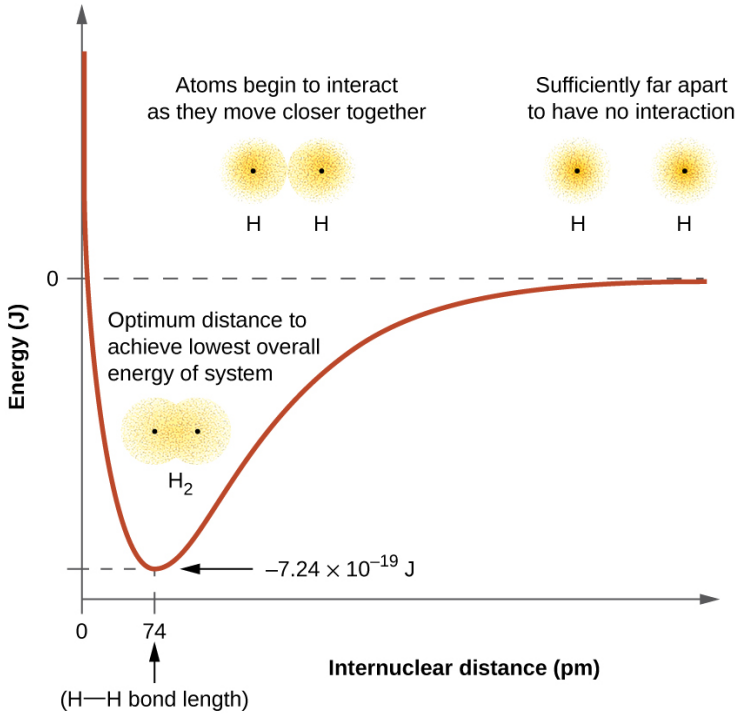


Figure* 4.3.1*: *The interaction of two hydrogen atoms changes as a function of distance. The energy of the system changes as the atoms interact. The lowest (most stable) energy occurs at a distance of 74 pm, which is the bond length observed for the H_2 molecule.*

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 4.3.1, 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 our earlier description of 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 4.3.1. 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 $H{-}CH_2C_6H_5$ (a common paint thinner) requires 375.5 kJ/mol.

Table* 4.3.1*: *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
C ≡ N	116.1	891	Cl–Cl	198.8	243

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 **4.3.2** 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.

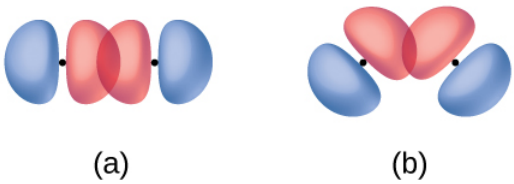


***Figure* 4.3.2:** *(a) The overlap of two p orbitals is greatest when the orbitals are directed end to end. (b) Any other arrangement results in less overlap. The dots indicate the locations of the nuclei.*

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 **4.3.3**. 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.

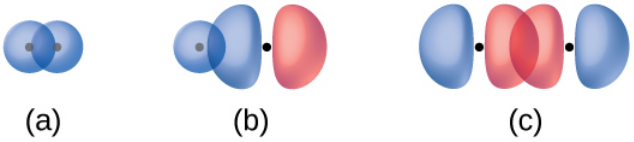


***Figure* 4.3.3**: *Sigma (σ) bonds form from the overlap of the following: (a) two s orbitals, (b) an s orbital and a p orbital, and (c) two p orbitals. The dots indicate the locations of the nuclei.*

A pi bond (π bond) is a type of covalent bond that results from the side-by-side overlap of two *p* orbitals, as illustrated in Figure **4.3.4**. 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.

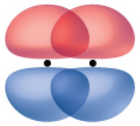
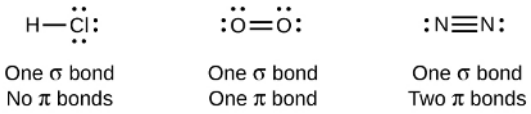


***Figure* 4.3.4**: *Pi (π) bonds form from the side-by-side overlap of two p orbitals. The dots indicate the location of the nuclei.*

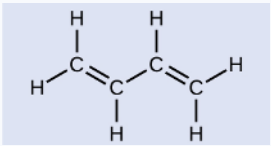
While all single bonds are σ bonds, multiple bonds consist of both σ and π bonds. As the Lewis structures suggest, O_2 contains a double bond, and N_2 contains a triple bond. The double bond consists of one σ bond and one π bond, and the triple bond consists of one σ bond and two π bonds. Between any 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 Table **4.3.1**, 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 4.3.1: 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

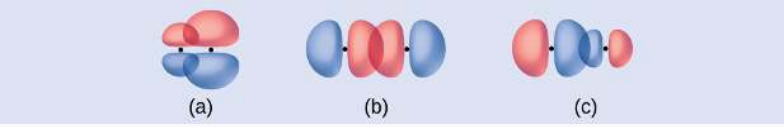
Solution

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 4.3.1

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.

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 **4.3.5**, 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.

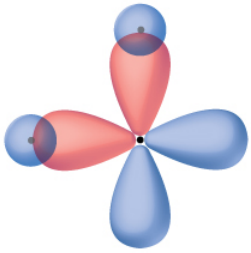


Figure* 4.3.5: The hypothetical overlap of two of the 2p orbitals on an oxygen atom (red) with the 1s orbitals of two hydrogen atoms (blue) would produce a bond angle of 90°. This is not consistent with experimental evidence.*[1]

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 **4.3.6**). 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.

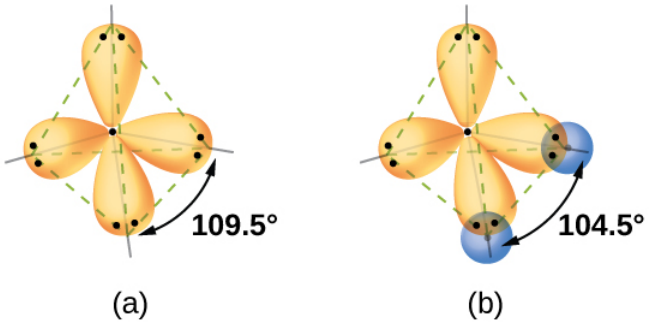


Figure* 4.3.6: (a) A water molecule has four regions of electron density, so VSEPR theory predicts a tetrahedral arrangement of hybrid orbitals. (b) Two of the hybrid orbitals on oxygen contain lone pairs, and the other two overlap with the 1s orbitals of hydrogen atoms to form the O–H bonds in H_2O. This description is more consistent with the experimental structure.*

The following ideas are important in understanding hybridization:

1. Hybrid orbitals do not exist in isolated atoms. They are formed only in covalently bonded atoms.
2. Hybrid orbitals have shapes and orientations that are very different from those of the atomic orbitals in isolated atoms.
3. A set of hybrid orbitals is generated by combining atomic orbitals. The number of hybrid orbitals in a set is equal to the number of atomic orbitals that were combined to produce the set.
4. All orbitals in a set of hybrid orbitals are equivalent in shape and energy.
5. The type of hybrid orbitals formed in a bonded atom depends on its electron-pair geometry as predicted by the VSEPR theory.
6. Hybrid orbitals overlap to form σ bonds. Unhybridized orbitals overlap to form π bonds.

In the following sections, we shall discuss the common types of hybrid orbitals.

sp Hybridization

The beryllium atom in a gaseous $BeCl_2$ molecule is an example of a central atom with no lone pairs of electrons in a linear arrangement of three atoms. There are two regions of valence electron density in the $BeCl_2$ molecule that correspond to the two covalent Be–Cl bonds. To accommodate these two electron domains, two of the Be atom's four valence orbitals will mix to yield two hybrid orbitals. This hybridization process involves mixing of the valence *s* orbital with one of the valence *p* orbitals to yield two equivalent *sp* hybrid orbitals that are oriented in a linear geometry (Figure **4.3.7**). 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.

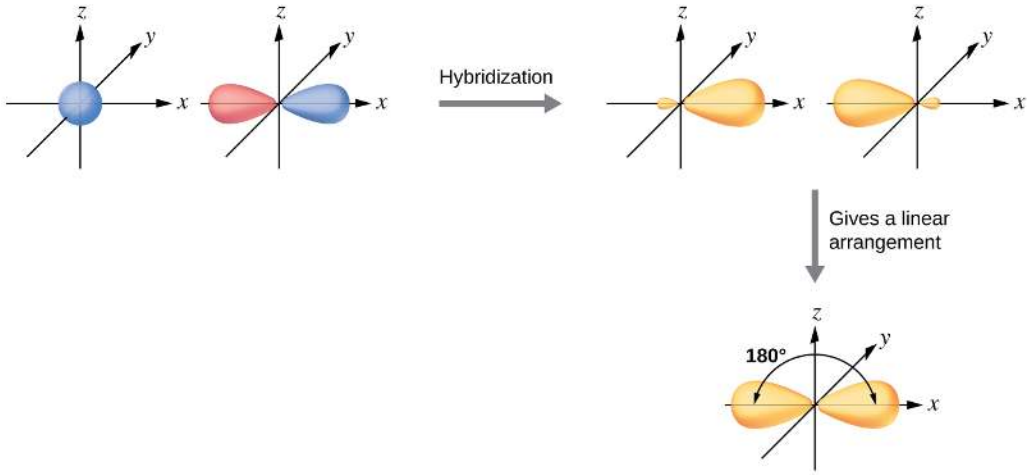


***Figure* 4.3.7:** *Hybridization of an s orbital (blue) and a p orbital (red) of the same atom produces two sp hybrid orbitals (yellow). Each hybrid orbital is oriented primarily in just one direction. Note that each sp orbital contains one lobe that is significantly larger than the other. The set of two sp orbitals are oriented at 180°, which is consistent with the geometry for two domains.*

We illustrate the electronic differences in an isolated Be atom and in the bonded Be atom in the orbital energy-level diagram in Figure **4.3.8**. 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.

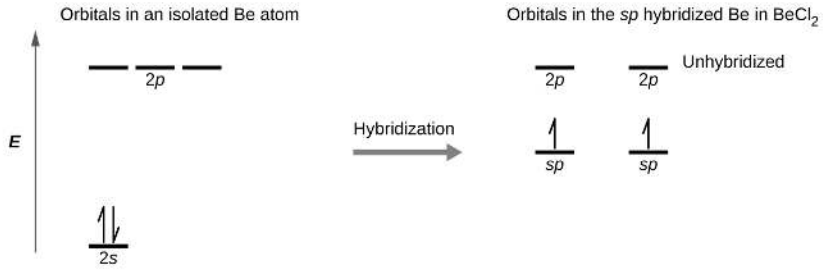


***Figure* 4.3.8:** *This orbital energy-level diagram shows the sp hybridized orbitals on Be in the linear $BeCl_2$ molecule. Each of the two sp hybrid orbitals holds one electron and is thus half filled and available for bonding via overlap with a Cl 3p orbital.*

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.

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 **4.3.9**).

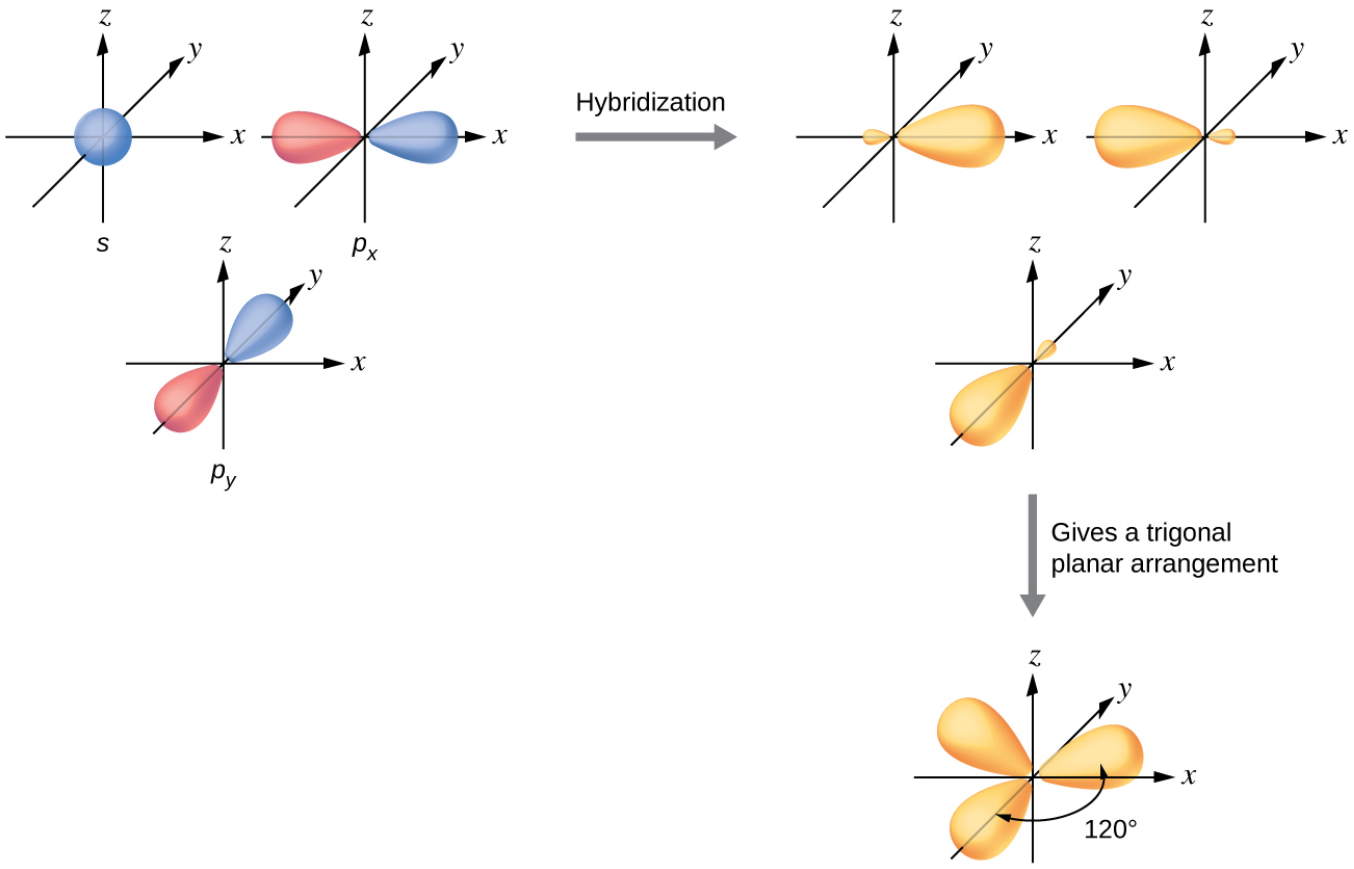


***Figure* 4.3.9:** *The hybridization of an s orbital (blue) and two p orbitals (red) produces three equivalent sp^2 hybridized orbitals (yellow) oriented at 120° with respect to each other. The remaining unhybridized p orbital is not shown here, but is located along the z axis.*

Although quantum mechanics yields the "plump" orbital lobes as depicted in Figure **4.3.5**, sometimes for clarity these orbitals are drawn thinner and without the minor lobes, as in Figure **4.3.10**, 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.

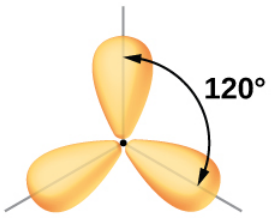


***Figure* 4.3.10:** *This alternate way of drawing the trigonal planar sp^2 hybrid orbitals is sometimes used in more crowded figures.*

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 **4.3.11**).

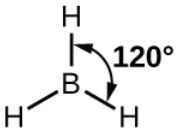


Figure* 4.3.11*: *BH_3 is an electron-deficient molecule with a trigonal planar structure.*

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 **4.3.12**. 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.

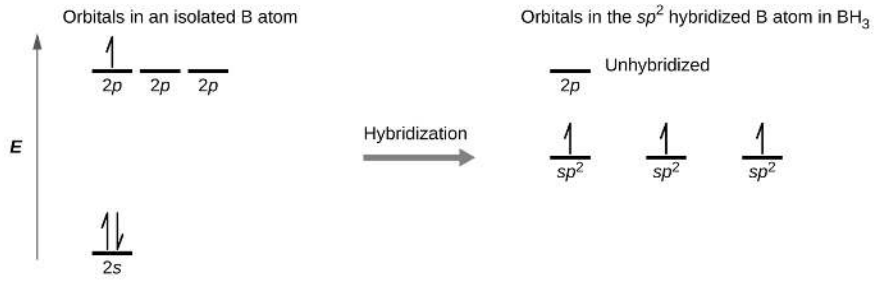


Figure* 4.3.12*: *In an isolated B atom, there are one 2s and three 2p valence orbitals. When boron is in a molecule with three regions of electron density, three of the orbitals hybridize and create a set of three sp^2 orbitals and one unhybridized 2p orbital. The three half-filled hybrid orbitals each overlap with an orbital from a hydrogen atom to form three σ bonds in BH_3.*

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 **4.3.13**), 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.

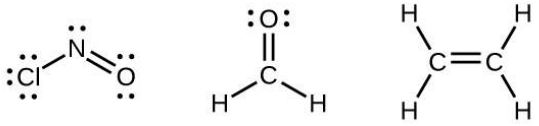


Figure* 4.3.13*: *The central atom(s) in each of the structures shown contain three regions of electron density and are sp^2 hybridized. As we know from the discussion of VSEPR theory, a region of electron density contains all of the electrons that point in one direction. A lone pair, an unpaired electron, a single bond, or a multiple bond would each count as one region of electron density.*

sp^3 Hybridization

The valence orbitals of an atom surrounded by a tetrahedral arrangement of bonding pairs and lone pairs consist of a set of four sp^3 hybrid orbitals. The hybrids result from the mixing of one *s* orbital and all three *p* orbitals that produces four identical sp^3 hybrid orbitals (Figure **4.3.14**). Each of these hybrid orbitals points toward a different corner of a tetrahedron.

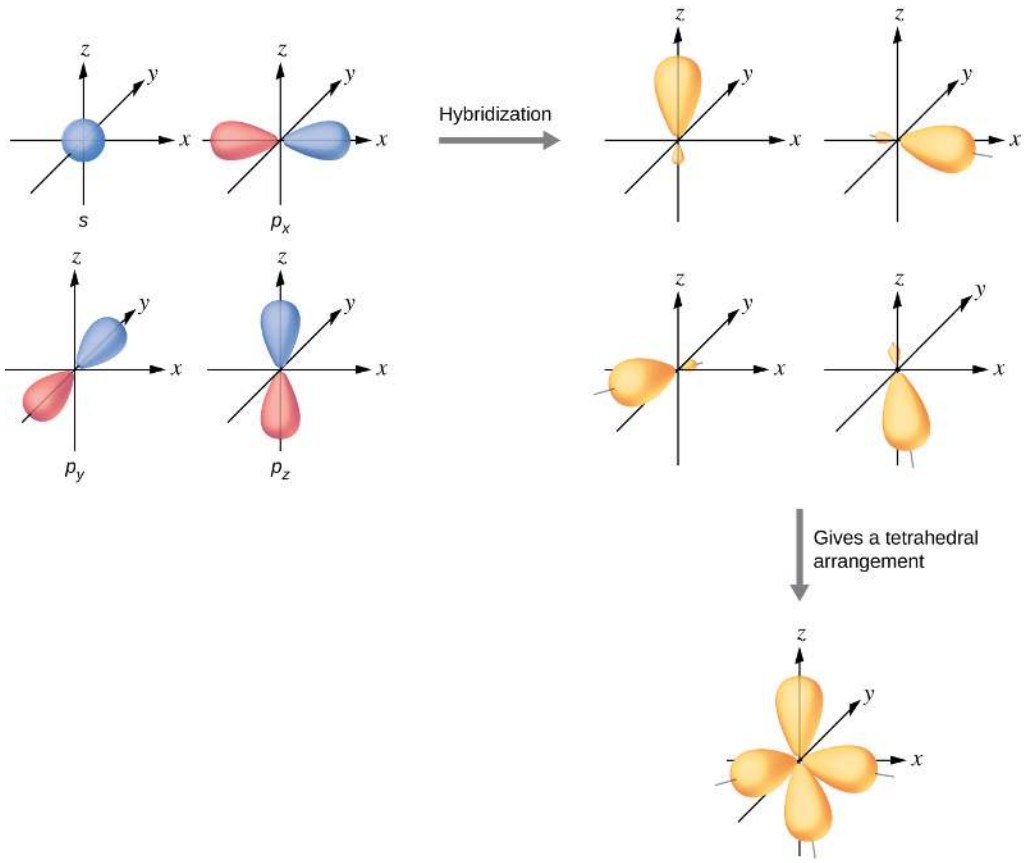


Figure* 4.3.14*: *The hybridization of an s orbital (blue) and three p orbitals (red) produces four equivalent sp^3 hybridized orbitals (yellow) oriented at 109.5° with respect to each other.*

A 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 **4.3.15**. 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.

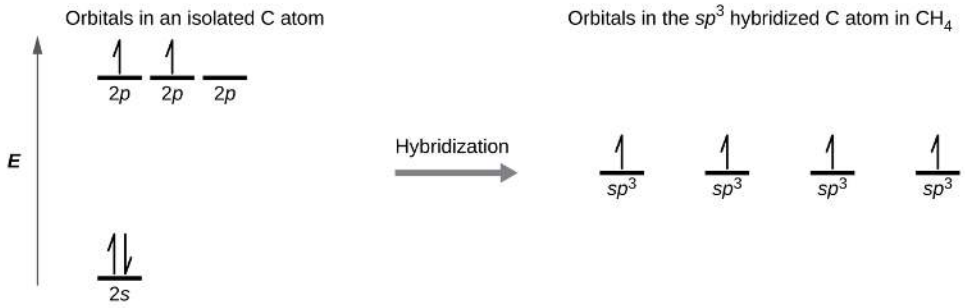


Figure* 4.3.15*: *The four valence atomic orbitals from an isolated carbon atom all hybridize when the carbon bonds in a molecule like CH_4 with four regions of electron density. This creates four equivalent sp^3 hybridized orbitals. Overlap of each of the hybrid orbitals with a hydrogen orbital creates a C–H σ bond.*

In a methane molecule, the 1*s* orbital of each of the four hydrogen atoms overlaps with one of the four sp^3 orbitals of the carbon atom to form a sigma (σ) bond. This results in the formation of four strong, equivalent covalent bonds between the carbon atom and each of the hydrogen atoms to produce the methane molecule, CH_4.

The structure of ethane, C_2H_6, is similar to that of methane in that each carbon in ethane has four neighboring atoms arranged at the corners of a tetrahedron—three hydrogen atoms and one carbon atom (Figure **4.3.10**). 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 **4.3.16**. 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.

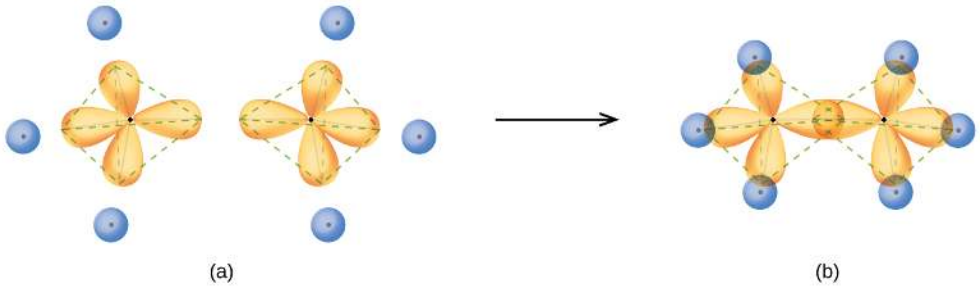


Figure* 4.3.16*: *(a) In the ethane molecule, C_2H_6, each carbon has four sp^3 orbitals. (b) These four orbitals overlap to form seven σ bonds.*

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.

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 **4.3.16**. 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 **4.3.17** that corresponds to this geometry.

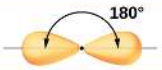
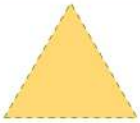
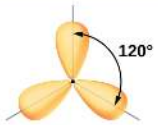
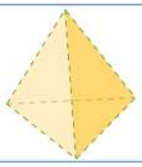
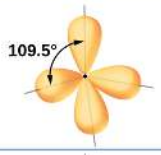
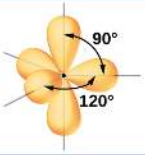
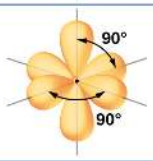
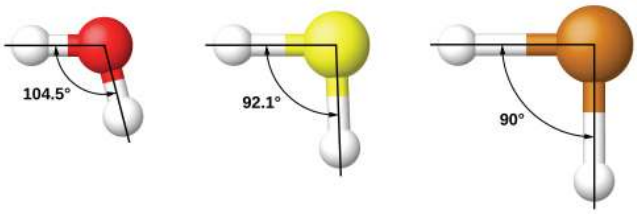
Regions of Electron Density	Arrangement		Hybridization	
2		linear	*sp*	
3		trigonal planar	sp^2	
4		tetrahedral	sp^3	
5		trigonal bipyramidal	sp^3d	
6		octahedral	sp^3d^2	

***Figure* 4.3.17**: 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.

> *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.



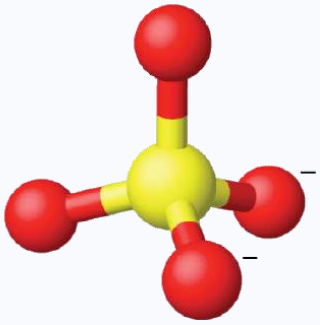
For example, we have discussed the H–O–H bond angle in H_2O, 104.5°, which is more consistent with sp^3 hybrid orbitals (109.5°) on the central atom than with 2*p* orbitals (90°). Sulfur is in the same group as oxygen, and H_2S has a similar Lewis structure. However, it has a much smaller bond angle (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 4.3.2: 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.



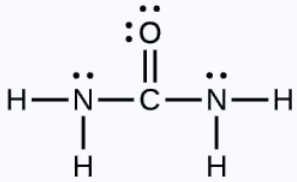
The hybridization is sp^3. since the carbon has a tetrahedral geometry (Figure **4.3.17**).

Example 4.3.3: 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

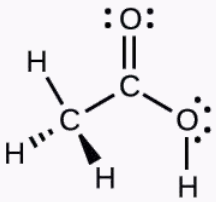


The nitrogen atoms are surrounded by four regions of electron density, which arrange themselves in a tetrahedral electron-pair geometry. The hybridization in a tetrahedral arrangement is sp^3 (Figure **4.3.17**). This is the hybridization of the nitrogen atoms in urea.

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 **4.3.17**), which is the hybridization of the carbon atom in urea.

Exercise 4.3.2

Acetic acid, $H_3CC(O)OH$, is the molecule that gives vinegar its odor and sour taste. What is the hybridization of the two carbon atoms in acetic acid?



Answer

$H_3\underline{C}$, sp^3; $\underline{C}(O)OH$, sp^2

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Summary



Video* 4.3.2*: *An overview of electron involvment in bonding.* *Good luck getting this tune out of your head.*

Valence bond theory describes bonding as a consequence of the overlap of two separate atomic orbitals on different atoms that creates a region with one pair of electrons shared between the two atoms. When the orbitals overlap along an axis containing the nuclei, they form a σ bond. When they overlap in a fashion that creates a node along this axis, they form a π bond.

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. Pi (π) bonds are formed from unhybridized atomic orbitals (*p* or *d* orbitals).

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.

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

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

***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

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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4.3.1: Valence Bond Theory and Hybrid Orbitals (Problems)

PROBLEM 4.3.1.1

Explain how σ and π bonds are similar and how they are different.

Answer

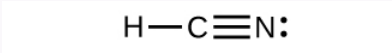
Similarities: Both types of bonds result from overlap of atomic orbitals on adjacent atoms and contain a maximum of two electrons. **Differences**: σ bonds are stronger and result from end-to-end overlap and all single bonds are σ bonds; π bonds between the same two atoms are weaker because they result from side-by-side overlap, and multiple bonds contain one or more π bonds (in addition to a σ bond).

PROBLEM 4.3.1.2

How many σ and π bonds are present in the molecule HCN?

Answer

H–C≡N has two σ (H–C and C–N) and two π (making the CN triple bond).

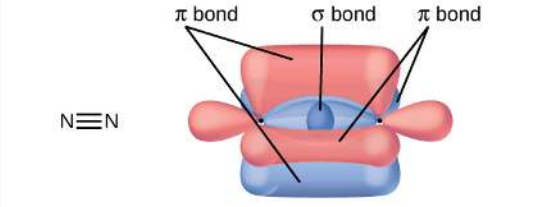


PROBLEM 4.3.1.3

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?

Answer

No, two of the *p* orbitals (one on each N) will be oriented end-to-end and will form a σ bond.



PROBLEM 4.3.1.4

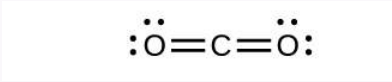
Draw the Lewis structures for CO_2 and CO, and predict the number of σ and π bonds for each molecule.

a. CO_2

b. CO

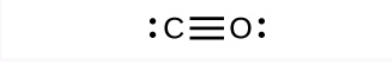
Answer a

2 σ 2 π



Answer b

1 σ 2 π



PROBLEM 4.3.1.5

Why is the concept of hybridization required in valence bond theory?

Answer

Hybridization is introduced to explain the geometry of bonding orbitals in valance bond theory.

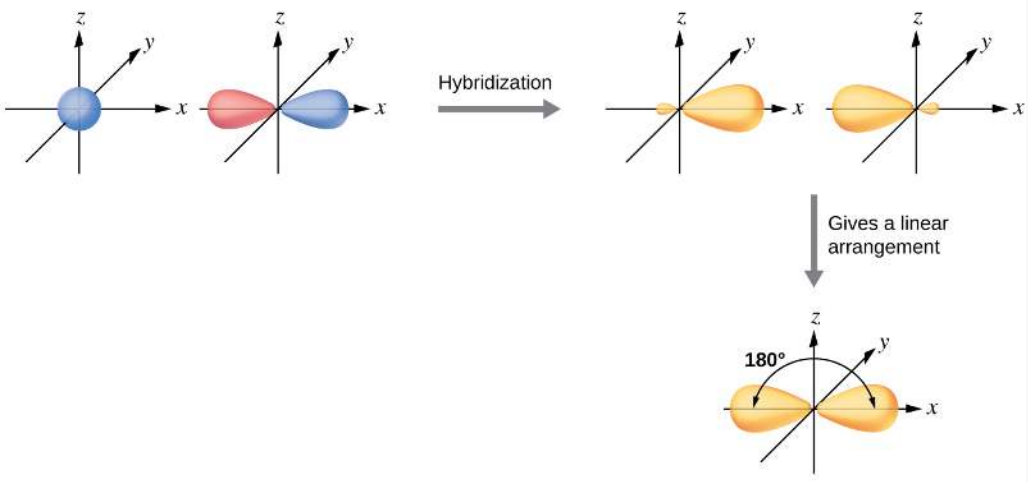
PROBLEM 4.3.1.6

Give the shape that describes each hybrid orbital set:

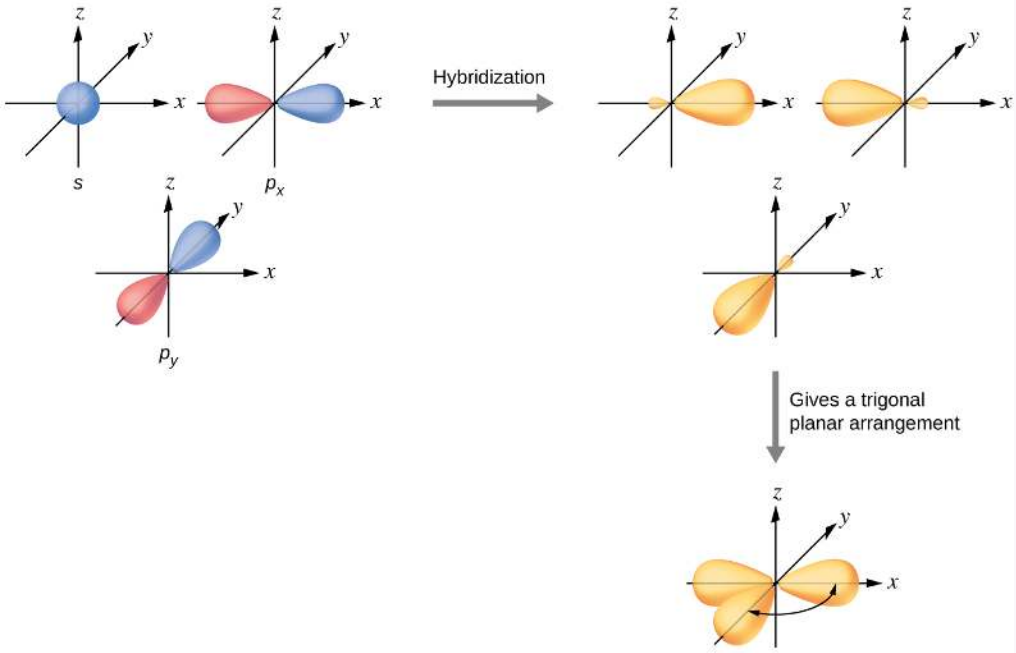
(a) sp^2

(b) sp

Answer a



Answer b



PROBLEM 4.3.1.7

What is the hybridization of the central atom in each of the following?

(a) BeH_2

(b) PO_4^{3-}

Answer a

linear

Answer b

tetrahedral

PROBLEM 4.3.1.8

A molecule with the formula AB_3 could have one of two different shapes. Give the shape and the hybridization of the central A atom for each.

Answer

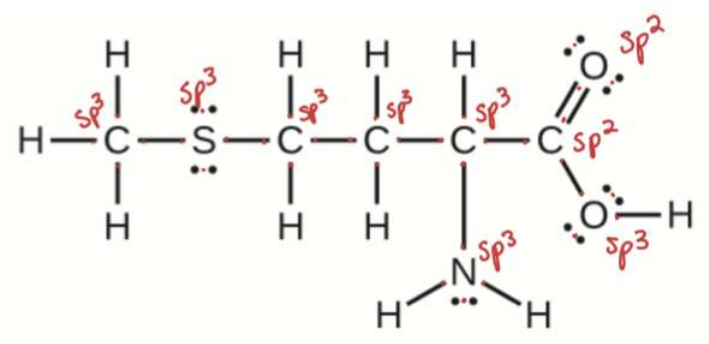
trigonal planar, sp^2; trigonal pyramidal (one lone pair on A) sp^3

PROBLEM 4.3.1.9

Methionine, $CH_3SCH_2CH_2CH(NH_2)CO_2H$, is an amino acid found in proteins. Based on the 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.

Answer



Click here to see a video of the solution



PROBLEM 4.3.1.10

Two important industrial chemicals, ethene, C_2H_4, and propene, C_3H_6, are produced by the steam (or thermal) cracking process:

$$2\,C_3H_8(g) \longrightarrow C_2H_4(g) + C_3H_6(g) + CH_4(g) + H_2(g)$$

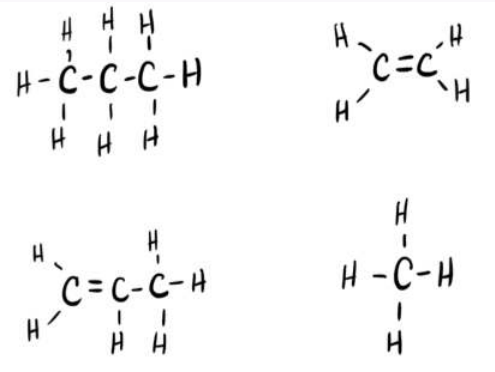
For each of the four carbon compounds, do the following:

(a) Draw a Lewis structure.

(b) Predict the geometry about the carbon atom.

(c) Determine the hybridization of each type of carbon atom.

Answer a



Answer b

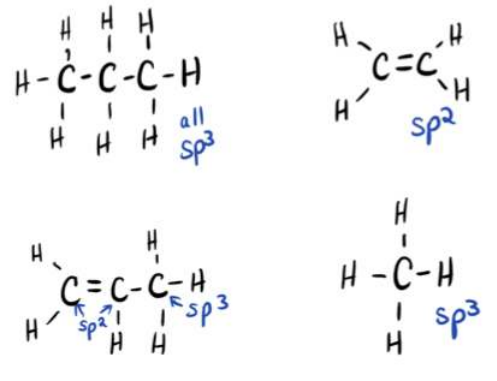
C_3H_8: tetrahedral

C_2H_4: trigonal planar

C_3H_6: trigonal planar (1&2) and tetrahedral (3)

CH_4: tetrahedral

Answer c



Click here to see a video of the solution

PROBLEM 4.3.1.11

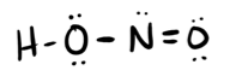
Consider nitrous acid, HNO_2 (HONO).

(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?

Answer a



Answer b

Electron pair: O: tetrahedral, N: trigonal planar

Molecular geometry: O: bent (109), N: trigonal planar

Answer c

O: sp^3

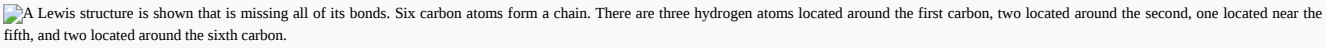
N: sp^2

Click here to see a video of the solution

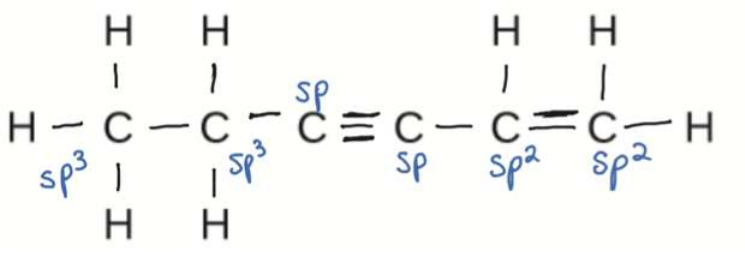


PROBLEM 4.3.1.12

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.

Answer



Click here to see a video of the solution



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).

- Adelaide Clark, Oregon Institute of Technology

Feedback

Think one of the answers above is wrong? Let us know here.

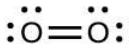
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4.4: Bond Types and Molecular Orbital Theory

Skills to Develop

- 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

For almost every covalent molecule that exists, we can now draw the Lewis structure, predict the electron-pair geometry, predict the molecular geometry, and come close to predicting bond angles. However, one of the most important molecules we know, the oxygen molecule O_2, presents a problem with respect to its Lewis structure. We would write the following Lewis structure for O_2:



This electronic structure adheres to all the rules governing Lewis theory. There is an O=O double bond, and each oxygen atom has eight electrons around it. However, this picture is at odds with the magnetic behavior of oxygen. By itself, O_2 is not magnetic, but it is attracted to magnetic fields. Thus, when we pour liquid oxygen past a strong magnet, it collects between the poles of the magnet and defies gravity. Such attraction to a magnetic field is called paramagnetism, and it arises in molecules that have unpaired electrons. And yet, the Lewis structure of O_2 indicates that all electrons are paired. How do we account for this discrepancy?

Magnetic susceptibility measures the force experienced by a substance in a magnetic field. When we compare the weight of a sample to the weight measured in a magnetic field (Figure **4.4.1**), 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.

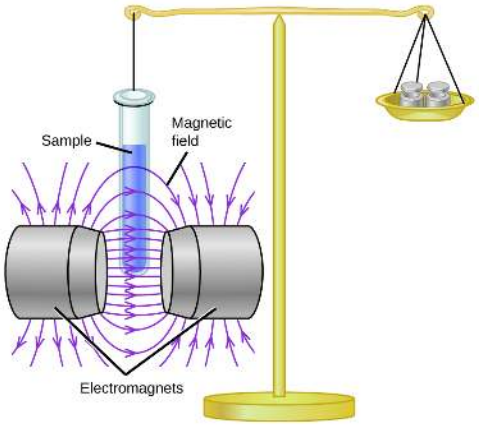


Figure* 4.4.1*: *A Gouy balance compares the mass of a sample in the presence of a magnetic field with the mass with the electromagnet turned off to determine the number of unpaired electrons in a sample.*

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* 4.4.1**: *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 (https://www.youtube.com/watch?v=A1vyB-O5i6E)*

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 **4.4.1** summarizes the main points of the two complementary bonding theories. Both theories provide different, useful ways of describing molecular structure.

***Table* 4.4.1**: *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 **4.4.2**). 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.

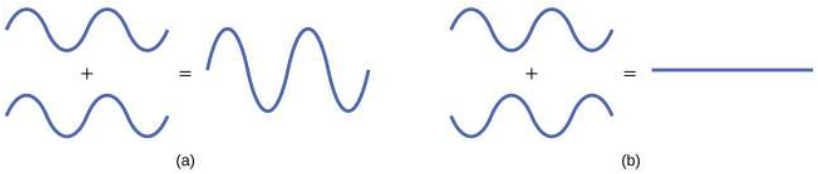


***Figure* 4.4.2:** *(a) When in-phase waves combine, constructive interference produces a wave with greater amplitude. (b) When out-of-phase waves combine, destructive interference produces a wave with less (or no) amplitude.*

There are two types of molecular orbitals that can form from the overlap of two atomic *s* orbitals on adjacent atoms. The two types are illustrated in Figure 8.4.3. 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.

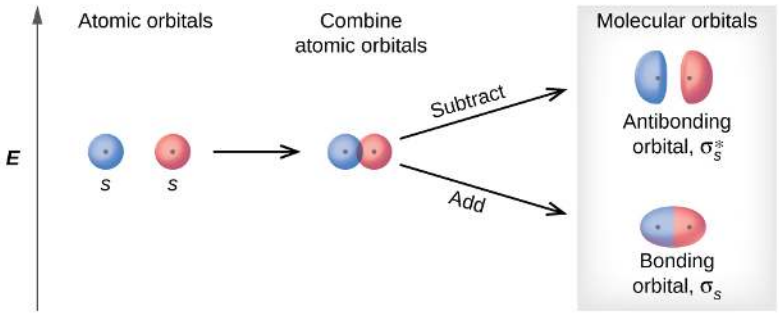


***Figure* 4.4.3:** *Sigma (σ) and sigma-star (σ*) molecular orbitals are formed by the combination of two s atomic orbitals. The plus (+) signs indicate the locations of nuclei.*

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 **4.4.4**). 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.

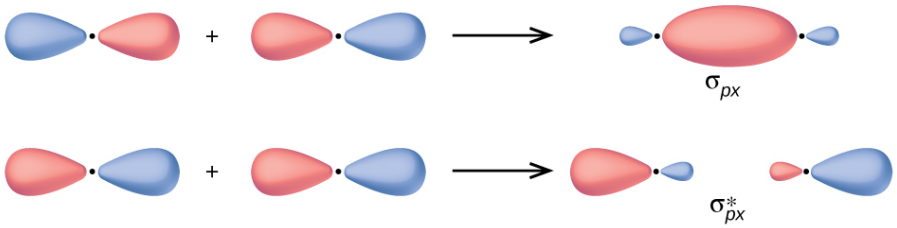


Figure* 4.4.4*: Combining wave functions of two *p* atomic orbitals along the internuclear axis creates two molecular orbitals, σ_p and σ^*_p.

The side-by-side overlap of two *p* orbitals gives rise to a pi (π) bonding molecular orbital and a π* antibonding molecular orbital, as shown in Figure 4.4.5. 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.

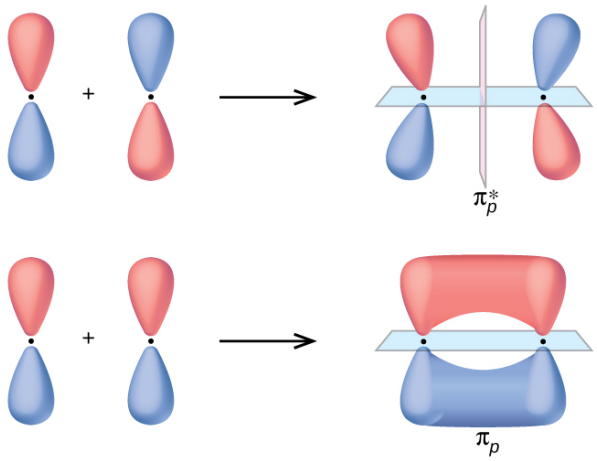
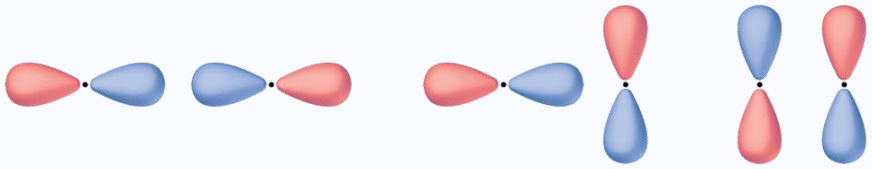


Figure* 4.4.5*: *Side-by-side overlap of each two p orbitals results in the formation of two π molecular orbitals. Combining the out-of-phase orbitals results in an antibonding molecular orbital with two nodes. One contains the internuclear axis, and one is perpendicular to the axis. Combining the in-phase 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.*

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 4.4.1

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.



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 4.4.1

Label the molecular orbital shown as σ or π, bonding or antibonding and indicate where the node occurs.



Answer

The orbital is located along the internuclear axis, so it is a σ orbital. There is a node bisecting the internuclear axis, so it is an antibonding orbital.



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 **4.4.6**). 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.

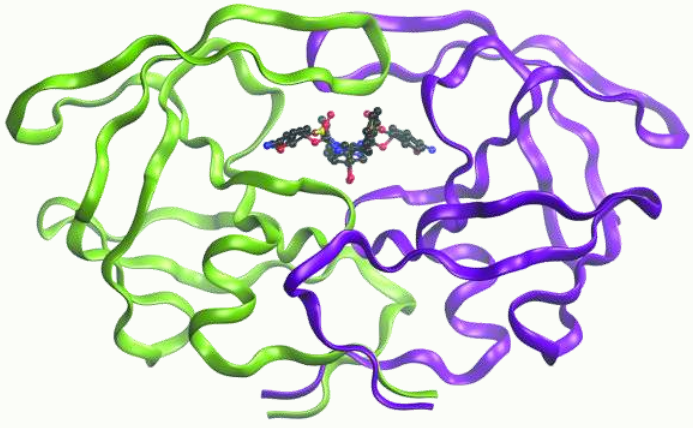


***Figure* 4.4.6:** *The molecule shown, HIV-1 protease, is an important target for pharmaceutical research. By designing molecules that bind to this protein, scientists are able to drastically inhibit the progress of the disease.*

Molecular Orbital Energy Diagrams

The relative energy levels of atomic and molecular orbitals are typically shown in a molecular orbital diagram (Figure **4.4.7**). 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*).

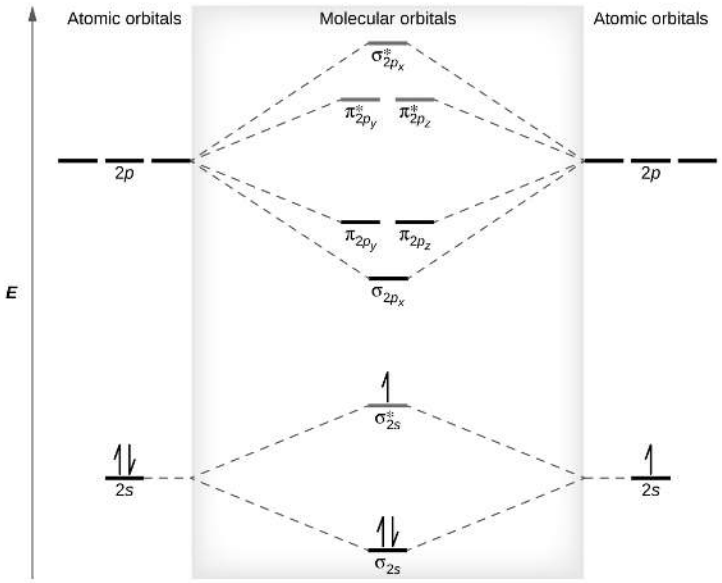


***Figure* 4.4.7**: *This is the molecular orbital diagram for the homonuclear diatomic* Be_2^+*, showing the molecular orbitals of the valence shell only. The molecular orbitals are filled in the same manner as atomic orbitals, using the Aufbau principle and Hund's rule.*

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 **4.4.7**). 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.

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:

$$\text{bond order} = \frac{(\text{number of bonding electrons}) - (\text{number of antibonding electrons})}{2} \tag{4.4.1}$$

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.

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 **4.4.8**) in which a single upward arrow indicates one electron in an orbital, and two (upward and downward) arrows indicate two electrons of opposite spin.

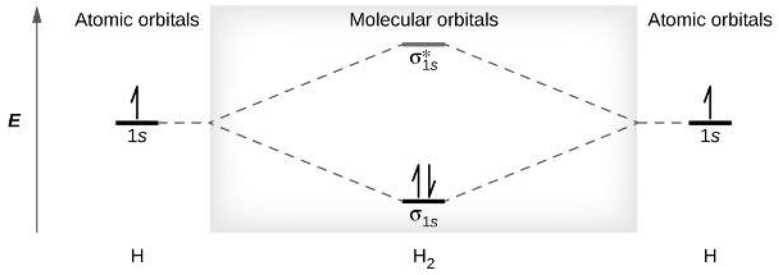


***Figure* 4.4.8**:*The molecular orbital energy diagram predicts that H_2 will be a stable molecule with lower energy than the separated atoms.*

PREVIEW: Band Theory in Extended Systems

When two identical atomic orbitals on different atoms combine, two molecular orbitals result (e.g., H_2 in Figure **4.4.8**). 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 **4.4.9**) shows the bands for three important classes of materials: insulators, semiconductors, and conductors.

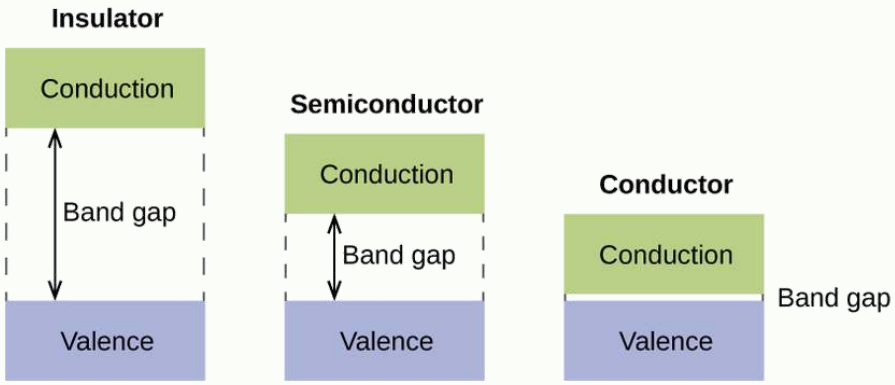


***Figure* 4.4.9**: *Molecular orbitals in solids are so closely spaced that they are described as bands. The valence band is lower in energy and the conduction band is higher in energy. The type of solid is determined by the size of the "band gap" between the valence and conduction bands. Only a very small amount of energy is required to move electrons from the valence band to the conduction band in a conductor, and so they conduct electricity well. In an insulator, the band gap is large, so that very few electrons move, and they are poor conductors of electricity. Semiconductors are in between: they conduct electricity better than insulators, but not as well as conductors.*

In order to conduct electricity, electrons must move from the filled valence band to the empty conduction band where they can move throughout the solid. The size of the band gap, or the energy difference between the top of the valence band and the bottom of the conduction band, determines how easy it is to move electrons between the bands. Only a small amount of energy is required in a conductor because the band gap is very small. This small energy difference is "easy" to overcome, so they are good conductors of electricity. In an insulator, the band gap is so "large" that very few electrons move into the conduction band; as a result, insulators are poor conductors of electricity. Semiconductors conduct electricity when "moderate" amounts of energy are provided to move electrons out of the valence band and into the conduction band. Semiconductors, such as silicon, are found in many electronics.

Semiconductors are used in devices such as computers, smartphones, and solar cells. Solar cells produce electricity when light provides the energy to move electrons out of the valence band. The electricity that is generated may then be used to power a light or tool, or it can be stored for later use by charging a battery. As of December 2014, up to 46% of the energy in sunlight could be converted into electricity using solar cells.

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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4.4.1: Bond Types and Molecular Orbital Theory (Problems)

PROBLEM 4.4.1.1

How are the following similar, and how do they differ?

(a) σ molecular orbitals and π molecular orbitals

(b) bonding orbitals and antibonding orbitals

Answer 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

Answer b

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.

PROBLEM 4.4.1.2

Can a molecule with an odd number of electrons ever be diamagnetic? Explain why or why not.

Answer

An odd number of electrons can never be paired, regardless of the arrangement of the molecular orbitals. It will always be paramagnetic.

PROBLEM 4.4.1.3

Can a molecule with an even number of electrons ever be paramagnetic? Explain why or why not.

Answer

Yes, you could potentially have unpaired electrons in each orbital

PROBLEM 4.4.1.4

Why are bonding molecular orbitals lower in energy than the parent atomic orbitals?

Answer

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.

PROBLEM 4.4.1.5

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.

Answer

The pairing of the two bonding electrons lowers the energy of the system relative to the energy of the nonbonded electrons.

Have a video solution request?

Let your professors know here.

***Please know that you are helping future students - videos will be made in time for next term's class.

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CHAPTER OVERVIEW

5: Intermolecular Forces

Unit Objectives

- Distinguish between adhesive and cohesive forces
- Define viscosity, surface tension, and capillary rise
- Describe the roles of intermolecular attractive forces in each of these properties/phenomena
- Define phase transitions and phase transition temperatures
- Explain the relation between phase transition temperatures and intermolecular attractive forces
- Explain the construction and use of a typical phase diagram
- Use phase diagrams to identify stable phases at given temperatures and pressures, and to describe phase transitions result from changes in these properties

5.1: Intermolecular Forces

5.1.1: Intermolecular Forces (Problems)

5.2: Soap

5.3: Surface Tension, Viscosity, and Capillary Action

5.3.1: Surface Tension, Viscosity, and Capillary Action (Problems)

5.4: Vapor Pressure

5.4.1: Vapor Pressure (Problems)

5.5: Heating Curves and Phase Changes

5.5.1: Heating Curves and Phase Changes (Problems)

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5.1: Intermolecular Forces

Skills to Develop

- Describe the types of intermolecular forces possible between atoms or molecules in condensed phases (dispersion forces, dipole-dipole attractions, and hydrogen bonding)
- Identify the types of intermolecular forces experienced by specific molecules based on their structures
- Explain the relation between the intermolecular forces present within a substance and the temperatures associated with changes in its physical state

The great distances between atoms and molecules in a gaseous phase, and the corresponding absence of any significant interactions between them, allows for simple descriptions of many physical properties that are the same for all gases, regardless of their chemical identities. As described last term when we explored gases, this situation changes at high pressures and low temperatures —conditions that permit the atoms and molecules to interact to a much greater extent.



Figure* 5.1.1*: *Solid carbon dioxide ("dry ice", left) sublimes vigorously when placed in a liquid (right), cooling the liquid and generating a fog of condensed water vapor above the cylinder. (credit: modification of work by Paul Flowers)*

In the liquid and solid states, these interactions are of considerable strength and play an important role in determining a number of physical properties that *do* depend on the chemical identity of the substance. In this chapter, the nature of these interactions and their effects on various physical properties of liquid and solid phases will be examined.

As was the case for gaseous substances, the kinetic molecular theory may be used to explain the behavior of solids and liquids. In the following description, the term *particle* will be used to refer to an atom, molecule, or ion. Note that we will use the popular phrase "intermolecular attraction" to refer to attractive forces between the particles of a substance, regardless of whether these particles are molecules, atoms, or ions.

Consider these two aspects of the molecular-level environments in solid, liquid, and gaseous matter:

- Particles in a solid are tightly packed together and often arranged in a regular pattern; in a liquid, they are close together with no regular arrangement; in a gas, they are far apart with no regular arrangement.
- Particles in a solid vibrate about fixed positions and do not generally move in relation to one another; in a liquid, they move past each other but remain in essentially constant contact; in a gas, they move independently of one another except when they collide.

The differences in the properties of a solid, liquid, or gas reflect the strengths of the attractive forces between the atoms, molecules, or ions that make up each phase. The phase in which a substance exists depends on the relative extents of its intermolecular forces (IMFs) and the kinetic energies (KE) of its molecules. IMFs are the various forces of attraction that may exist between the atoms and molecules of a substance due to electrostatic phenomena, as will be detailed in this module. These forces serve to hold particles close together, whereas the particles' KE provides the energy required to overcome the attractive forces and thus increase the distance between particles. Figure **5.1.2** illustrates how changes in physical state may be induced by changing the temperature, hence, the average KE, of a given substance.

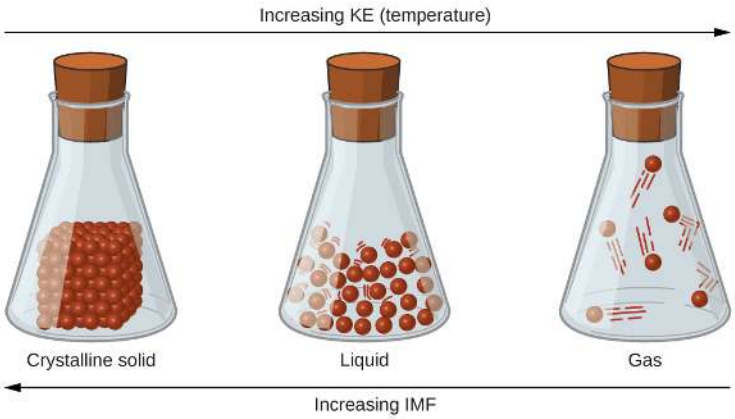


Figure* 5.1.2: Transitions between solid, liquid, and gaseous states of a substance occur when conditions of temperature or pressure favor the associated changes in intermolecular forces. (Note: The space between particles in the gas phase is much greater than shown.)*

As an example of the processes depicted in this figure, consider a sample of water. When gaseous water is cooled sufficiently, the attractions between H_2O molecules will be capable of holding them together when they come into contact with each other; the gas condenses, forming liquid H_2O. For example, liquid water forms on the outside of a cold glass as the water vapor in the air is cooled by the cold glass, as seen in Figure **5.1.2**.



Figure* 5.1.3: Condensation forms when water vapor in the air is cooled enough to form liquid water, such as (a) on the outside of a cold beverage glass or (b) in the form of fog. (credit a: modification of work by Jenny Downing; credit b: modification of work by Cory Zanker)*

We can also liquefy many gases by compressing them, if the temperature is not too high. The increased pressure brings the molecules of a gas closer together, such that the attractions between the molecules become strong relative to their KE. Consequently, they form liquids. Butane, C_4H_{10}, is the fuel used in disposable lighters and is a gas at standard temperature and pressure. Inside the lighter's fuel compartment, the butane is compressed to a pressure that results in its condensation to the liquid state, as shown in Figure **5.1.4**.



Figure* 5.1.4*: *Gaseous butane is compressed within the storage compartment of a disposable lighter, resulting in its condensation to the liquid state. (credit: modification of work by "Sam-Cat"/Flickr)*

Finally, if the temperature of a liquid becomes sufficiently low, or the pressure on the liquid becomes sufficiently high, the molecules of the liquid no longer have enough KE to overcome the IMF between them, and a solid forms. A more thorough discussion of these and other changes of state, or phase transitions, is provided in a later module of this chapter.

Forces between Molecules

Under appropriate conditions, the attractions between all gas molecules will cause them to form liquids or solids. This is due to intermolecular forces, not *intra*molecular forces. *Intra*molecular forces are those *within* the molecule that keep the molecule together, for example, the bonds between the atoms. *Inter*molecular forces are the attractions *between* molecules, which determine many of the physical properties of a substance. Figure 5.1.5 illustrates these different molecular forces. The strengths of these attractive forces vary widely, though usually the IMFs between small molecules are weak compared to the intramolecular forces that bond atoms together within a molecule. For example, to overcome the IMFs in one mole of liquid HCl and convert it into gaseous HCl requires only about 17 kilojoules. However, to break the covalent bonds between the hydrogen and chlorine atoms in one mole of HCl requires about 25 times more energy—430 kilojoules.

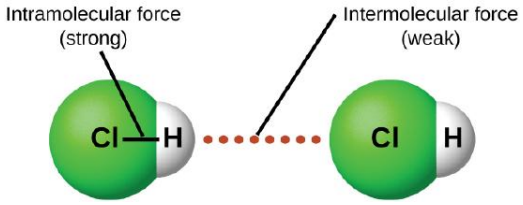


Figure* 5.1.5*: *Intramolecular forces keep a molecule intact. Intermolecular forces hold multiple molecules together and determine many of a substance's properties.*

All of the attractive forces between neutral atoms and molecules are known as van der Waals forces, although they are usually referred to more informally as intermolecular attraction. We will consider the various types of IMFs in the next three sections of this module.

Dispersion Forces

One of the three van der Waals forces is present in all condensed phases, regardless of the nature of the atoms or molecules composing the substance. This attractive force is called the London dispersion force in honor of German-born American physicist Fritz London who, in 1928, first explained it. This force is often referred to as simply the dispersion force. Because the electrons of an atom or molecule are in constant motion (or, alternatively, the electron's location is subject to quantum-mechanical variability), at any moment in time, an atom or molecule can develop a temporary, instantaneous dipole if its electrons are distributed asymmetrically. The presence of this dipole can, in turn, distort the electrons of a neighboring atom or molecule, producing an induced dipole. These two rapidly fluctuating, temporary dipoles thus result in a relatively weak electrostatic attraction between the species—a so-called dispersion force like that illustrated in Figure 5.1.6.

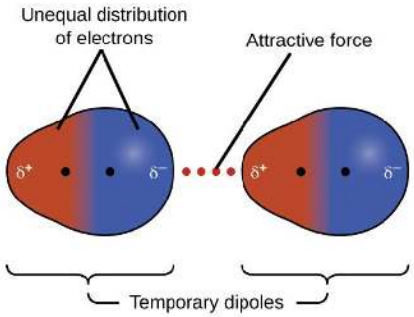


***Figure* 5.1.6**: *Dispersion forces result from the formation of temporary dipoles, as illustrated here for two nonpolar diatomic molecules.*

Dispersion forces that develop between atoms in different molecules can attract the two molecules to each other. The forces are relatively weak, however, and become significant only when the molecules are very close. Larger and heavier atoms and molecules exhibit stronger dispersion forces than do smaller and lighter atoms and molecules. F_2 and Cl_2 are gases at room temperature (reflecting weaker attractive forces); Br_2 is a liquid, and I_2 is a solid (reflecting stronger attractive forces). Trends in observed melting and boiling points for the halogens clearly demonstrate this effect, as seen in Table **5.1.1**.

***Table* 5.1.1**: *Melting and Boiling Points of the Halogens*

Halogen	Molar Mass	Atomic Radius	Melting Point	Boiling Point
fluorine, F_2	38 g/mol	72 pm	53 K	85 K
chlorine, Cl_2	71 g/mol	99 pm	172 K	238 K
bromine, Br_2	160 g/mol	114 pm	266 K	332 K
iodine, I_2	254 g/mol	133 pm	387 K	457 K
astatine, At_2	420 g/mol	150 pm	575 K	610 K

The increase in melting and boiling points with increasing atomic/molecular size may be rationalized by considering how the strength of dispersion forces is affected by the electronic structure of the atoms or molecules in the substance. In a larger atom, the valence electrons are, on average, farther from the nuclei than in a smaller atom. Thus, they are less tightly held and can more easily form the temporary dipoles that produce the attraction. The measure of how easy or difficult it is for another electrostatic charge (for example, a nearby ion or polar molecule) to distort a molecule's charge distribution (its electron cloud) is known as polarizability. A molecule that has a charge cloud that is easily distorted is said to be very polarizable and will have large dispersion forces; one with a charge cloud that is difficult to distort is not very polarizable and will have small dispersion forces.

Example 5.1.1: London Forces and Their Effects

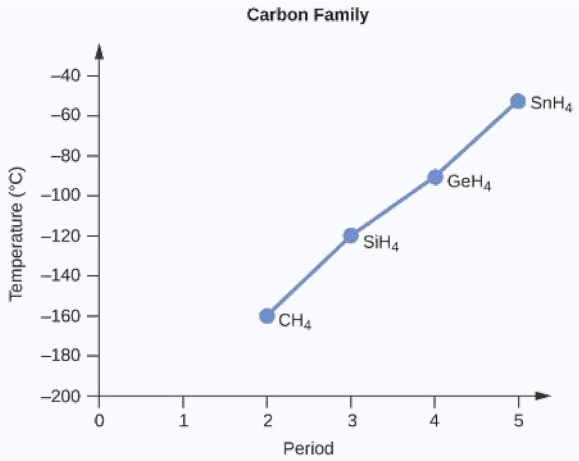
Order the following compounds of a group 14 element and hydrogen from lowest to highest boiling point: CH_4, SiH_4, GeH_4, and SnH_4. Explain your reasoning.

Solution

Applying the skills acquired in the chapter on chemical bonding and molecular geometry, all of these compounds are predicted to be nonpolar, so they may experience only dispersion forces: the smaller the molecule, the less polarizable and the weaker the dispersion forces; the larger the molecule, the larger the dispersion forces. The molar masses of CH_4, SiH_4, GeH_4, and SnH_4 are approximately 16 g/mol, 32 g/mol, 77 g/mol, and 123 g/mol, respectively. Therefore, CH_4 is expected to have the lowest boiling point and SnH_4 the highest boiling point. The ordering from lowest to highest boiling point is expected to be

$$CH_4 < SiH_4 < GeH_4 < SnH_4$$

A graph of the actual boiling points of these compounds versus the period of the group 14 elements shows this prediction to be correct:



Exercise 5.1.1

Order the following hydrocarbons from lowest to highest boiling point: C_2H_6, C_3H_8, and C_4H_{10}.

Answer

All of these compounds are nonpolar and only have London dispersion forces: the larger the molecule, the larger the dispersion forces and the higher the boiling point. The ordering from lowest to highest boiling point is therefore

$$C_2H_6 < C_3H_8 < C_4H_{10}.$$

The shapes of molecules also affect the magnitudes of the dispersion forces between them. For example, boiling points for the isomers *n*-pentane, isopentane, and neopentane (shown in Figure **5.1.7**) are 36 °C, 27 °C, and 9.5 °C, respectively. Even though these compounds are composed of molecules with the same chemical formula, C_5H_{12}, the difference in boiling points suggests that dispersion forces in the liquid phase are different, being greatest for *n*-pentane and least for neopentane. The elongated shape of *n*-pentane provides a greater surface area available for contact between molecules, resulting in correspondingly stronger dispersion forces. The more compact shape of isopentane offers a smaller surface area available for intermolecular contact and, therefore, weaker dispersion forces. Neopentane molecules are the most compact of the three, offering the least available surface area for intermolecular contact and, hence, the weakest dispersion forces. This behavior is analogous to the connections that may be formed between strips of VELCRO brand fasteners: the greater the area of the strip's contact, the stronger the connection.

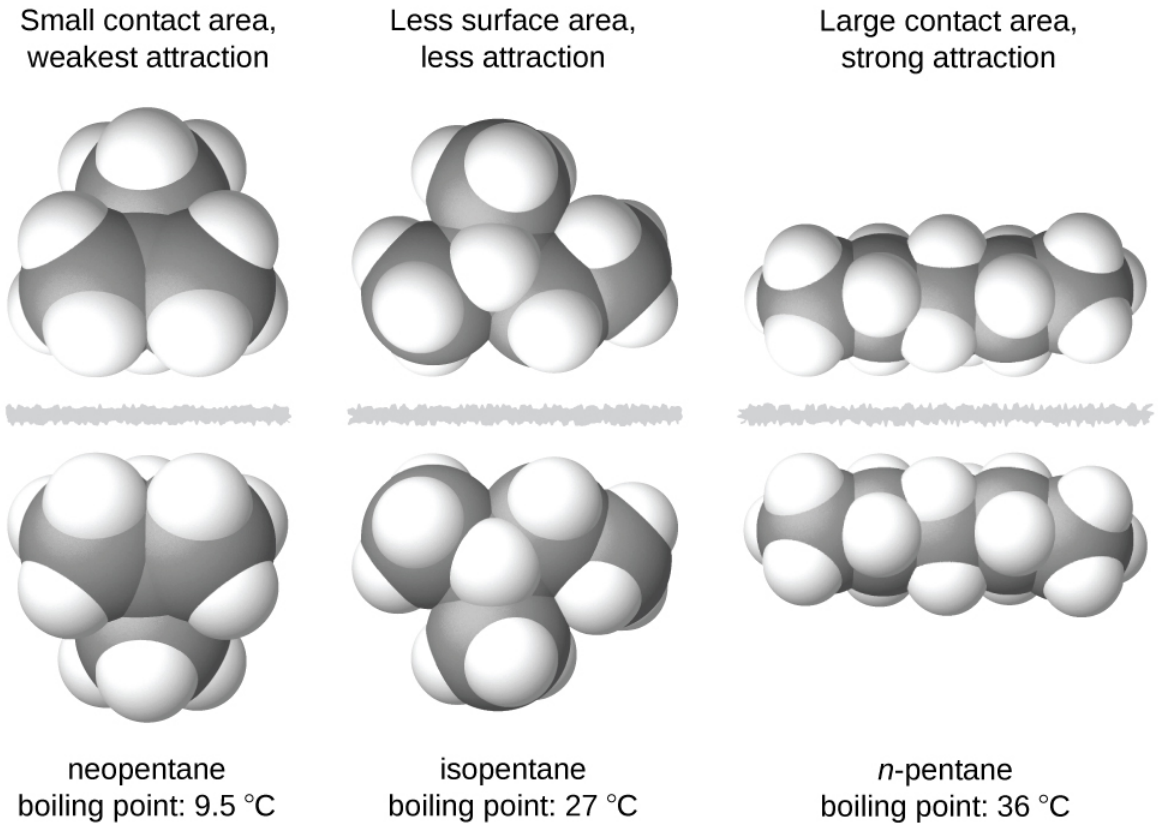


***Figure* 5.1.7**: *The strength of the dispersion forces increases with the contact area between molecules, as demonstrated by the boiling points of these pentane isomers.*

Applications: Geckos and Intermolecular Forces

Geckos have an amazing ability to adhere to most surfaces. They can quickly run up smooth walls and across ceilings that have no toe-holds, and they do this without having suction cups or a sticky substance on their toes. And while a gecko can lift its feet easily as it walks along a surface, if you attempt to pick it up, it sticks to the surface. How are geckos (as well as spiders and some other insects) able to do this? Although this phenomenon has been investigated for hundreds of years, scientists only recently uncovered the details of the process that allows geckos' feet to behave this way.

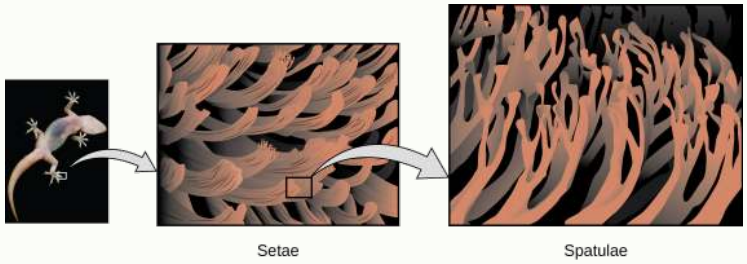


***Figure* 5.1.7**: *Geckos' toes contain large numbers of tiny hairs (setae), which branch into many triangular tips (spatulae). Geckos adhere to surfaces because of van der Waals attractions between the surface and a gecko's millions of spatulae. By changing how the spatulae contact the surface, geckos can turn their stickiness "on" and "off." (credit photo: modification of work by "JC*+A!"/Flickr)*

Geckos' toes are covered with hundreds of thousands of tiny hairs known as *setae*, with each seta, in turn, branching into hundreds of tiny, flat, triangular tips called *spatulae*. The huge numbers of spatulae on its setae provide a gecko, shown in Figure **5.1.7**, with a large total surface area for sticking to a surface. In 2000, Kellar Autumn, who leads a multi-institutional gecko research team, found that geckos adhered equally well to both polar silicon dioxide and nonpolar gallium arsenide. This proved that geckos stick to surfaces because of dispersion forces—weak intermolecular attractions arising from temporary,

synchronized charge distributions between adjacent molecules. Although dispersion forces are very weak, the total attraction over millions of spatulae is large enough to support many times the gecko's weight.

In 2014, two scientists developed a model to explain how geckos can rapidly transition from "sticky" to "non-sticky." Alex Greaney and Congcong Hu at Oregon State University described how geckos can achieve this by changing the angle between their spatulae and the surface. Geckos' feet, which are normally nonsticky, become sticky when a small shear force is applied. By curling and uncurling their toes, geckos can alternate between sticking and unsticking from a surface, and thus easily move across it. Further investigations may eventually lead to the development of better adhesives and other applications.



Video* 5.1.1: Watch this video to learn more about Kellar Autumn's research that determined that van der Waals forces are responsible for a gecko's ability to cling and climb.*

Dipole-Dipole Attractions

Recall from the chapter on chemical bonding and molecular geometry that *polar* molecules have a partial positive charge on one side and a partial negative charge on the other side of the molecule—a separation of charge called a *dipole*. Consider a polar molecule such as hydrogen chloride, HCl. In the HCl molecule, the more electronegative Cl atom bears the partial negative charge, whereas the less electronegative H atom bears the partial positive charge. An attractive force between HCl molecules results from the attraction between the positive end of one HCl molecule and the negative end of another. This attractive force is called a dipole-dipole attraction—the electrostatic force between the partially positive end of one polar molecule and the partially negative end of another, as illustrated in Figure 5.1.8.

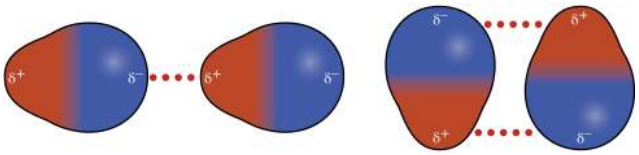


Figure* 5.1.8: This image shows two arrangements of polar molecules, such as HCl, that allow an attraction between the partial negative end of one molecule and the partial positive end of another.*

The effect of a dipole-dipole attraction is apparent when we compare the properties of HCl molecules to nonpolar F_2 molecules. Both HCl and F_2 consist of the same number of atoms and have approximately the same molecular mass. At a temperature of 150 K, molecules of both substances would have the same average KE. However, the dipole-dipole attractions between HCl molecules are sufficient to cause them to "stick together" to form a liquid, whereas the relatively weaker dispersion forces between nonpolar F_2 molecules are not, and so this substance is gaseous at this temperature. The higher normal boiling point of HCl (188 K) compared to F_2 (85 K) is a reflection of the greater strength of dipole-dipole attractions between HCl molecules, compared to the attractions between nonpolar F_2 molecules. We will often use values such as boiling or freezing points, or enthalpies of vaporization or fusion, as indicators of the relative strengths of IMFs of attraction present within different substances.

Example 5.1.2: Dipole-Dipole Forces and Their Effects

Predict which will have the higher boiling point: N_2 or CO. Explain your reasoning.

Solution

CO and N_2 are both diatomic molecules with masses of about 28 amu, so they experience similar London dispersion forces. Because CO is a polar molecule, it experiences dipole-dipole attractions. Because N_2 is nonpolar, its molecules cannot exhibit dipole-dipole attractions. The dipole-dipole attractions between CO molecules are comparably stronger than the dispersion forces between nonpolar N_2 molecules, so CO is expected to have the higher boiling point.

A common method for preparing oxygen is the decomposition

Exercise 5.1.2

Predict which will have the higher boiling point: **ICl** or **Br_2**. Explain your reasoning.

Answer

ICl. ICl and Br_2 have similar masses (~160 amu) and therefore experience similar London dispersion forces. ICl is polar and thus also exhibits dipole-dipole attractions; Br_2 is nonpolar and does not. The relatively stronger dipole-dipole attractions require more energy to overcome, so ICl will have the higher boiling point.

Hydrogen Bonding

Nitrosyl fluoride (ONF, molecular mass 49 amu) is a gas at room temperature. Water (H_2O, molecular mass 18 amu) is a liquid, even though it has a lower molecular mass. We clearly cannot attribute this difference between the two compounds to dispersion forces. Both molecules have about the same shape and ONF is the heavier and larger molecule. It is, therefore, expected to experience more significant dispersion forces. Additionally, we cannot attribute this difference in boiling points to differences in the dipole moments of the molecules. Both molecules are polar and exhibit comparable dipole moments. The large difference between the boiling points is due to a particularly strong dipole-dipole attraction that may occur when a molecule contains a hydrogen atom bonded to a fluorine, oxygen, or nitrogen atom (the three most electronegative elements). The very large difference in electronegativity between the H atom (2.1) and the atom to which it is bonded (4.0 for an F atom, 3.5 for an O atom, or 3.0 for a N atom), combined with the very small size of a H atom and the relatively small sizes of F, O, or N atoms, leads to *highly concentrated partial charges* with these atoms. Molecules with F-H, O-H, or N-H moieties are very strongly attracted to similar moieties in nearby molecules, a particularly strong type of dipole-dipole attraction called hydrogen bonding. Examples of hydrogen bonds include HF···HF, H_2O···HOH, and H_3N···HNH_2, in which the hydrogen bonds are denoted by dots. Figure **5.1.9** illustrates hydrogen bonding between water molecules.

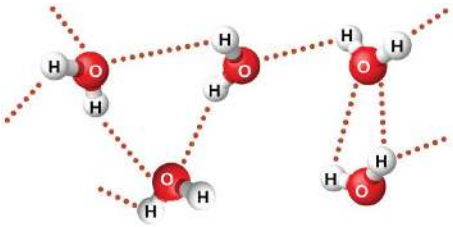


Figure* 5.1.9: Water molecules participate in multiple hydrogen-bonding interactions with nearby water molecules.*

Despite use of the word “bond,” keep in mind that hydrogen bonds are *intermolecular* attractive forces, not *intramolecular* attractive forces (covalent bonds). Hydrogen bonds are much weaker than covalent bonds, only about 5 to 10% as strong, but are generally much stronger than other dipole-dipole attractions and dispersion forces.

Hydrogen bonds have a pronounced effect on the properties of condensed phases (liquids and solids). For example, consider the trends in boiling points for the binary hydrides of group 15 (NH_3, PH_3, AsH_3, and SbH_3), group 16 hydrides (H_2O, H_2S, H_2Se, and H_2Te), and group 17 hydrides (HF, HCl, HBr, and HI). The boiling points of the heaviest three hydrides for each group are plotted in Figure **5.1.10**. As we progress down any of these groups, the polarities of the molecules decrease slightly, whereas the sizes of the molecules increase substantially. The effect of increasingly stronger dispersion forces dominates that of increasingly weaker dipole-dipole attractions, and the boiling points are observed to increase steadily.

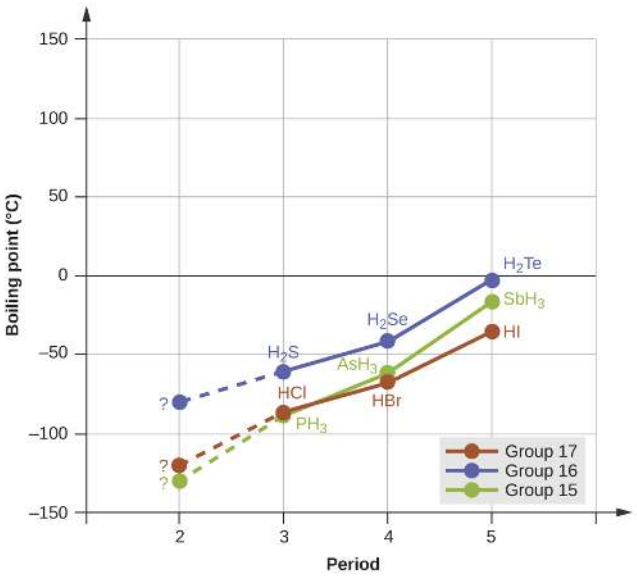


***Figure* 5.1.10**: *For the group 15, 16, and 17 hydrides, the boiling points for each class of compounds increase with increasing molecular mass for elements in periods 3, 4, and 5.*

If we use this trend to predict the boiling points for the lightest hydride for each group, we would expect NH_3 to boil at about −120 °C, H_2O to boil at about −80 °C, and HF to boil at about −110 °C. However, when we measure the boiling points for these compounds, we find that they are dramatically higher than the trends would predict, as shown in Figure **5.1.11**. The stark contrast between our naïve predictions and reality provides compelling evidence for the strength of hydrogen bonding.

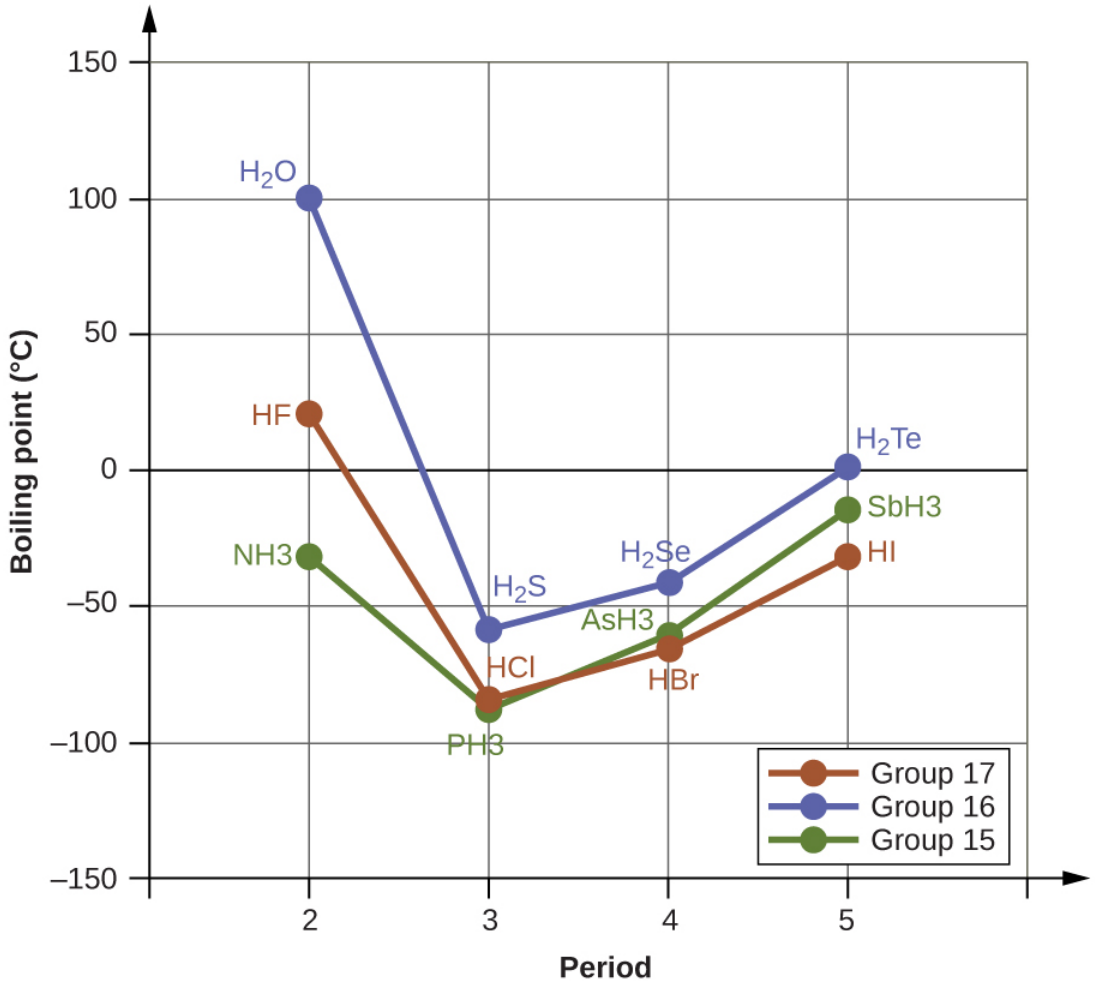


***Figure* 5.1.11**: *In comparison to periods 3−5, the binary hydrides of period 2 elements in groups 17, 16 and 15 (F, O and N, respectively) exhibit anomalously high boiling points due to hydrogen bonding.*

Example 5.1.3: Effect of Hydrogen Bonding on Boiling Points

Consider the compounds dimethylether (CH_3OCH_3), ethanol (CH_3CH_2OH), and propane ($CH_3CH_2CH_3$). Their boiling points, not necessarily in order, are −42.1 °C, −24.8 °C, and 78.4 °C. Match each compound with its boiling point. Explain your reasoning.

Solution

The VSEPR-predicted shapes of CH_3OCH_3, CH_3CH_2OH, and $CH_3CH_2CH_3$ are similar, as are their molar masses (46 g/mol, 46 g/mol, and 44 g/mol, respectively), so they will exhibit similar dispersion forces. Since $CH_3CH_2CH_3$ is nonpolar, it may exhibit *only* dispersion forces. Because CH_3OCH_3 is polar, it will also experience dipole-dipole attractions. Finally, CH_3CH_2OH has an −OH group, and so it will experience the uniquely strong dipole-dipole attraction known as hydrogen bonding. So the ordering in terms of strength of IMFs, and thus boiling points, is $CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CH_2OH$. The boiling point of propane is −42.1 °C, the boiling point of dimethylether is −24.8 °C, and the boiling point of ethanol is 78.5 °C.

Exercise 5.1.2

Ethane (CH_3CH_3) has a melting point of −183 °C and a boiling point of −89 °C. Predict the melting and boiling points for methylamine (CH_3NH_2). Explain your reasoning.

Answer:

The melting point and boiling point for methylamine are predicted to be significantly greater than those of ethane. CH_3CH_3 and CH_3NH_2 are similar in size and mass, but methylamine possesses an −NH group and therefore may exhibit hydrogen bonding. This greatly increases its IMFs, and therefore its melting and boiling points. It is difficult to predict values, but the known values are a melting point of −93 °C and a boiling point of −6 °C.

Hydrogen Bonding and DNA

Deoxyribonucleic acid (DNA) is found in every living organism and contains the genetic information that determines the organism's characteristics, provides the blueprint for making the proteins necessary for life, and serves as a template to pass this information on to the organism's offspring. A DNA molecule consists of two (anti-)parallel chains of repeating nucleotides, which form its well-known double helical structure, as shown in Figure **5.1.12**.

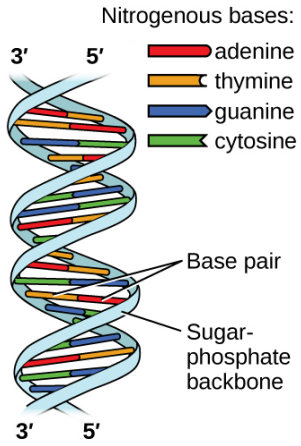
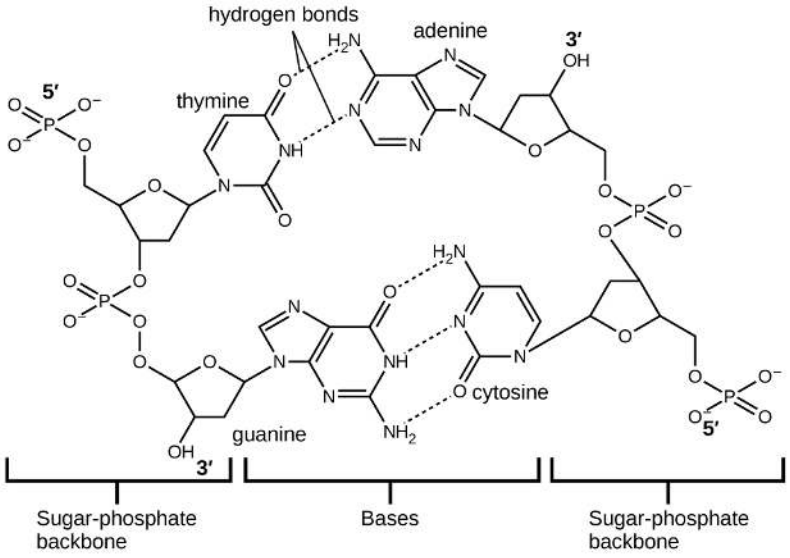


***Figure* 5.1.12**: *Two separate DNA molecules form a double-stranded helix in which the molecules are held together via hydrogen bonding. (credit: modification of work by Jerome Walker, Dennis Myts)*

Each nucleotide contains a (deoxyribose) sugar bound to a phosphate group on one side, and one of four nitrogenous bases on the other. Two of the bases, cytosine (C) and thymine (T), are single-ringed structures known as pyrimidines. The other two, adenine (A) and guanine (G), are double-ringed structures called purines. These bases form complementary base pairs consisting of one purine and one pyrimidine, with adenine pairing with thymine, and cytosine with guanine. Each base pair is held together by hydrogen bonding. A and T share two hydrogen bonds, C and G share three, and both pairings have a similar shape and structure Figure **5.1.13**



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***Figure* 5.1.13**: *The geometries of the base molecules result in maximum hydrogen bonding between adenine and thymine (AT) and between guanine and cytosine (GC), so-called "complementary base pairs."*

The cumulative effect of millions of hydrogen bonds effectively holds the two strands of DNA together. Importantly, the two strands of DNA can relatively easily "unzip" down the middle since hydrogen bonds are relatively weak compared to the covalent bonds that hold the atoms of the individual DNA molecules together. This allows both strands to function as a template for replication.

Summary



***Video* 5.1.2**: *An overview of intermolecular forces.*

The physical properties of condensed matter (liquids and solids) can be explained in terms of the kinetic molecular theory. In a liquid, intermolecular attractive forces hold the molecules in contact, although they still have sufficient kinetic energy to move past each other. Intermolecular attractive forces, collectively referred to as van der Waals forces, are responsible for the behavior of liquids and solids and are electrostatic in nature. Dipole-dipole attractions result from the electrostatic attraction of the partial negative end of one dipolar molecule for the partial positive end of another. The temporary dipole that results from the motion of the electrons in an atom can induce a dipole in an adjacent atom and give rise to the London dispersion force. London forces increase with increasing molecular size. Hydrogen bonds are a special type of dipole-dipole attraction that results when hydrogen is bonded to one of the three most electronegative elements: F, O, or N.

Glossary

dipole-dipole attraction
: intermolecular attraction between two permanent dipoles

dispersion force
: (also, London dispersion force) attraction between two rapidly fluctuating, temporary dipoles; significant only when particles are very close together

hydrogen bonding
: occurs when exceptionally strong dipoles attract; bonding that exists when hydrogen is bonded to one of the three most electronegative elements: F, O, or N

induced dipole
: temporary dipole formed when the electrons of an atom or molecule are distorted by the instantaneous dipole of a neighboring atom or molecule

instantaneous dipole
: temporary dipole that occurs for a brief moment in time when the electrons of an atom or molecule are distributed asymmetrically

intermolecular force

noncovalent attractive force between atoms, molecules, and/or ions

polarizability

measure of the ability of a charge to distort a molecule's charge distribution (electron cloud)

van der Waals force

attractive or repulsive force between molecules, including dipole-dipole, dipole-induced dipole, and London dispersion forces; does not include forces due to covalent or ionic bonding, or the attraction between ions and molecules

Contributors

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5.1.1: Intermolecular Forces (Problems)

PROBLEM 5.1.1.1

In terms of their bulk properties, how do liquids and solids differ? How are they similar?

Answer

Liquids and solids are similar in that they are matter composed of atoms, ions, or molecules. They are incompressible and have similar densities that are both much larger than those of gases. They are different in that liquids have no fixed shape, and solids are rigid.

PROBLEM 5.1.1.2

In terms of the kinetic molecular theory, in what ways are liquids similar to solids? In what ways are liquids different from solids?

Answer

Particles in liquids and solids are close together, but in liquids they have no regular arrangement or fixed positions.

PROBLEM 5.1.1.3

In terms of the kinetic molecular theory, in what ways are liquids similar to gases? In what ways are liquids different from gases?

Answer

They are similar in that the atoms or molecules are free to move from one position to another. They differ in that the particles of a liquid are confined to the shape of the vessel in which they are placed. In contrast, a gas will expand without limit to fill the space into which it is placed.

PROBLEM 5.1.1.4

Explain why liquids assume the shape of any container into which they are poured, whereas solids are rigid and retain their shape.

Answer

Particles in a solid vibrate about fixed positions and do not generally move in relation to one another; in a liquid, they move past each other but remain in essentially constant contact

PROBLEM 5.1.1.5

What is the evidence that all neutral atoms and molecules exert attractive forces on each other?

Answer

All atoms and molecules will condense into a liquid or solid in which the attractive forces exceed the kinetic energy of the molecules, at sufficiently low temperature.

PROBLEM 5.1.1.6

The types of intermolecular forces in a substance are identical whether it is a solid, a liquid, or a gas. Why then does a substance change phase from a gas to a liquid or to a solid?

Answer

Intermolecular forces serve to hold particles close together, whereas the particles' kinetic energy provides the energy required to overcome the attractive forces and thus increase the distance between particles. Changes in physical state may be induced by changing the temperature, hence, the average KE, of a given substance

PROBLEM 5.1.1.7

Why do the boiling points of the noble gases increase in the order He < Ne < Ar < Kr < Xe?

Answer

The London forces typically increase as the number of electrons increase.

PROBLEM 5.1.1.8

Neon and HF have approximately the same molecular masses.

a. Explain why the boiling points of Neon and HF differ.
b. Compare the change in the boiling points of Ne, Ar, Kr, and Xe with the change of the boiling points of HF, HCl, HBr, and HI, and explain the difference between the changes with increasing atomic or molecular mass.

Answer a

Ne has only dispersion forces, whereas HF is polar covalent and has hydrogen bonding, dipole-dipole, and dispersion forces.

Answer b

Compound	Boiling Point (°C)		Compound	Boiling Point (°C)
Ne	-246		HF	19.5
Ar	-185.8		HCl	-85
Kr	-153.4		HBr	-66
Xe	-108.1		HI	-34

The boiling point of the noble gases increases as you increase the molecular weight because of the increasing strength of the dispersion forces.

For the hydrogen halides, HF does not follow this pattern because it has hydrogen bonding while the other three only has dipole-dipole interactions.

PROBLEM 5.1.1.9

Arrange each of the following sets of compounds in order of increasing boiling point temperature:

a. HCl, H_2O, SiH_4
b. F_2, Cl_2, Br_2
c. CH_4, C_2H_6, C_3H_8
d. O_2, NO, N_2

Answer a

SiH_4 < HCl < H_2O

Answer b

F_2 < Cl_2 < Br_2

Answer c

CH_4 < C_2H_6 < C_3H_8

Answer d

$N_2 < O_2 < NO$

PROBLEM 5.1.1.10

The molecular mass of butanol, C_4H_9OH, is 74.14; that of ethylene glycol, $CH_2(OH)CH_2OH$, is 62.08, yet their boiling points are 117.2 °C and 174 °C, respectively. Explain the reason for the difference.

Answer

ethylene glycol contains two OH groups which increase the polarity

PROBLEM 5.1.1.11

On the basis of intermolecular attractions, explain the differences in the boiling points of *n*–butane (−1 °C) and chloroethane (12 °C), which have similar molar masses.

Answer

Only rather small dipole-dipole interactions from C-H bonds are available to hold *n*-butane in the liquid state. Chloroethane, however, has rather large dipole interactions because of the Cl-C bond; the interaction is therefore stronger, leading to a higher boiling point.

PROBLEM 5.1.1.12

On the basis of dipole moments and/or hydrogen bonding, explain in a qualitative way the differences in the boiling points of acetone (56.2 °C) and 1-propanol (97.4 °C), which have similar molar masses.

Answer

1-propanol contains an OH group, which makes it more polar.

PROBLEM 5.1.1.13

The melting point of $H_2O(s)$ is 0 °C. Would you expect the melting point of $H_2S(s)$ to be −85 °C, 0 °C, or 185 °C? Explain your answer.

Answer

−85 °C. Water has stronger hydrogen bonds so it melts at a higher temperature.

PROBLEM 5.1.1.14

Identify the intermolecular forces present in the following solids:

a. CH_3CH_2OH
b. $CH_3CH_2CH_3$
c. CH_3CH_2Cl

Answer a

hydrogen bonding and dispersion forces

Answer b

dispersion forces

Answer c

dipole-dipole attraction and dispersion forces

Contributors

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5.2: Soap

Soap is a mixture of sodium salts of various naturally occurring fatty acids. Air bubbles added to a molten soap will decrease the density of the soap and thus it will float on water. If the fatty acid salt has potassium rather than sodium, a softer lather is the result. Soap is produced by a saponification or basic hydrolysis reaction of a fat or oil. Currently, sodium carbonate or sodium hydroxide is used to neutralize the fatty acid and convert it to the salt.

Introduction

General overall hydrolysis reaction:

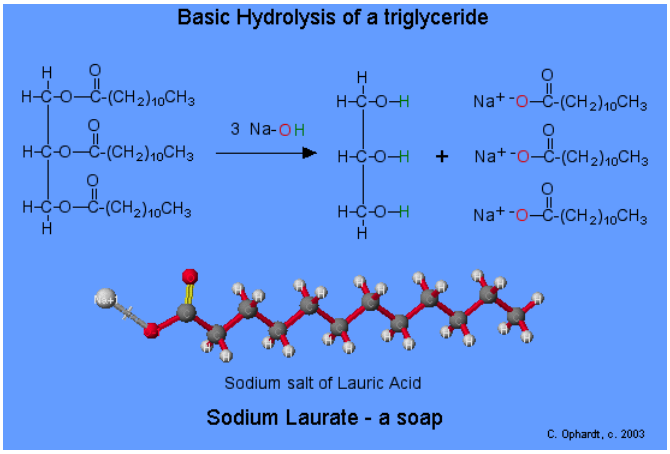
fat + NaOH → glycerol + sodium salt of fatty acid

Although the reaction is shown as a one step reaction, it is in fact two steps. The net effect as that the ester bonds are broken. The glycerol turns back into an alcohol (addition of the green H's). The fatty acid portion is turned into a salt because of the presence of a basic solution of the NaOH. In the carboxyl group, one oxygen (red) now has a negative charge that attracts the positive sodium ion.

Types of Soap

The type of fatty acid and length of the carbon chain determines the unique properties of various soaps. Tallow or animal fats give primarily sodium stearate (18 carbons) a very hard, insoluble soap. Fatty acids with longer chains are even more insoluble. As a matter of fact, zinc stearate is used in talcum powders because it is water repellent.

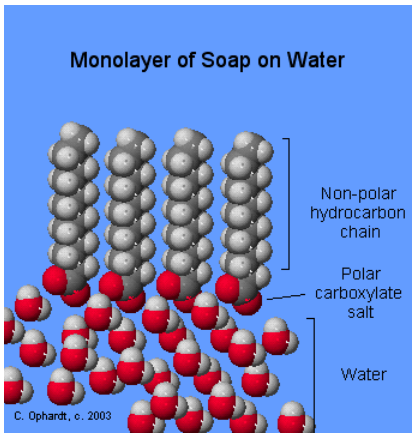
Coconut oil is a source of lauric acid (12 carbons) which can be made into sodium laurate. This soap is very soluble and will lather easily even in sea water. Fatty acids with only 10 or fewer carbons are not used in soaps because they irritate the skin and have objectionable odors.



Cleansing Action of Soap

The cleansing action of soap is determined by its polar and non-polar structures in conjunction with an application of solubility principles. The long hydrocarbon chain is of course non-polar and hydrophobic (repelled by water). The "salt" end of the soap molecule is ionic and hydrophilic (water soluble).

Monolayer: When soap is added to water, the ionic-salt end of the molecule is attracted to water and dissolved in it. The non-polar hydrocarbon end of the soap molecule is repelled by water. A drop or two of soap in water forms a monolayer on the water surface as shown in the graphics on the left. The soap molecules "stand up" on the surface as the polar carboxyl salt end is attracted to the polar water. The non-polar hydrocarbon tails are repelled by the water, which makes them appear to stand up.

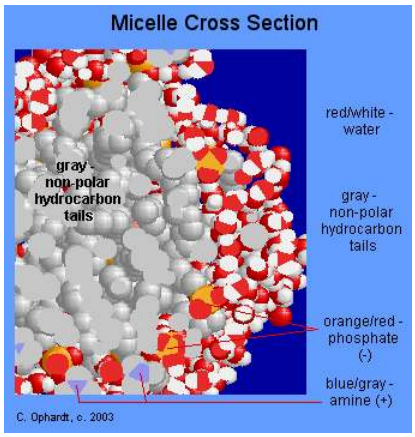


Soap vs. oil vs. water

Water alone is not able to penetrate grease or oil because they are of opposite polarity. When grease or oil (non-polar hydrocarbons) are mixed with a soap- water solution, the soap molecules work as a "bridge" between polar water molecules and non-polar oil molecules. Soap molecules have both properties of non-polar and polar at opposite ends of the molecule.

The oil is a pure hydrocarbon so it is non-polar. The non-polar hydrocarbon tail of the soap dissolves into the oil. That leaves the polar carboxylate ion of the soap molecules are sticking out of the oil droplets, the surface of each oil droplet is negatively charged. As a result, the oil droplets repel each other and remain suspended in solution (this is called an emulsion) to be washed away by a stream of water. The outside of the droplet is also coated with a layer of water molecules.

The graphic on the left although not strictly a representation of the above description is a micelle that works in much the same fashion. The oil would be a the center of the micelle. Click for more information on a micelle.



Effect of Hard Water

If soap is used in "hard" water, the soap will be precipitated as "bath-tub ring" by calcium or magnesium ions present in "hard" water. The effects of "hard" water calcium or magnesium ions are minimized by the addition of "builders". The most common "builder" used to be sodium trimetaphosphate. The phosphates react with the calcium or magnesium ions and keeps them in solution but away from the soap molecule. The soap molecule can then do its job without interference from calcium or magnesium ions. Other "builders" include sodium carbonate, borax, and sodium silicate are currently in detergents.

Problems

- Use the solubility principles to complete a diagram showing many soap molecules as "bridges" between water and oil. Label and explain the diagram further.

Outside Links

- Ceretti, Helena; Hughes, Enrique A.; Zalts, Anita. "The Softening of Hard Water and Complexometric Titrations: An Undergraduate Experiment." *J. Chem. Educ.* **1999** *76* 1420.
- "Soapmaking." *J. Chem. Educ.* **1999**, *76*, 192A.

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5.3: Surface Tension, Viscosity, and Capillary Action

Skills to Develop

- Distinguish between adhesive and cohesive forces
- Define viscosity, surface tension, and capillary rise
- Describe the roles of intermolecular attractive forces in each of these properties/phenomena

When you pour a glass of water, or fill a car with gasoline, you observe that water and gasoline flow freely. But when you pour syrup on pancakes or add oil to a car engine, you note that syrup and motor oil do not flow as readily. The viscosity of a liquid is a measure of its resistance to flow. Water, gasoline, and other liquids that flow freely have a low viscosity. Honey, syrup, motor oil, and other liquids that do not flow freely, like those shown in Figure **5.3.1**, have higher viscosities. We can measure viscosity by measuring the rate at which a metal ball falls through a liquid (the ball falls more slowly through a more viscous liquid) or by measuring the rate at which a liquid flows through a narrow tube (more viscous liquids flow more slowly).



***Figure* 5.3.1:** *(a) Honey and (b) motor oil are examples of liquids with high viscosities; they flow slowly. (credit a: modification of work by Scott Bauer; credit b: modification of work by David Nagy)*

The IMFs between the molecules of a liquid, the size and shape of the molecules, and the temperature determine how easily a liquid flows. As Table **5.3.1** shows, the more structurally complex are the molecules in a liquid and the stronger the IMFs between them, the more difficult it is for them to move past each other and the greater is the viscosity of the liquid. As the temperature increases, the molecules move more rapidly and their kinetic energies are better able to overcome the forces that hold them together; thus, the viscosity of the liquid decreases.

***Table* 5.3.1:** *Viscosities of Common Substances at 25 °C*

Substance	Formula	Viscosity (mPa·s)
water	H_2O	0.890
mercury	Hg	1.526
ethanol	C_2H_5OH	1.074
octane	C_8H_{18}	0.508
ethylene glycol	$CH_2(OH)CH_2(OH)$	16.1
honey	variable	~2,000–10,000
motor oil	variable	~50–500

The various IMFs between identical molecules of a substance are examples of cohesive forces. The molecules within a liquid are surrounded by other molecules and are attracted equally in all directions by the cohesive forces within the liquid. However, the molecules on the surface of a liquid are attracted only by about one-half as many molecules. Because of the unbalanced molecular attractions on the surface molecules, liquids contract to form a shape that minimizes the number of molecules on the surface—that is, the shape with the minimum surface area. A small drop of liquid tends to assume a spherical shape, as shown in Figure **5.3.2**, because in a sphere, the ratio of surface area to volume is at a minimum. Larger drops are more greatly affected by gravity, air resistance, surface interactions, and so on, and as a result, are less spherical.

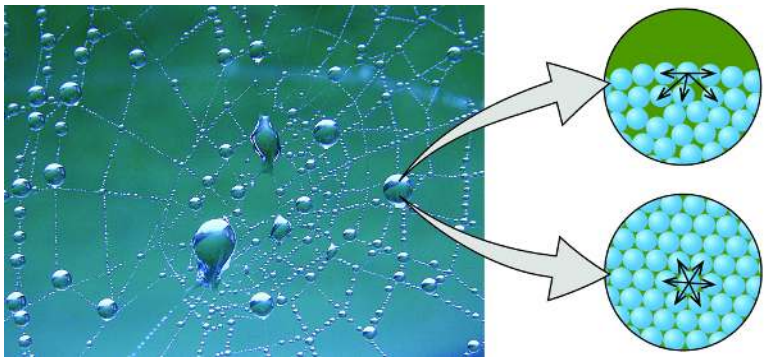


***Figure* 5.3.2**: *Attractive forces result in a spherical water drop that minimizes surface area; cohesive forces hold the sphere together; adhesive forces keep the drop attached to the web. (credit photo: modification of work by "OliBac"/Flickr)*

Surface tension is defined as the energy required to increase the surface area of a liquid, or the force required to increase the length of a liquid surface by a given amount. This property results from the cohesive forces between molecules at the surface of a liquid, and it causes the surface of a liquid to behave like a stretched rubber membrane. Surface tensions of several liquids are presented in Table **5.3.2**.

***Table* 5.3.2**: *Surface Tensions of Common Substances at 25 °C*

Substance	Formula	Surface Tension (mN/m)
water	H_2O	71.99
mercury	Hg	458.48
ethanol	C_2H_5OH	21.97
octane	C_8H_{18}	21.14
ethylene glycol	$CH_2(OH)CH_2(OH)$	47.99

Among common liquids, water exhibits a distinctly high surface tension due to strong hydrogen bonding between its molecules. As a result of this high surface tension, the surface of water represents a relatively "tough skin" that can withstand considerable force without breaking. A steel needle carefully placed on water will float. Some insects, like the one shown in Figure **5.3.3**, even though they are denser than water, move on its surface because they are supported by the surface tension.

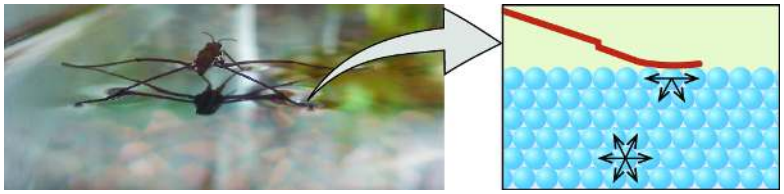


***Figure* 5.3.3**: *Surface tension (right) prevents this insect, a "water strider," from sinking into the water.*

The IMFs of attraction between two *different* molecules are called adhesive forces. Consider what happens when water comes into contact with some surface. If the adhesive forces between water molecules and the molecules of the surface are weak compared to

the cohesive forces between the water molecules, the water does not “wet” the surface. For example, water does not wet waxed surfaces or many plastics such as polyethylene. Water forms drops on these surfaces because the cohesive forces within the drops are greater than the adhesive forces between the water and the plastic. Water spreads out on glass because the adhesive force between water and glass is greater than the cohesive forces within the water. When water is confined in a glass tube, its meniscus (surface) has a concave shape because the water wets the glass and creeps up the side of the tube. On the other hand, the cohesive forces between mercury atoms are much greater than the adhesive forces between mercury and glass. Mercury therefore does not wet glass, and it forms a convex meniscus when confined in a tube because the cohesive forces within the mercury tend to draw it into a drop (Figure 5.3.4).

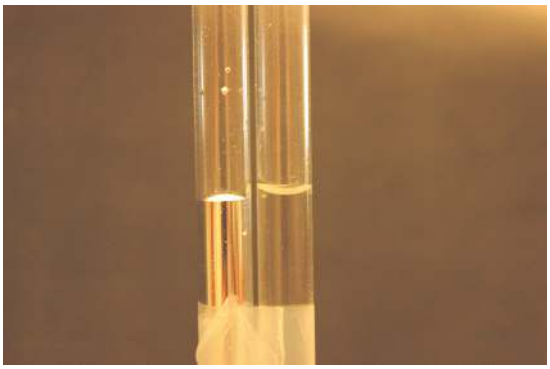


Figure 5.3.4*: Differences in the relative strengths of cohesive and adhesive forces result in different meniscus shapes for mercury (left) and water (right) in glass tubes. (credit: Mark Ott)*

If you place one end of a paper towel in spilled wine, as shown in Figure 5.3.5, the liquid wicks up the paper towel. A similar process occurs in a cloth towel when you use it to dry off after a shower. These are examples of capillary action—when a liquid flows within a porous material due to the attraction of the liquid molecules to the surface of the material and to other liquid molecules. The adhesive forces between the liquid and the porous material, combined with the cohesive forces within the liquid, may be strong enough to move the liquid upward against gravity.

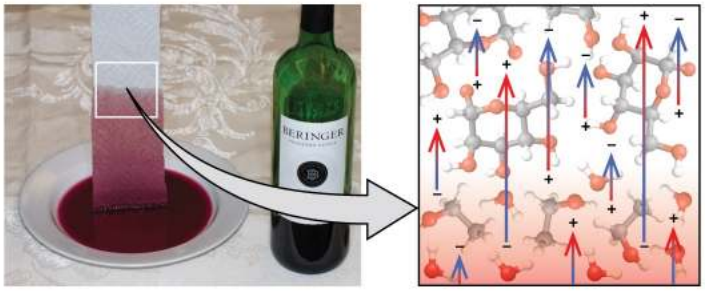


Figure 5.3.5*: Wine wicks up a paper towel (left) because of the strong attractions of water (and ethanol) molecules to the −OH groups on the towel’s cellulose fibers and the strong attractions of water molecules to other water (and ethanol) molecules (right). (credit photo: modification of work by Mark Blaser)*

Towels soak up liquids like water because the fibers of a towel are made of molecules that are attracted to water molecules. Most cloth towels are made of cotton, and paper towels are generally made from paper pulp. Both consist of long molecules of cellulose that contain many −OH groups. Water molecules are attracted to these −OH groups and form hydrogen bonds with them, which draws the H_2O molecules up the cellulose molecules. The water molecules are also attracted to each other, so large amounts of water are drawn up the cellulose fibers.

Capillary action can also occur when one end of a small diameter tube is immersed in a liquid, as illustrated in Figure 5.3.6. If the liquid molecules are strongly attracted to the tube molecules, the liquid creeps up the inside of the tube until the weight of the liquid and the adhesive forces are in balance. The smaller the diameter of the tube is, the higher the liquid climbs. It is partly by capillary action occurring in plant cells called xylem that water and dissolved nutrients are brought from the soil up through the roots and into a plant. Capillary action is the basis for thin layer chromatography, a laboratory technique commonly used to separate small

quantities of mixtures. You depend on a constant supply of tears to keep your eyes lubricated and on capillary action to pump tear fluid away.

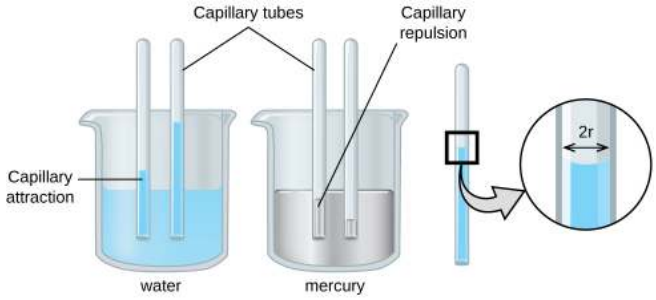


***Figure* 5.3.6:** *Depending upon the relative strengths of adhesive and cohesive forces, a liquid may rise (such as water) or fall (such as mercury) in a glass capillary tube. The extent of the rise (or fall) is directly proportional to the surface tension of the liquid and inversely proportional to the density of the liquid and the radius of the tube.*

The height to which a liquid will rise in a capillary tube is determined by several factors as shown in the following equation:

$$h = \frac{2T\cos\theta}{r\rho g} \tag{5.3.1}$$

where

- h is the height of the liquid inside the capillary tube relative to the surface of the liquid outside the tube,
- T is the surface tension of the liquid,
- θ is the contact angle between the liquid and the tube,
- r is the radius of the tube, ρ is the density of the liquid, and
- g is the acceleration due to gravity, 9.8 m/s^2.

When the tube is made of a material to which the liquid molecules are strongly attracted, they will spread out completely on the surface, which corresponds to a contact angle of 0°. This is the situation for water rising in a glass tube. We will not concern ourselves with calculating capillary height in this course.

Applications: Capillary Action is Used to Draw Blood

Many medical tests require drawing a small amount of blood, for example to determine the amount of glucose in someone with diabetes or the hematocrit level in an athlete. This procedure can be easily done because of capillary action, the ability of a liquid to flow up a small tube against gravity, as shown in Figure **5.3.7**. When your finger is pricked, a drop of blood forms and holds together due to surface tension—the unbalanced intermolecular attractions at the surface of the drop. Then, when the open end of a narrow-diameter glass tube touches the drop of blood, the adhesive forces between the molecules in the blood and those at the glass surface draw the blood up the tube. How far the blood goes up the tube depends on the diameter of the tube (and the type of fluid). A small tube has a relatively large surface area for a given volume of blood, which results in larger (relative) attractive forces, allowing the blood to be drawn farther up the tube. The liquid itself is held together by its own cohesive forces. When the weight of the liquid in the tube generates a downward force equal to the upward force associated with capillary action, the liquid stops rising.



***Figure* 5.3.7:**: Blood is collected for medical analysis by capillary action, which draws blood into a small diameter glass tube. (credit: modification of work by Centers for Disease Control and Prevention)

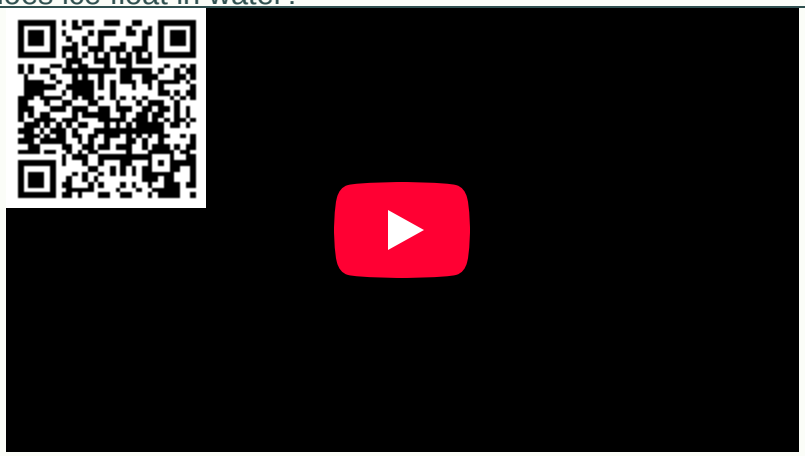
Summary



***Video* 5.3.1**: *An overview of intermolecular forces in action as surface tension, viscosity, and capillary action.*

The intermolecular forces between molecules in the liquid state vary depending upon their chemical identities and result in corresponding variations in various physical properties. Cohesive forces between like molecules are responsible for a liquid's viscosity (resistance to flow) and surface tension (elasticity of a liquid surface). Adhesive forces between the molecules of a liquid and different molecules composing a surface in contact with the liquid are responsible for phenomena such as surface wetting and capillary rise.

Learn More: Why does ice float in water?



***Video* 5.3.2:** Ice floating in water is one of the unique properties of water.

Glossary

adhesive force

force of attraction between molecules of different chemical identities

capillary action

flow of liquid within a porous material due to the attraction of the liquid molecules to the surface of the material and to other liquid molecules

cohesive force

force of attraction between identical molecules

surface tension

energy required to increase the area, or length, of a liquid surface by a given amount

viscosity

measure of a liquid’s resistance to flow

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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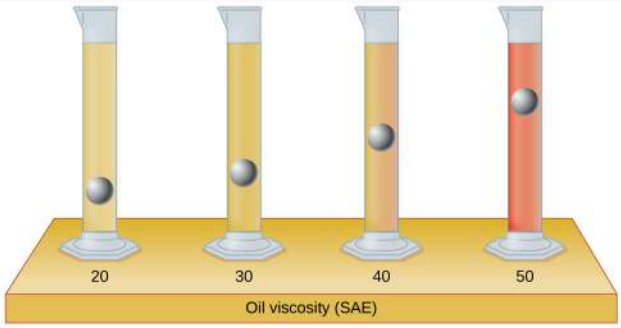
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5.3.1: Surface Tension, Viscosity, and Capillary Action (Problems)

PROBLEM 5.3.1.1

The test tubes shown here contain equal amounts of the specified motor oils. Identical metal spheres were dropped at the same time into each of the tubes, and a brief moment later, the spheres had fallen to the heights indicated in the illustration. Rank the motor oils in order of increasing viscosity, and explain your reasoning:



Answer

20 < 30 < 40 < 50

PROBLEM 5.3.1.2

Although steel is denser than water, a steel needle or paper clip placed carefully lengthwise on the surface of still water can be made to float. Explain at a molecular level how this is possible:



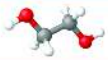
(credit: Cory Zanker)

Answer

The water molecules have strong intermolecular forces of hydrogen bonding. The water molecules are thus attracted strongly to one another and exhibit a relatively large surface tension, forming a type of “skin” at its surface. This skin can support a bug or paper clip if gently placed on the water.

PROBLEM 5.3.1.3

The surface tension and viscosity values for diethyl ether, acetone, ethanol, and ethylene glycol are shown here.

Compound	Molecule	Surface Tension (mN/m)	Viscosity (mPa s)
diethyl ether $C_2H_5OC_2H_5$		17	0.22
acetone $C_2H_5OC_2H_5$		23	0.31
ethanol C_2H_5OH		22	1.07
ethylene glycol $CH_2(OH)CH_2(OH)$		48	16.1

a. Explain their differences in viscosity in terms of the size and shape of their molecules and their IMFs.
b. Explain their differences in surface tension in terms of the size and shape of their molecules and their IMFs.

Answer a

The viscosity increases as the molecular weight (size) of the molecules increases. Additionally, the more polar the molecule, the more viscous.

Answer b

The surface tension increases as the molecular weight of the molecule increases. Additionally, the more polar the molecule, the higher the surface tension.

PROBLEM 5.3.1.4

You may have heard someone use the figure of speech “slower than molasses in winter” to describe a process that occurs slowly. Explain why this is an apt idiom, using concepts of molecular size and shape, molecular interactions, and the effect of changing temperature.

Answer

Temperature has an effect on intermolecular forces: the higher the temperature, the greater the kinetic energies of the molecules and the greater the extent to which their intermolecular forces are overcome, and so the more fluid (less viscous) the liquid; the lower the temperature, the lesser the intermolecular forces are overcome, and so the more viscous the liquid.

PROBLEM 5.3.1.5

It is often recommended that you let your car engine run idle to warm up before driving, especially on cold winter days. While the benefit of prolonged idling is dubious, it is certainly true that a warm engine is more fuel efficient than a cold one. Explain the reason for this.

Answer

The fluids in the engine are warmer, decreasing their viscosity, which aids in lubricating the moving parts of the engine causing it to run smoother.

PROBLEM 5.3.1.6

The surface tension and viscosity of water at several different temperatures are given in this table.

Water	Surface Tension (mN/m)	Viscosity (mPa s)
0 °C	75.6	1.79
20 °C	72.8	1.00
60 °C	66.2	0.47
100 °C	58.9	0.28

a. As temperature increases, what happens to the surface tension of water? Explain why this occurs, in terms of molecular interactions and the effect of changing temperature.
b. As temperature increases, what happens to the viscosity of water? Explain why this occurs, in terms of molecular interactions and the effect of changing temperature.

Answer a

As the water reaches higher temperatures, the increased kinetic energies of its molecules are more effective in overcoming hydrogen bonding, and so its surface tension decreases. Surface tension and intermolecular forces are directly related.

Answer b

The same trend in viscosity is seen as in surface tension, and for the same reason.

Contributors

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- Adelaide Clark, Oregon Institute of Technology

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5.4: Vapor Pressure

Skills to Develop

- Define phase transitions and phase transition temperatures
- Explain the relation between phase transition temperatures and intermolecular attractive forces

We witness and utilize changes of physical state, or phase transitions, in a great number of ways. As one example of global significance, consider the evaporation, condensation, freezing, and melting of water. These changes of state are essential aspects of our earth's water cycle as well as many other natural phenomena and technological processes of central importance to our lives. In this module, the essential aspects of phase transitions are explored.

Vaporization and Condensation

When a liquid vaporizes in a closed container, gas molecules cannot escape. As these gas phase molecules move randomly about, they will occasionally collide with the surface of the condensed phase, and in some cases, these collisions will result in the molecules re-entering the condensed phase. The change from the gas phase to the liquid is called condensation. When the rate of condensation becomes equal to the rate of vaporization, neither the amount of the liquid nor the amount of the vapor in the container changes. The vapor in the container is then said to be *in equilibrium* with the liquid. Keep in mind that this is not a static situation, as molecules are continually exchanged between the condensed and gaseous phases. Such is an example of a dynamic equilibrium, the status of a system in which reciprocal processes (for example, vaporization and condensation) occur at equal rates. The pressure exerted by the vapor in equilibrium with a liquid in a closed container at a given temperature is called the liquid's vapor pressure (or equilibrium vapor pressure). The area of the surface of the liquid in contact with a vapor and the size of the vessel have no effect on the vapor pressure, although they do affect the time required for the equilibrium to be reached. We can measure the vapor pressure of a liquid by placing a sample in a closed container, like that illustrated in Figure **5.4.1**, and using a manometer to measure the increase in pressure that is due to the vapor in equilibrium with the condensed phase.

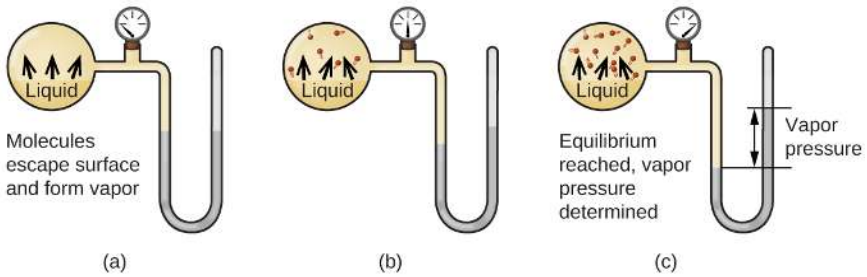
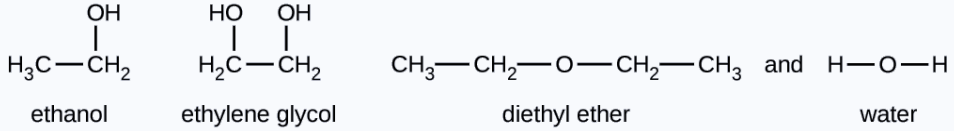


Figure* 5.4.1*: *In a closed container, dynamic equilibrium is reached when (a) the rate of molecules escaping from the liquid to become the gas (b) increases and eventually (c) equals the rate of gas molecules entering the liquid. When this equilibrium is reached, the vapor pressure of the gas is constant, although the vaporization and condensation processes continue.*

The chemical identities of the molecules in a liquid determine the types (and strengths) of intermolecular attractions possible; consequently, different substances will exhibit different equilibrium vapor pressures. Relatively strong intermolecular attractive forces will serve to impede vaporization as well as favoring "recapture" of gas-phase molecules when they collide with the liquid surface, resulting in a relatively low vapor pressure. Weak intermolecular attractions present less of a barrier to vaporization, and a reduced likelihood of gas recapture, yielding relatively high vapor pressures. The following example illustrates this dependence of vapor pressure on intermolecular attractive forces.

Example 5.4.1: Explaining Vapor Pressure in Terms of IMFs

Given the shown structural formulas for these four compounds, explain their relative vapor pressures in terms of types and extents of IMFs:



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Solution

Diethyl ether has a very small dipole and most of its intermolecular attractions are London forces. Although this molecule is the largest of the four under consideration, its IMFs are the weakest and, as a result, its molecules most readily escape from the liquid. It also has the highest vapor pressure. Due to its smaller size, ethanol exhibits weaker dispersion forces than diethyl ether. However, ethanol is capable of hydrogen bonding and, therefore, exhibits stronger overall IMFs, which means that fewer molecules escape from the liquid at any given temperature, and so ethanol has a lower vapor pressure than diethyl ether. Water is much smaller than either of the previous substances and exhibits weaker dispersion forces, but its extensive hydrogen bonding provides stronger intermolecular attractions, fewer molecules escaping the liquid, and a lower vapor pressure than for either diethyl ether or ethanol. Ethylene glycol has two −OH groups, so, like water, it exhibits extensive hydrogen bonding. It is much larger than water and thus experiences larger London forces. Its overall IMFs are the largest of these four substances, which means its vaporization rate will be the slowest and, consequently, its vapor pressure the lowest.

Exercise 5.4.1

At 20 °C, the vapor pressures of several alcohols are given in this table. Explain these vapor pressures in terms of types and extents of IMFs for these alcohols:

Compound	methanol CH_3OH	ethanol C_2H_5OH	propanol C_3H_7OH	butanol C_4H_9OH
Vapor Pressure at 20 °C	11.9 kPa	5.95 kPa	2.67 kPa	0.56 kPa

Answer

All these compounds exhibit hydrogen bonding; these strong IMFs are difficult for the molecules to overcome, so the vapor pressures are relatively low. As the size of molecule increases from methanol to butanol, dispersion forces increase, which means that the vapor pressures decrease as observed:

$$P_{methanol} > P_{ethanol} > P_{propanol} > P_{butanol}$$

As temperature increases, the vapor pressure of a liquid also increases due to the increased average KE of its molecules. Recall that at any given temperature, the molecules of a substance experience a range of kinetic energies, with a certain fraction of molecules having a sufficient energy to overcome IMF and escape the liquid (vaporize). At a higher temperature, a greater fraction of molecules have enough energy to escape from the liquid, as shown in Figure **5.4.2**. The escape of more molecules per unit of time and the greater average speed of the molecules that escape both contribute to the higher vapor pressure.

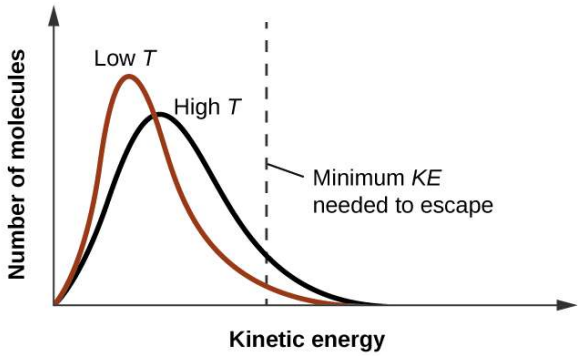


***Figure* 5.4.2**: *Temperature affects the distribution of kinetic energies for the molecules in a liquid. At the higher temperature, more molecules have the necessary kinetic energy, KE, to escape from the liquid into the gas phase.*



***Video* 5.4.1**: *Mercury (Hg) boils at room pressure at 356 °C.*

When the vapor pressure increases enough to equal the external atmospheric pressure, the liquid reaches its boiling point. The boiling point of a liquid is the temperature at which its equilibrium vapor pressure is equal to the pressure exerted on the liquid by its gaseous surroundings. For liquids in open containers, this pressure is that due to the earth's atmosphere. The normal boiling point of a liquid is defined as its boiling point when surrounding pressure is equal to 1 atm (101.3 kPa). Figure **5.4.3** shows the variation in vapor pressure with temperature for several different substances. Considering the definition of boiling point, these curves may be seen as depicting the dependence of a liquid's boiling point on surrounding pressure.

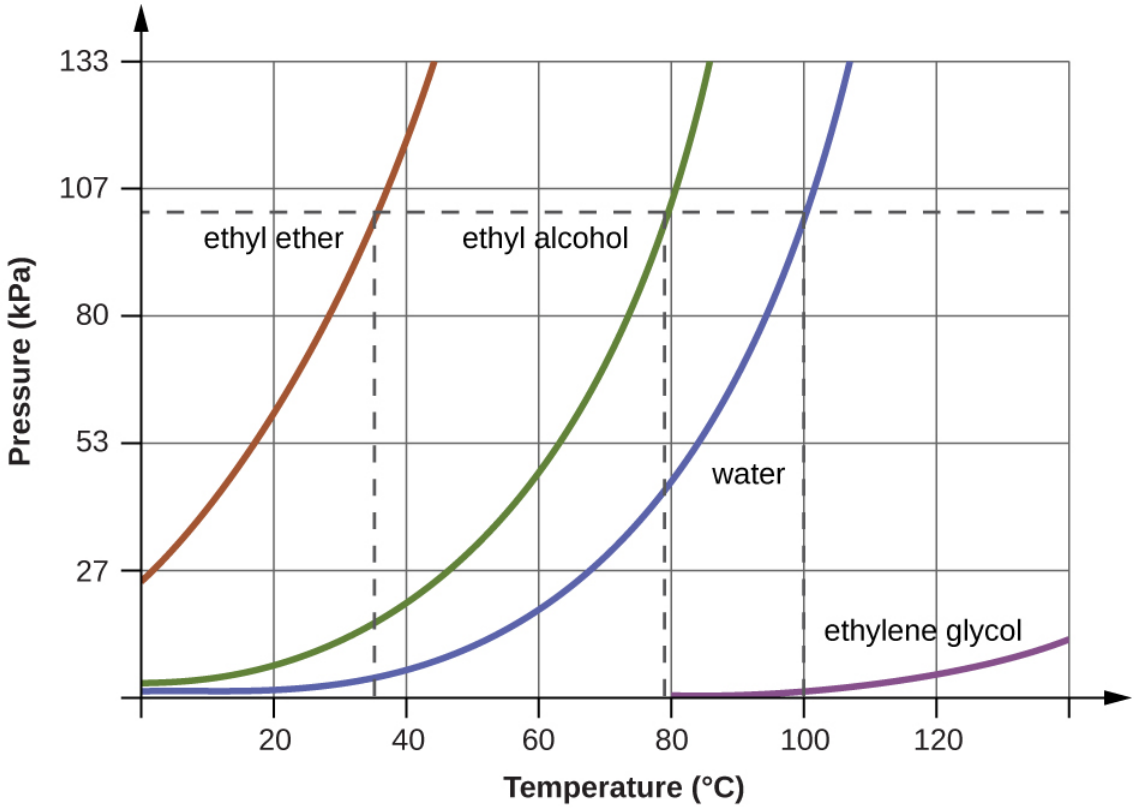


***Figure* 5.4.3**: *The boiling points of liquids are the temperatures at which their equilibrium vapor pressures equal the pressure of the surrounding atmosphere. Normal boiling points are those corresponding to a pressure of 1 atm (101.3 kPa.)*

Example 5.4.2: A Boiling Point at Reduced Pressure

A typical atmospheric pressure in Leadville, Colorado (elevation 10,200 feet) is 68 kPa. Use the graph in Figure **5.4.3** to determine the boiling point of water at this elevation.

Solution

The graph of the vapor pressure of water versus temperature in Figure **5.4.3** indicates that the vapor pressure of water is 68 kPa at about 90 °C. Thus, at about 90 °C, the vapor pressure of water will equal the atmospheric pressure in Leadville, and water will boil.

Exercise 5.4.2

The boiling point of ethyl ether was measured to be 10 °C at a base camp on the slopes of Mount Everest. Use Figure **5.4.3** to determine the approximate atmospheric pressure at the camp.

Answer

Approximately 40 kPa (0.4 atm)

The quantitative relation between a substance's vapor pressure and its temperature is described by the Clausius-Clapeyron equation:

$$P = Ae^{-\Delta H_{vap}/RT} \tag{5.4.1}$$

where

- ΔH_{vap} is the enthalpy of vaporization for the liquid,
- R is the gas constant, and
- $\ln A$ is a constant whose value depends on the chemical identity of the substance.

Equation 5.4.1 is often rearranged into logarithmic form to yield the linear equation:

$$\ln P = -\frac{\Delta H_{\text{vap}}}{RT} + \ln A \tag{5.4.2}$$

This linear equation may be expressed in a two-point format that is convenient for use in various computations, as demonstrated in the examples and exercises that follow. If at temperature T_1, the vapor pressure is P_1, and at temperature T_2, the vapor pressure is T_2, the corresponding linear equations are:

$$\ln P_1 = -\frac{\Delta H_{\text{vap}}}{RT_1} + \ln A \tag{5.4.3}$$

and

$$\ln P_2 = -\frac{\Delta H_{\text{vap}}}{RT_2} + \ln A \tag{5.4.4}$$

Since the constant, ln A, is the same, these two equations may be rearranged to isolate $\ln A$ and then set them equal to one another:

$$\ln P_1 + \frac{\Delta H_{\text{vap}}}{RT_1} = \ln P_2 + \frac{\Delta H_{\text{vap}}}{RT_2}$$

which can be combined into:

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{5.4.5}$$

Example 5.4.3: Estimating Enthalpy of Vaporization

Isooctane (2,2,4-trimethylpentane) has an octane rating of 100. It is used as one of the standards for the octane-rating system for gasoline. At 34.0 °C, the vapor pressure of isooctane is 10.0 kPa, and at 98.8 °C, its vapor pressure is 100.0 kPa. Use this information to estimate the enthalpy of vaporization for isooctane.

Solution

The enthalpy of vaporization, ΔH_{vap}, can be determined by using the Clausius-Clapeyron equation (Equation 5.4.5):

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Since we have two vapor pressure-temperature values

- $T_1 = 34.0°C = 307.2\,K$
- $P_1 = 10.0\,kPa$ and
- $T_2 = 98.8°C = 372.0\,K$
- $P_2 = 100\,kPa$

we can substitute them into this equation and solve for ΔH_{vap}. Rearranging the Clausius-Clapeyron equation and solving for ΔH_{vap} yields:

$$\begin{aligned}\Delta H_{vap} &= \frac{R \cdot \ln\left(\frac{P_2}{P_1}\right)}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} \\ &= \frac{(8.3145\ J/mol \cdot K) \cdot \ln\left(\frac{100\,kPa}{10.0\,kPa}\right)}{\left(\frac{1}{307.2\,K} - \frac{1}{372.0\,K}\right)} \\ &= 33,800\,J/mol = 33.8\,kJ/mol\end{aligned}$$

Note that the pressure can be in any units, so long as they agree for both P values, but the temperature must be in kelvin for the Clausius-Clapeyron equation to be valid.

Exercise 5.4.3

At 20.0 °C, the vapor pressure of ethanol is 5.95 kPa, and at 63.5 °C, its vapor pressure is 53.3 kPa. Use this information to estimate the enthalpy of vaporization for ethanol.

Answer

47,782 J/mol = 47.8 kJ/mol

Example 5.4.4: Estimating Temperature (or Vapor Pressure)

For benzene (C_6H_6), the normal boiling point is 80.1 °C and the enthalpy of vaporization is 30.8 kJ/mol. What is the boiling point of benzene in Denver, where atmospheric pressure = 83.4 kPa?

Solution

If the temperature and vapor pressure are known at one point, along with the enthalpy of vaporization, $\Delta H_{vap,}$ then the temperature that corresponds to a different vapor pressure (or the vapor pressure that corresponds to a different temperature) can be determined by using the Clausius-Clapeyron equation (Equation 5.4.1) :

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Since the normal boiling point is the temperature at which the vapor pressure equals atmospheric pressure at sea level, we know one vapor pressure-temperature value (T_1 = 80.1 °C = 353.3 K, P_1 = 101.3 kPa, ΔH_{vap} = 30.8 kJ/mol) and want to find the temperature (T_2) that corresponds to vapor pressure P_2 = 83.4 kPa. We can substitute these values into the Clausius-Clapeyron equation and then solve for T_2. Rearranging the Clausius-Clapeyron equation and solving for T_2 yields:

$$T_2 = \left(\frac{-R \cdot \ln\left(\frac{P_2}{P_1}\right)}{\Delta H_{vap}} + \frac{1}{T_1} \right)^{-1}$$

$$= \left(\frac{-(8.3145\ \text{J/mol·K}) \cdot \ln\left(\frac{83.4\ \text{kPa}}{101.3\ \text{kPa}}\right)}{30{,}800\ \text{J/mol}} + \frac{1}{353.3\ \text{K}} \right)^{-1}$$

$$= 346.9\ \text{K or } 73.8°\text{C}$$

Exercise 5.4.4

For acetone $(CH_3)_2CO$, the normal boiling point is 56.5 °C and the enthalpy of vaporization is 31.3 kJ/mol. What is the vapor pressure of acetone at 25.0 °C?

Answer

30.1 kPa



***Video* 5.4.2:** *An overview of the role of vapor pressure on boiling point.*

Enthalpy of Vaporization

Vaporization is an endothermic process. The cooling effect can be evident when you leave a swimming pool or a shower. When the water on your skin evaporates, it removes heat from your skin and causes you to feel cold. The energy change associated with the vaporization process is the enthalpy of vaporization, ΔH_{vap}. For example, the vaporization of water at standard temperature is represented by:

$$H_2O(l) \longrightarrow H_2O(g) \quad \Delta H_{vap} = 44.01\ \text{kJ/mol} \tag{5.4.6}$$

As described in the chapter on thermochemistry, the reverse of an endothermic process is exothermic. And so, the condensation of a gas releases heat:

$$H_2O(g) \longrightarrow H_2O(l) \quad \Delta H_{con} = -\Delta H_{vap} = -44.01\ \text{kJ/mol} \tag{5.4.7}$$

Example 5.4.5: Using Enthalpy of Vaporization

One way our body is cooled is by evaporation of the water in sweat (Figure **5.4.4**). In very hot climates, we can lose as much as 1.5 L of sweat per day. Although sweat is not pure water, we can get an approximate value of the amount of heat removed by evaporation by assuming that it is. How much heat is required to evaporate 1.5 L of water (1.5 kg) at T = 37 °C (normal body temperature); $\Delta H_{vap} = 43.46\ kJ/mol$ at 37 °C.



***Figure* 5.4.4:** *Evaporation of sweat helps cool the body. (credit: "Kullez"/Flickr)*

Solution We start with the known volume of sweat (approximated as just water) and use the given information to convert to the amount of heat needed:

$$1.5 \cancel{L} \times \frac{1000 \cancel{g}}{1 \cancel{L}} \times \frac{1 \cancel{\text{mol}}}{18 \cancel{g}} \times \frac{43.46 \text{ kJ}}{1 \cancel{\text{mol}}} = 3.6 \times 10^3 \text{ kJ}$$

Thus, 3600 kJ of heat are removed by the evaporation of 1.5 L of water.

Exercise 5.4.5: Boiling Ammonia

How much heat is required to evaporate 100.0 g of liquid ammonia, NH_3, at its boiling point if its enthalpy of vaporization is 4.8 kJ/mol?

Answer

28 kJ

Melting and Freezing

When we heat a crystalline solid, we increase the average energy of its atoms, molecules, or ions and the solid gets hotter. At some point, the added energy becomes large enough to partially overcome the forces holding the molecules or ions of the solid in their fixed positions, and the solid begins the process of transitioning to the liquid state, or melting. At this point, the temperature of the solid stops rising, despite the continual input of heat, and it remains constant until all of the solid is melted. Only after all of the solid has melted will continued heating increase the temperature of the liquid (Figure 5.4.5.



***Figure* 5.4.5:** *(a) This beaker of ice has a temperature of −12.0 °C. (b) After 10 minutes the ice has absorbed enough heat from the air to warm to 0 °C. A small amount has melted. (c) Thirty minutes later, the ice has absorbed more heat, but its temperature is still 0 °C. The ice melts without changing its temperature. (d) Only after all the ice has melted does the heat absorbed cause the temperature to increase to 22.2 °C. (credit: modification of work by Mark Ott).*

If we stop heating during melting and place the mixture of solid and liquid in a perfectly insulated container so no heat can enter or escape, the solid and liquid phases remain in equilibrium. This is almost the situation with a mixture of ice and water in a very good thermos bottle; almost no heat gets in or out, and the mixture of solid ice and liquid water remains for hours. In a mixture of solid

and liquid at equilibrium, the reciprocal processes of melting and freezing occur at equal rates, and the quantities of solid and liquid therefore remain constant. The temperature at which the solid and liquid phases of a given substance are in equilibrium is called the melting point of the solid or the freezing point of the liquid. Use of one term or the other is normally dictated by the direction of the phase transition being considered, for example, solid to liquid (melting) or liquid to solid (freezing).

The enthalpy of fusion and the melting point of a crystalline solid depend on the strength of the attractive forces between the units present in the crystal. Molecules with weak attractive forces form crystals with low melting points. Crystals consisting of particles with stronger attractive forces melt at higher temperatures.

The amount of heat required to change one mole of a substance from the solid state to the liquid state is the enthalpy of fusion, ΔHfus of the substance. The enthalpy of fusion of ice is 6.0 kJ/mol at 0 °C. Fusion (melting) is an endothermic process:

$$\mathrm{H_2O_{(s)} \rightarrow H_2O_{(l)} \quad \Delta H_{fus} = 6.01\ kJ/mol} \tag{5.4.8}$$

The reciprocal process, freezing, is an exothermic process whose enthalpy change is −6.0 kJ/mol at 0 °C:

$$\mathrm{H_2O_{(l)} \rightarrow H_2O_{(s)} \quad \Delta H_{frz} = -\Delta H_{fus} = -6.01\ kJ/mol} \tag{5.4.9}$$

Sublimation and Deposition

Some solids can transition directly into the gaseous state, bypassing the liquid state, via a process known as sublimation. At room temperature and standard pressure, a piece of dry ice (solid CO_2) sublimes, appearing to gradually disappear without ever forming any liquid. Snow and ice sublime at temperatures below the melting point of water, a slow process that may be accelerated by winds and the reduced atmospheric pressures at high altitudes. When solid iodine is warmed, the solid sublimes and a vivid purple vapor forms (Figure **5.4.6**). The reverse of sublimation is called deposition, a process in which gaseous substances condense directly into the solid state, bypassing the liquid state. The formation of frost is an example of deposition.



Figure 5.4.6: *Sublimation of solid iodine in the bottom of the tube produces a purple gas that subsequently deposits as solid iodine on the colder part of the tube above. (credit: modification of work by Mark Ott)*

Like vaporization, the process of sublimation requires an input of energy to overcome intermolecular attractions. The enthalpy of sublimation, ΔHsub, is the energy required to convert one mole of a substance from the solid to the gaseous state. For example, the sublimation of carbon dioxide is represented by:

$$\mathrm{CO_2(s) \longrightarrow CO_2(g) \quad \Delta H_{sub} = 26.1\ kJ/mol} \tag{5.4.10}$$

Likewise, the enthalpy change for the reverse process of deposition is equal in magnitude but opposite in sign to that for sublimation:

$$\mathrm{CO_2(g) \longrightarrow CO_2(s) \quad \Delta H_{dep} = -\Delta H_{sub} = -26.1\ kJ/mol} \tag{5.4.11}$$

Consider the extent to which intermolecular attractions must be overcome to achieve a given phase transition. Converting a solid into a liquid requires that these attractions be only partially overcome; transition to the gaseous state requires that they be completely overcome. As a result, the enthalpy of fusion for a substance is less than its enthalpy of vaporization. This same logic can be used to derive an approximate relation between the enthalpies of all phase changes for a given substance. Though not an entirely accurate description, sublimation may be conveniently modeled as a sequential two-step process of melting followed by vaporization in order to apply Hess's Law.

$$\begin{array}{l} \text{solid} \longrightarrow \text{liquid} \quad \Delta H_{\text{fus}} \\ \underline{\text{liquid} \longrightarrow \text{gas} \quad \Delta H_{\text{vap}}} \\ \text{solid} \longrightarrow \text{gas} \quad \Delta H_{\text{sub}} = \Delta H_{\text{fus}} + \Delta H_{\text{vap}} \end{array} \tag{5.4.12}$$

Viewed in this manner, the enthalpy of sublimation for a substance may be estimated as the sum of its enthalpies of fusion and vaporization, as illustrated in Figure 5.4.7. For example:

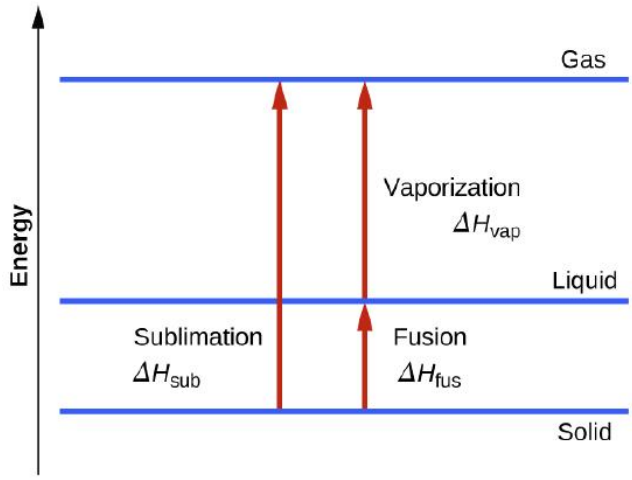


***Figure* 5.4.7**: *For a given substance, the sum of its enthalpy of fusion and enthalpy of vaporization is approximately equal to its enthalpy of sublimation.*

Summary



***Video* 5.4.3**: *An overview of phase changes with regards to kinetics.*

Phase transitions are processes that convert matter from one physical state into another. There are six phase transitions between the three phases of matter. Melting, vaporization, and sublimation are all endothermic processes, requiring an input of heat to overcome intermolecular attractions. The reciprocal transitions of freezing, condensation, and deposition are all exothermic processes, involving heat as intermolecular attractive forces are established or strengthened. The temperatures at which phase transitions occur are determined by the relative strengths of intermolecular attractions and are, therefore, dependent on the chemical identity of the substance.

Key Equations

- $P = Ae^{-\Delta H_{\text{vap}}/RT}$
- $\ln P = -\dfrac{\Delta H_{\text{vap}}}{RT} + \ln A$
- $\ln\left(\dfrac{P_2}{P_1}\right) = \dfrac{\Delta H_{\text{vap}}}{R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$

Glossary

boiling point
temperature at which the vapor pressure of a liquid equals the pressure of the gas above it

Clausius-Clapeyron equation
mathematical relationship between the temperature, vapor pressure, and enthalpy of vaporization for a substance

condensation
change from a gaseous to a liquid state

deposition
change from a gaseous state directly to a solid state

dynamic equilibrium
state of a system in which reciprocal processes are occurring at equal rates

freezing
change from a liquid state to a solid state

freezing point
temperature at which the solid and liquid phases of a substance are in equilibrium; see also *melting point*

melting
change from a solid state to a liquid state

melting point
temperature at which the solid and liquid phases of a substance are in equilibrium; see also *freezing point*

normal boiling point
temperature at which a liquid's vapor pressure equals 1 atm (760 torr)

sublimation
change from solid state directly to gaseous state

vapor pressure
(also, equilibrium vapor pressure) pressure exerted by a vapor in equilibrium with a solid or a liquid at a given temperature

vaporization
change from liquid state to gaseous state

Contributors

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- Adelaide Clark, Oregon Institute of Technology
- Crash Course Chemistry: Crash Course is a division of Complexly and videos are free to stream for educational purposes.
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5.4.1: Vapor Pressure (Problems)

PROBLEM 5.4.1.1

Heat is added to boiling water. Explain why the temperature of the boiling water does not change. What does change?

Answer

The heat is absorbed by the water, providing the energy required to partially overcome intermolecular attractive forces in the liquid and causing a phase transition to gaseous water. The solution remains at 100 °C until all the water is boiled. Only the amount of water existing as liquid water changes until the liquid disappears. Then the temperature of the water can rise.

PROBLEM 5.4.1.2

Heat is added to ice at 0 °C. Explain why the temperature of the ice does not change. What does change?

Answer

The heat is absorbed by the ice, providing the energy required to partially overcome intermolecular attractive forces in the solid and causing a phase transition to liquid water. The solution remains at 0 °C until all the ice is melted. Only the amount of water existing as ice changes until the ice disappears. Then the temperature of the water can rise.

PROBLEM 5.4.1.3

What is the relationship between the intermolecular forces in a liquid and its vapor pressure?

Answer

The vapor pressure of a liquid decreases as the strength of its intermolecular forces increases.

PROBLEM 5.4.1.4

What is the relationship between the intermolecular forces in a solid and its melting temperature?

Answer

The stronger the intermolecular forces, the higher the melting point.

PROBLEM 5.4.1.5

Why does spilled gasoline evaporate more rapidly on a hot day than on a cold day?

Answer

As the temperature increases, the average kinetic energy of the molecules of gasoline increases and so a greater fraction of molecules have sufficient energy to escape from the liquid than at lower temperatures.

PROBLEM 5.4.1.6

When is the boiling point of a liquid equal to its normal boiling point?

Answer

When the pressure of gas above the liquid is exactly 1 atm

PROBLEM 5.4.1.7

How does the boiling of a liquid differ from its evaporation?

Answer

boiling implies an application of energy in the form of heat.

PROBLEM 5.4.1.8

Explain the following observations:

a. It takes longer to cook an egg in Klamath Falls, Oregon (altitude, 4200 feet above sea level) than it does in Boston (at sea level).
b. Perspiring is a mechanism for cooling the body.

Answer a

At 4200 feet, the atmospheric pressure is lower than at sea level, and water will therefore boil at a lower temperature. This lower temperature will cause the physical and chemical changes involved in cooking the egg to proceed more slowly, and a longer time is required to fully cook the egg.

Answer b

As long as the air surrounding the body contains less water vapor than the maximum that air can hold at that temperature, perspiration will evaporate, thereby cooling the body by removing the heat of vaporization required to vaporize the water.

PROBLEM 5.4.1.9

Explain why the molar enthalpies of vaporization of the following substances increase in the order $CH_4 < C_2H_6 < C_3H_8$, even though all three substances experience the same dispersion forces when in the liquid state.

Answer

Dispersion forces increase with molecular mass or size. As the number of atoms composing the molecules in this homologous series increases, so does the extent of intermolecular attraction via dispersion forces and, consequently, the energy required to overcome these forces and vaporize the liquids.

PROBLEM 5.4.1.10

Explain why the enthalpies of vaporization of the following substances increase in the order $CH_4 < NH_3 < H_2O$, even though all three substances have approximately the same molar mass.

Answer

CH_4 is non-polar (dispersion forces only)

NH_3 is polar (dipole-dipole interactions)

H_2O is polar (hydrogen bonding)

PROBLEM 5.4.1.11

Which contains the compounds listed correctly in order of increasing boiling points?

a. $N_2 < CS_2 < H_2O < KCl$
b. $H_2O < N_2 < CS_2 < KCl$
c. $N_2 < KCl < CS_2 < H_2O$
d. $CS_2 < N_2 < KCl < H_2O$
e. $KCl < H_2O < CS_2 < N_2$

Answer

a is correct; N_2 is nonpolar, CS_2 is polar (dipole-dipole), H_2O is polar (H-bonding), KCl is ionic (ion-dipole)

Contributors

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- Adelaide Clark, Oregon Institute of Technology

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5.5: Heating Curves and Phase Changes

Skills to Develop

- Describe the processes represented by typical heating and cooling curves, and compute heat flows and enthalpy changes accompanying these processes
- Explain the construction and use of a typical phase diagram
- Use phase diagrams to identify stable phases at given temperatures and pressures, and to describe phase transitions resulting from changes in these properties
- Describe the supercritical fluid phase of matter

Heating and Cooling Curves

In the Unit on Thermochemistry, the relation between the amount of heat absorbed or related by a substance, q, and its accompanying temperature change, ΔT, was introduced:

$$q = mc\Delta T \tag{5.5.1}$$

where m is the mass of the substance and c is its specific heat. The relation applies to matter being heated or cooled, but not undergoing a change in state. When a substance being heated or cooled reaches a temperature corresponding to one of its phase transitions, further gain or loss of heat is a result of diminishing or enhancing intermolecular attractions, instead of increasing or decreasing molecular kinetic energies. While a substance is undergoing a change in state, its temperature remains constant. Figure 5.5.1 shows a typical heating curve.

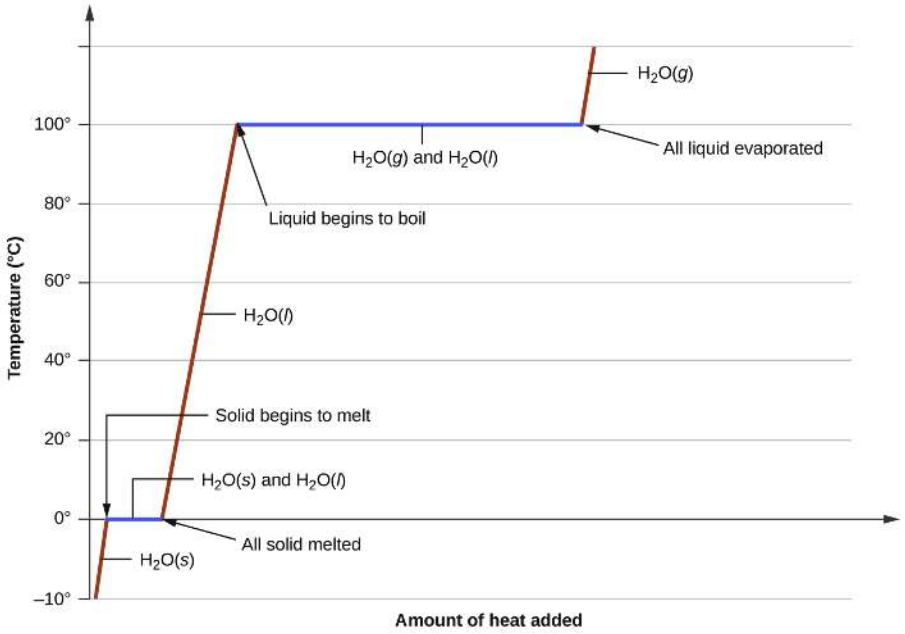


***Figure 5.5.1**: A typical heating curve for a substance depicts changes in temperature that result as the substance absorbs increasing amounts of heat. Plateaus in the curve (regions of constant temperature) are exhibited when the substance undergoes phase transitions.*

Consider the example of heating a pot of water to boiling. A stove burner will supply heat at a roughly constant rate; initially, this heat serves to increase the water's temperature. When the water reaches its boiling point, the temperature remains constant despite the continued input of heat from the stove burner. This same temperature is maintained by the water as long as it is boiling. If the burner setting is increased to provide heat at a greater rate, the water temperature does not rise, but instead the boiling becomes more vigorous (rapid). This behavior is observed for other phase transitions as well: For example, temperature remains constant while the change of state is in progress.

Example 5.5.1: Total Heat Needed to Change Temperature and Phase for a Substance

How much heat is required to convert 135 g of ice at −15 °C into water vapor at 120 °C?

Solution

The transition described involves the following steps:

1. Heat ice from −15 °C to 0 °C
2. Melt ice
3. Heat water from 0 °C to 100 °C
4. Boil water
5. Heat steam from 100 °C to 120 °C

The heat needed to change the temperature of a given substance (with no change in phase) is: $q = m \times c \times \Delta T$ (see previous chapter on thermochemistry). The heat needed to induce a given change in phase is given by $q = n \times \Delta H$.

Using these equations with the appropriate values for specific heat of ice, water, and steam, and enthalpies of fusion and vaporization, we have:

$$\begin{aligned} q_{\text{total}} &= (m \cdot c \cdot \Delta T)_{\text{ice}} + n \cdot \Delta H_{\text{fus}} + (m \cdot c \cdot \Delta T)_{\text{water}} + n \cdot \Delta H_{\text{vap}} + (m \cdot c \cdot \Delta T)_{\text{steam}} \\ &= (135\ \text{g} \cdot 2.09\ \text{J/g·°C} \cdot 15\text{°C}) + \left(135 \cdot \frac{1\ \text{mol}}{18.02\ \text{g}} \cdot 6.01\ \text{kJ/mol}\right) \\ &+ (135\ \text{g} \cdot 4.18\ \text{J/g·°C} \cdot 100\text{°C}) + \left(135\ \text{g} \cdot \frac{1\ \text{mol}}{18.02\ \text{g}} \cdot 40.67\ \text{kJ/mol}\right) \\ &+ (135\ \text{g} \cdot 1.84\ \text{J/g·°C} \cdot 20\text{°C}) \\ &= 4230\ \text{J} + 45.0\ \text{kJ} + 56,500\ \text{J} + 305\ \text{kJ} + 4970\ \text{J} \end{aligned}$$

Converting the quantities in J to kJ permits them to be summed, yielding the total heat required:

$$= 4.23\ \text{kJ} + 45.0\ \text{kJ} + 56.5\ \text{kJ} + 305\ \text{kJ} + 4.97\ \text{kJ} = 416\ \text{kJ}$$

Exercise 5.5.1

What is the total amount of heat released when 94.0 g water at 80.0 °C cools to form ice at −30.0 °C?

Answer

40.5 kJ

In the previous unit, the variation of a liquid's equilibrium vapor pressure with temperature was described. Considering the definition of boiling point, plots of vapor pressure versus temperature represent how the boiling point of the liquid varies with pressure. Also described was the use of heating and cooling curves to determine a substance's melting (or freezing) point. Making such measurements over a wide range of pressures yields data that may be presented graphically as a phase diagram. A phase diagram combines plots of pressure versus temperature for the liquid-gas, solid-liquid, and solid-gas phase-transition equilibria of a substance. These diagrams indicate the physical states that exist under specific conditions of pressure and temperature, and also provide the pressure dependence of the phase-transition temperatures (melting points, sublimation points, boiling points). A typical phase diagram for a pure substance is shown in Figure 5.5.2.

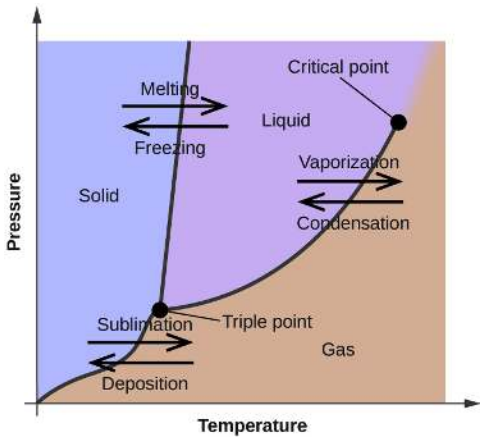


Figure* 5.5.2*: *The physical state of a substance and its phase-transition temperatures are represented graphically in a phase diagram.*

To illustrate the utility of these plots, consider the phase diagram for water shown in Figure **5.5.3**.

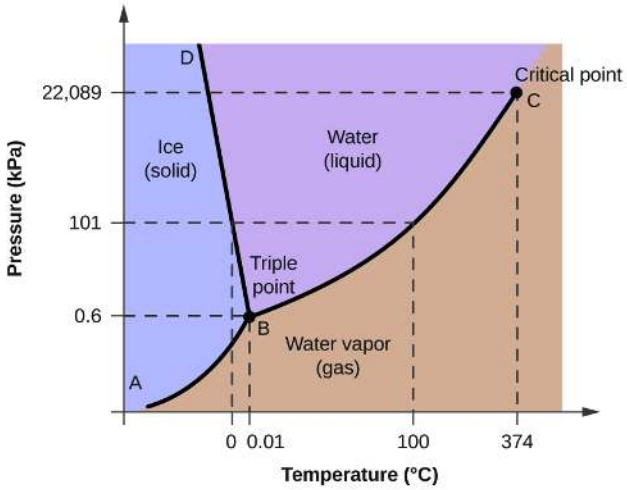


Figure* 5.5.3*: *The pressure and temperature axes on this phase diagram of water are not drawn to constant scale in order to illustrate several important properties.*

We can use the phase diagram to identify the physical state of a sample of water under specified conditions of pressure and temperature. For example, a pressure of 50 kPa and a temperature of −10 °C correspond to the region of the diagram labeled “ice.” Under these conditions, water exists only as a solid (ice). A pressure of 50 kPa and a temperature of 50 °C correspond to the “water” region—here, water exists only as a liquid. At 25 kPa and 200 °C, water exists only in the gaseous state. Note that on the H_2O phase diagram, the pressure and temperature axes are not drawn to a constant scale in order to permit the illustration of several important features as described here.

The curve BC in Figure **5.5.3** is the plot of vapor pressure versus temperature as described in the previous module of this chapter. This “liquid-vapor” curve separates the liquid and gaseous regions of the phase diagram and provides the boiling point for water at any pressure. For example, at 1 atm, the boiling point is 100 °C. Notice that the liquid-vapor curve terminates at a temperature of 374 °C and a pressure of 218 atm, indicating that water cannot exist as a liquid above this temperature, regardless of the pressure. The physical properties of water under these conditions are intermediate between those of its liquid and gaseous phases. This unique state of matter is called a supercritical fluid, a topic that will be described in the next section of this module.

The solid-vapor curve, labeled AB in Figure **5.5.3**, indicates the temperatures and pressures at which ice and water vapor are in equilibrium. These temperature-pressure data pairs correspond to the sublimation, or deposition, points for water. If we could zoom in on the solid-gas line in Figure **5.5.2**, we would see that ice has a vapor pressure of about 0.20 kPa at −10 °C. Thus, if we place a

frozen sample in a vacuum with a pressure less than 0.20 kPa, ice will sublime. This is the basis for the “freeze-drying” process often used to preserve foods, such as the ice cream shown in Figure 5.5.4.



Figure 5.5.4: *Freeze-dried foods, like this ice cream, are dehydrated by sublimation at pressures below the triple point for water. (credit: "lwao"/Flickr)*

The solid-liquid curve labeled BD shows the temperatures and pressures at which ice and liquid water are in equilibrium, representing the melting/freezing points for water. Note that this curve exhibits a slight negative slope (greatly exaggerated for clarity), indicating that the melting point for water decreases slightly as pressure increases. Water is an unusual substance in this regard, as most substances exhibit an increase in melting point with increasing pressure. This behavior is partly responsible for the movement of glaciers, like the one shown in Figure 5.5.5. The bottom of a glacier experiences an immense pressure due to its weight that can melt some of the ice, forming a layer of liquid water on which the glacier may more easily slide.



Figure 5.5.5: *The immense pressures beneath glaciers result in partial melting to produce a layer of water that provides lubrication to assist glacial movement. This satellite photograph shows the advancing edge of the Perito Moreno glacier in Argentina. (credit: NASA)*

The point of intersection of all three curves is labeled B in Figure 5.5.3. At the pressure and temperature represented by this point, all three phases of water coexist in equilibrium. This temperature-pressure data pair is called the triple point. At pressures lower than the triple point, water cannot exist as a liquid, regardless of the temperature.



Video* 5.5.1*: *Cyclohexane at the triple point.*

Example 5.5.2: Determining the State of Water

Using the phase diagram for water given in Figure 10.4.2, determine the state of water at the following temperatures and pressures:

a. −10 °C and 50 kPa
b. 25 °C and 90 kPa
c. 50 °C and 40 kPa
d. 80 °C and 5 kPa
e. −10 °C and 0.3 kPa
f. 50 °C and 0.3 kPa

Solution

Using the phase diagram for water, we can determine that the state of water at each temperature and pressure given are as follows: (a) solid; (b) liquid; (c) liquid; (d) gas; (e) solid; (f) gas.

Exercise 5.5.2

What phase changes can water undergo as the temperature changes if the pressure is held at 0.3 kPa? If the pressure is held at 50 kPa?

Answer:

At 0.3 kPa: s⟶ g at −58 °C. At 50 kPa: s⟶ l at 0 °C, l ⟶ g at 78 °C

Consider the phase diagram for carbon dioxide shown in Figure **5.5.6** as another example. The solid-liquid curve exhibits a positive slope, indicating that the melting point for CO_2 increases with pressure as it does for most substances (water being a notable exception as described previously). Notice that the triple point is well above 1 atm, indicating that carbon dioxide cannot exist as a liquid under ambient pressure conditions. Instead, cooling gaseous carbon dioxide at 1 atm results in its deposition into the solid state. Likewise, solid carbon dioxide does not melt at 1 atm pressure but instead sublimes to yield gaseous CO_2. Finally, notice that the critical point for carbon dioxide is observed at a relatively modest temperature and pressure in comparison to water.

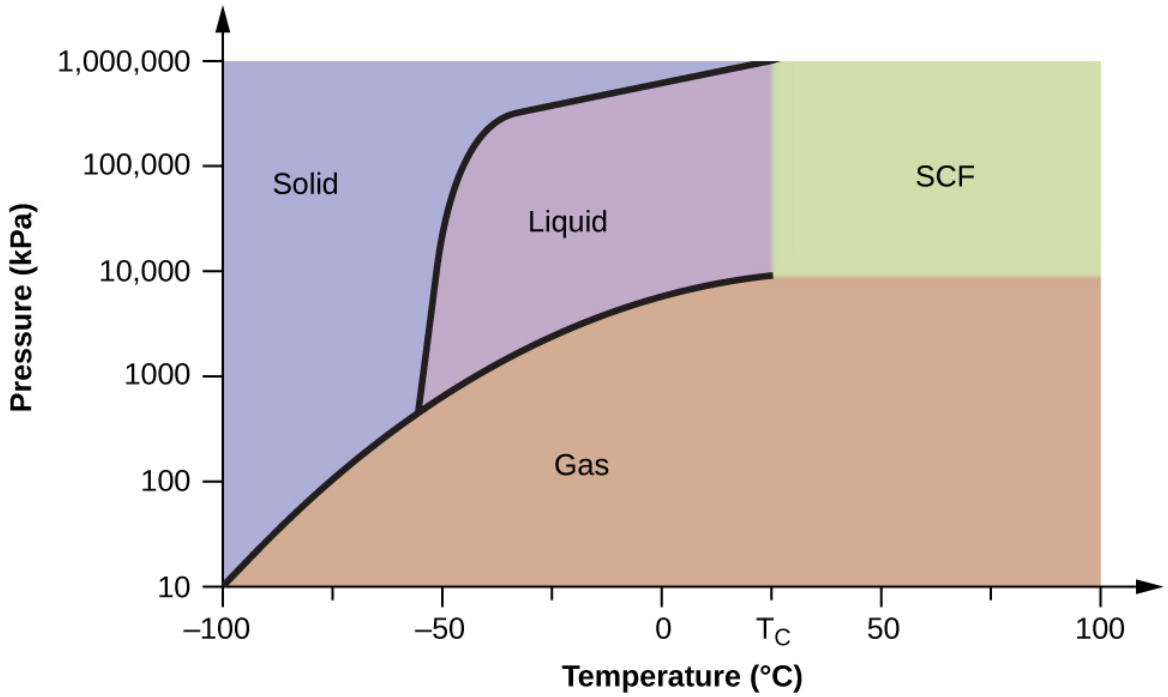


***Figure* 5.5.6**: *A phase diagram for carbon dioxide is shown. The pressure axis is plotted on a logarithmic scale to accommodate the large range of values.*

Example 5.5.3: Determining the State of Carbon Dioxide

Using the phase diagram for carbon dioxide shown in Figure 10.4.5, determine the state of CO_2 at the following temperatures and pressures:

a. −30 °C and 2000 kPa
b. −60 °C and 1000 kPa
c. −60 °C and 100 kPa
d. 20 °C and 1500 kPa
e. 0 °C and 100 kPa
f. 20 °C and 100 kPa

Solution

Using the phase diagram for carbon dioxide provided, we can determine that the state of CO_2 at each temperature and pressure given are as follows: (a) liquid; (b) solid; (c) gas; (d) liquid; (e) gas; (f) gas.

Exercise 5.5.3

Determine the phase changes carbon dioxide undergoes when its temperature is varied, thus holding its pressure constant at 1500 kPa? At 500 kPa? At what approximate temperatures do these phase changes occur?

Answer

at 1500 kPa: s⟶ l at −45 °C, l⟶ g at −10 °C; at 500 kPa: s⟶ g at −58 °C



Video* 5.5.2*: *Observe the behavior of supercritical fluids.*

If we place a sample of water in a sealed container at 25 °C, remove the air, and let the vaporization-condensation equilibrium establish itself, we are left with a mixture of liquid water and water vapor at a pressure of 0.03 atm. A distinct boundary between the more dense liquid and the less dense gas is clearly observed. As we increase the temperature, the pressure of the water vapor increases, as described by the liquid-gas curve in the phase diagram for water (Figure **5.5.3**), and a two-phase equilibrium of liquid and gaseous phases remains. At a temperature of 374 °C, the vapor pressure has risen to 218 atm, and any further increase in temperature results in the disappearance of the boundary between liquid and vapor phases. All of the water in the container is now present in a single phase whose physical properties are intermediate between those of the gaseous and liquid states. This phase of matter is called a supercritical fluid, and the temperature and pressure above which this phase exists is the critical point (Figure **5.5.5**). Above its critical temperature, a gas cannot be liquefied no matter how much pressure is applied. The pressure required to liquefy a gas at its critical temperature is called the critical pressure. The critical temperatures and critical pressures of some common substances are given in Table **5.5.1**.

Table* 5.5.1*: *Critical Temperatures and Critical Pressures of select substances*

Substance	Critical Temperature (K)	Critical Pressure (atm)
hydrogen	33.2	12.8
nitrogen	126.0	33.5
oxygen	154.3	49.7
carbon dioxide	304.2	73.0
ammonia	405.5	111.5
sulfur dioxide	430.3	77.7
water	647.1	217.7



***Video* 5.5.3:** *The liquid to supercritical fluid transition for carbon dioxide.*

Like a gas, a supercritical fluid will expand and fill a container, but its density is much greater than typical gas densities, typically being close to those for liquids. Similar to liquids, these fluids are capable of dissolving nonvolatile solutes. They exhibit essentially no surface tension and very low viscosities, however, so they can more effectively penetrate very small openings in a solid mixture and remove soluble components. These properties make supercritical fluids extremely useful solvents for a wide range of applications. For example, supercritical carbon dioxide has become a very popular solvent in the food industry, being used to decaffeinate coffee, remove fats from potato chips, and extract flavor and fragrance compounds from citrus oils. It is nontoxic, relatively inexpensive, and not considered to be a pollutant. After use, the CO_2 can be easily recovered by reducing the pressure and collecting the resulting gas.

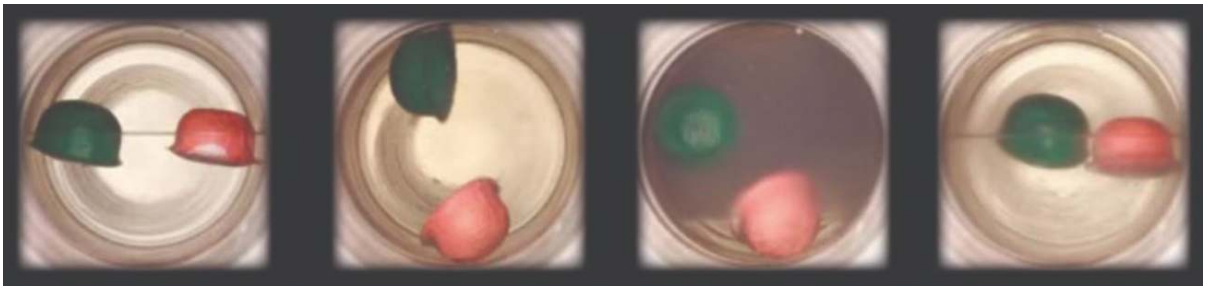


***Figure* 5.5.7:** *(a) A sealed container of liquid carbon dioxide slightly below its critical point is heated, resulting in (b) the formation of the supercritical fluid phase. Cooling the supercritical fluid lowers its temperature and pressure below the critical point, resulting in the reestablishment of separate liquid and gaseous phases (c and d). Colored floats illustrate differences in density between the liquid, gaseous, and supercritical fluid states. (credit: modification of work by "mrmrobin"/YouTube)*

Example 5.5.4: The Critical Temperature of Carbon Dioxide

If we shake a carbon dioxide fire extinguisher on a cool day (18 °C), we can hear liquid CO_2 sloshing around inside the cylinder. However, the same cylinder appears to contain no liquid on a hot summer day (35 °C). Explain these observations.

Solution

On the cool day, the temperature of the CO_2 is below the critical temperature of CO_2, 304 K or 31 °C (Table **5.5.1**), so liquid CO_2 is present in the cylinder. On the hot day, the temperature of the CO_2 is greater than its critical temperature of 31 °C. Above this temperature no amount of pressure can liquefy CO_2 so no liquid CO_2 exists in the fire extinguisher.

Exercise 5.5.4

Ammonia can be liquefied by compression at room temperature; oxygen cannot be liquefied under these conditions. Why do the two gases exhibit different behavior?

Answer

The critical temperature of ammonia is 405.5 K, which is higher than room temperature. The critical temperature of oxygen is below room temperature; thus oxygen cannot be liquefied at room temperature.

Decaffeinating Coffee Using Supercritical CO_2

Coffee is the world's second most widely traded commodity, following only petroleum. Across the globe, people love coffee's aroma and taste. Many of us also depend on one component of coffee—caffeine—to help us get going in the morning or stay alert in the afternoon. But late in the day, coffee's stimulant effect can keep you from sleeping, so you may choose to drink decaffeinated coffee in the evening.

Since the early 1900s, many methods have been used to decaffeinate coffee. All have advantages and disadvantages, and all depend on the physical and chemical properties of caffeine. Because caffeine is a somewhat polar molecule, it dissolves well in water, a polar liquid. However, since many of the other 400-plus compounds that contribute to coffee's taste and aroma also dissolve in H_2O, hot water decaffeination processes can also remove some of these compounds, adversely affecting the smell and taste of the decaffeinated coffee. Dichloromethane (CH_2Cl_2) and ethyl acetate ($CH_3CO_2C_2H_5$) have similar polarity to caffeine, and are therefore very effective solvents for caffeine extraction, but both also remove some flavor and aroma components, and their use requires long extraction and cleanup times. Because both of these solvents are toxic, health concerns have been raised regarding the effect of residual solvent remaining in the decaffeinated coffee.

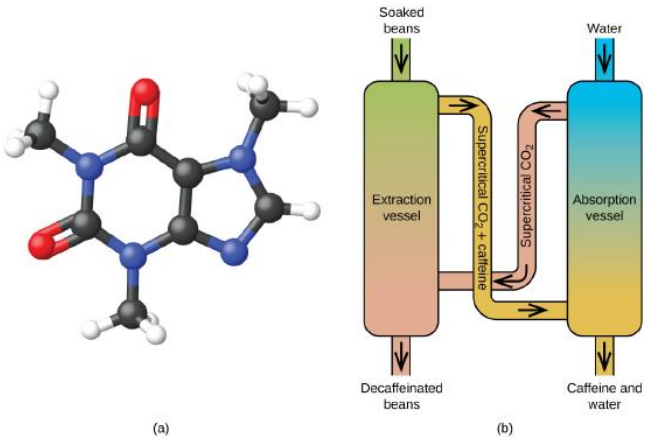
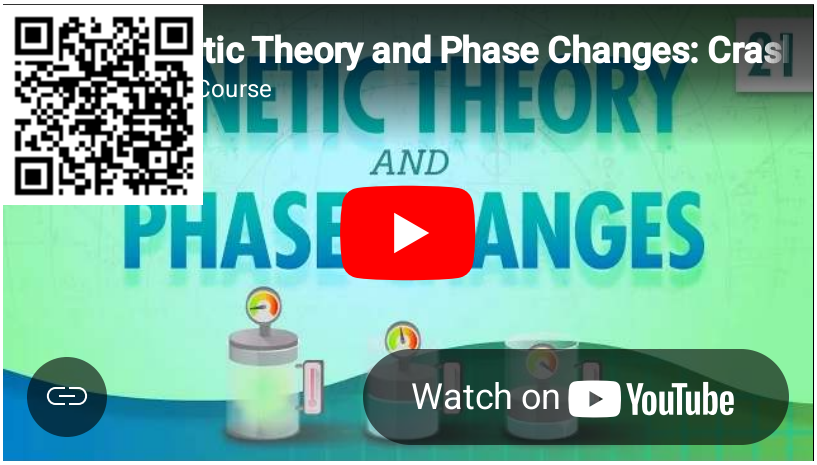


***Figure* 5.5.8:** *(a) Caffeine molecules have both polar and nonpolar regions, making it soluble in solvents of varying polarities. (b) The schematic shows a typical decaffeination process involving supercritical carbon dioxide.*

Supercritical fluid extraction using carbon dioxide is now being widely used as a more effective and environmentally friendly decaffeination method (Figure 5.5.8). At temperatures above 304.2 K and pressures above 7376 kPa, CO_2 is a supercritical fluid, with properties of both gas and liquid. Like a gas, it penetrates deep into the coffee beans; like a liquid, it effectively dissolves certain substances. Supercritical carbon dioxide extraction of steamed coffee beans removes 97−99% of the caffeine, leaving coffee's flavor and aroma compounds intact. Because CO_2 is a gas under standard conditions, its removal from the extracted coffee beans is easily accomplished, as is the recovery of the caffeine from the extract. The caffeine recovered from coffee beans via this process is a valuable product that can be used subsequently as an additive to other foods or drugs.

Summary



***Video* 5.5.4:** *An overview of phase changes and phase diagrams.*

The temperatures at which phase transitions occur are determined by the relative strengths of intermolecular attractions and are, therefore, dependent on the chemical identity of the substance. The temperature and pressure conditions at which a substance exists in solid, liquid, and gaseous states are summarized in a phase diagram for that substance. Phase diagrams are combined plots of three pressure-temperature equilibrium curves: solid-liquid, liquid-gas, and solid-gas. These curves represent the relationships between phase-transition temperatures and pressures. The point of intersection of all three curves represents the substance's triple point—the temperature and pressure at which all three phases are in equilibrium. At pressures below the triple point, a substance cannot exist in the liquid state, regardless of its temperature. The terminus of the liquid-gas curve represents the substance's critical point, the pressure and temperature above which a liquid phase cannot exist.

Key Equations

- $P = Ae^{-\Delta H_{vap}/RT}$
- $\ln P = -\frac{\Delta H_{vap}}{RT} + \ln A$
- $\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

Glossary

critical point
: temperature and pressure above which a gas cannot be condensed into a liquid

phase diagram
: pressure-temperature graph summarizing conditions under which the phases of a substance can exist

supercritical fluid
: substance at a temperature and pressure higher than its critical point; exhibits properties intermediate between those of gaseous and liquid states

triple point
: temperature and pressure at which the vapor, liquid, and solid phases of a substance are in equilibrium

Contributors

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5.5.1: Heating Curves and Phase Changes (Problems)

PROBLEM 5.5.1.1

From the phase diagram for water, determine the state of water at:

a. 35 °C and 85 kPa
b. −15 °C and 40 kPa
c. −15 °C and 0.1 kPa
d. 75 °C and 3 kPa
e. 40 °C and 0.1 kPa
f. 60 °C and 50 kPa

Answer a

Liquid

Answer b

solid

Answer c

solid

Answer d

gas

Answer e

gas

Answer f

liquid

PROBLEM 5.5.1.2

Evaporation of sweat requires energy and thus take excess heat away from the body. Some of the water that you drink may eventually be converted into sweat and evaporate. If you drink a 20-ounce bottle of water that had been in the refrigerator at 3.8 °C, how much heat is needed to convert all of that water into sweat and then to vapor?? (Note: Your body temperature is 36.6 °C. For the purpose of solving this problem, assume that the thermal properties of sweat are the same as for water.)

Answer

20 ounces water= 567 g $\quad \frac{567g}{18.0g/mole}$ = 31.5 moles

Heating 567 g from 3.8 °C to 100 °C q_1= m Cp ΔT = 567g x 4.18 J/g-°C x 96.2°C = 228 kJ

Vaporizing step q_2= n ΔH_vap = 31.5 moles x 30.67 kJ/mole =1281 kJ

Cooling the vapor from 100 °C to 38.6 °C q_3= m Cp ΔT =567g x 1.84 x (-61.4) = -64 kJ

$q_{Total} = q_1 + q_2 + q_3$ = 228kJ + 1281kJ -64kJ = 1445 kJ

PROBLEM 5.5.1.3

How much heat is required to convert 422 g of liquid H_2O at 23.5 °C into steam at 150 °C?

Answer

1130 kJ

Click here to see a video of the solution



PROBLEM 5.5.1.4

Titanium tetrachloride, $TiCl_4$, has a melting point of −23.2 °C and has a ΔH_{fusion} = 9.37 kJ/mol.

a. How much energy is required to melt 263.1 g $TiCl_4$?
b. For $TiCl_4$, which will likely have the larger magnitude: ΔH_{fusion} or $\Delta H_{vaporization}$? Explain your reasoning.

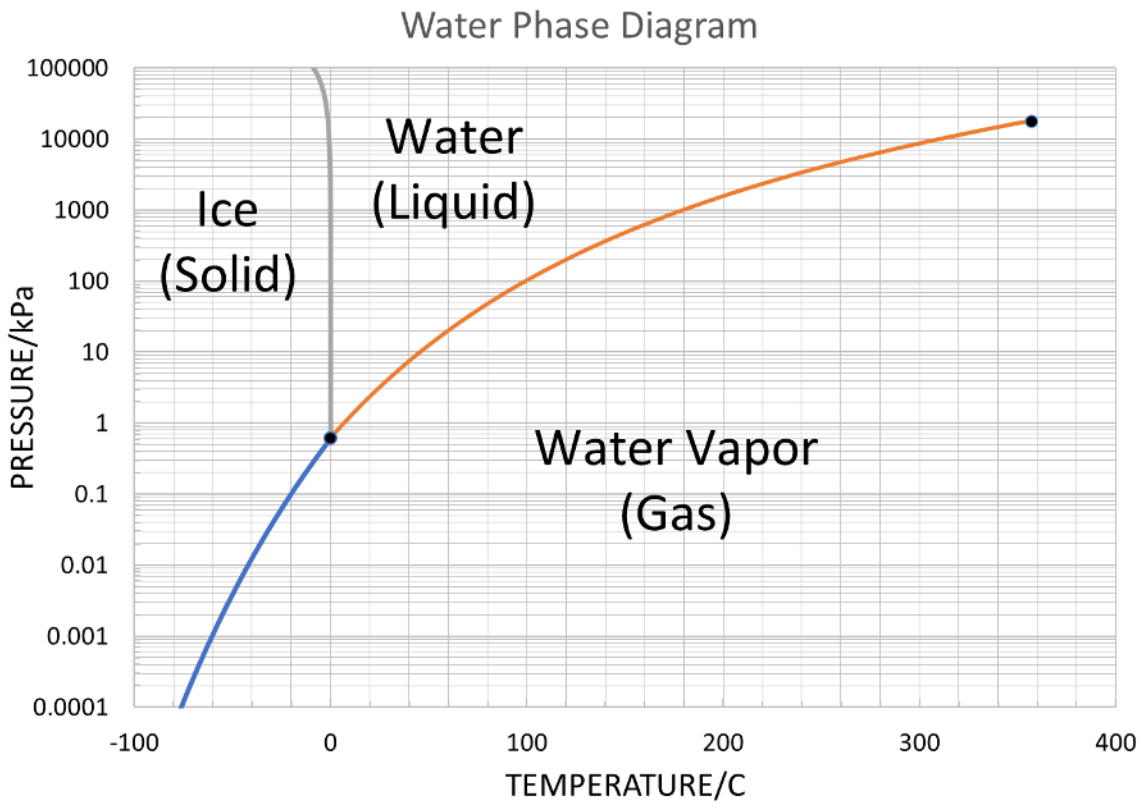
Answer a

13.0 kJ

Answer b

It is likely that the heat of vaporization will have a larger magnitude since in the case of vaporization the intermolecular interactions have to be completely overcome, while melting weakens or destroys only some of them.

PROBLEM 5.5.1.5



What phase changes will take place when water is subjected to varying pressure at a constant temperature of 0.005 °C? At 40 °C? At −40 °C?

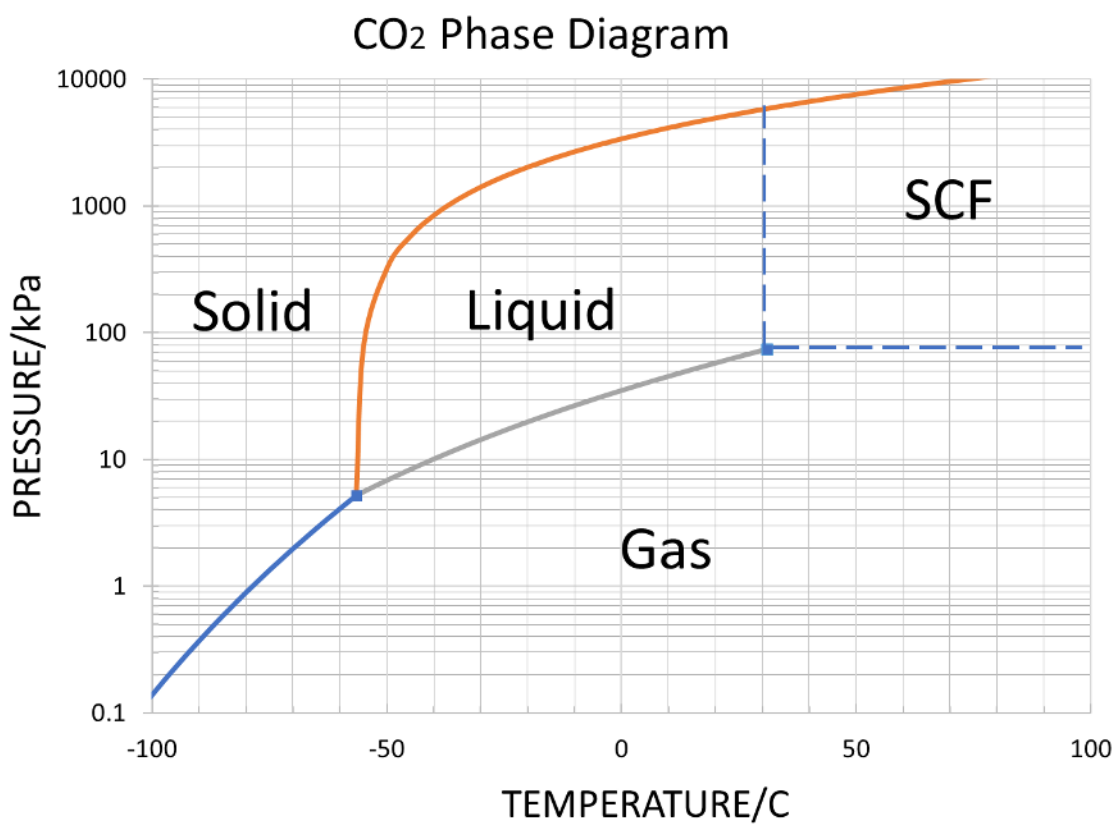
Answer

At 0.005 °C vapor to solid to liquid. The triple point is at +0.01 °C and the freezing point is ever so slightly lower at 0.00 °C. So if one raises the pressure at a constant 0.005 °C one passes just to the left of the triple point and the vapor will first solidify at 0.612 KPa and then the solid will melt and become a liquid between the 0.00 °C melting point and 0.612 kPa

At 40 °C vapor to liquid.

At - 40 °C vapor to solid

PROBLEM 5.5.1.6



From the phase diagram for carbon dioxide, determine the state of CO_2 at:

a. 20 °C and 1000 kPa
b. 10 °C and 2000 kPa
c. 10 °C and 100 kPa
d. −40 °C and 500 kPa
e. −80 °C and 1500 kPa
f. −80 °C and 10 kPa

Answer a

liquid

Answer b

liquid

Answer c

liquid

Answer d

liquid

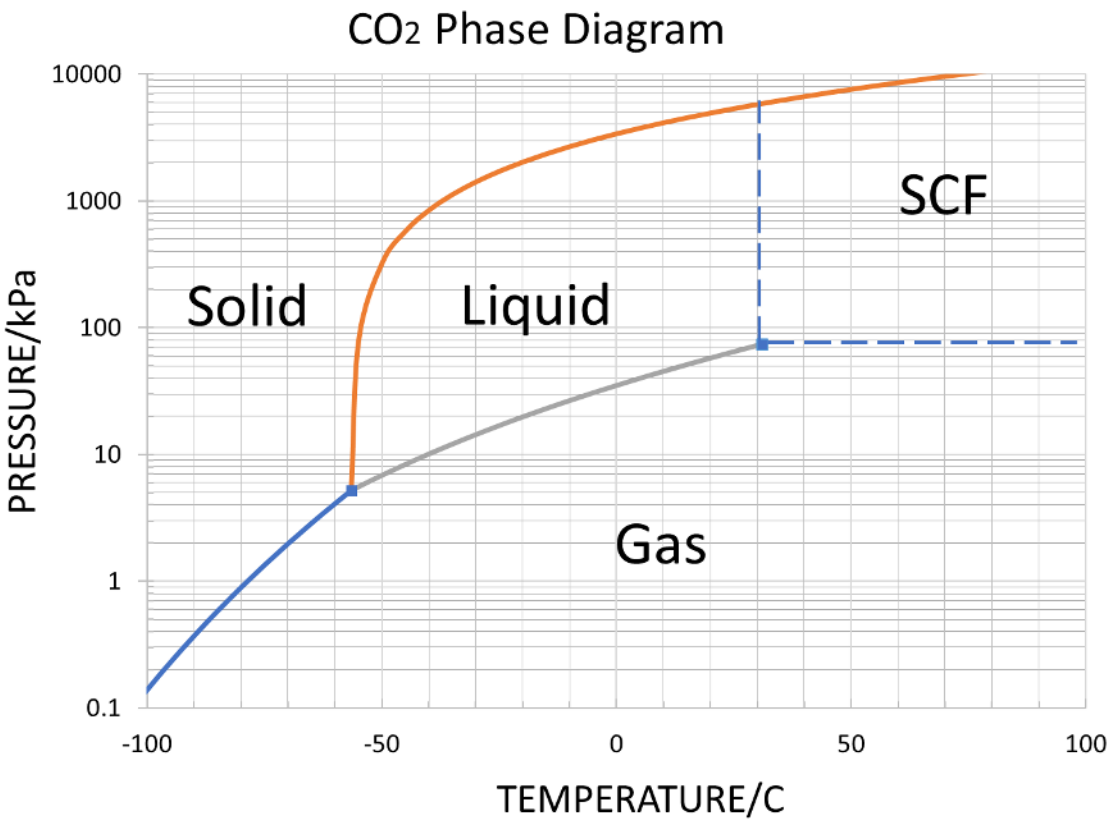
Answer e

solid

Answer f

solid

? PROBLEM 5.5.1.7



Determine the phase changes that carbon dioxide undergoes as the pressure changes if the temperature is held at −50 °C? If the temperature is held at −40 °C? At 20 °C?

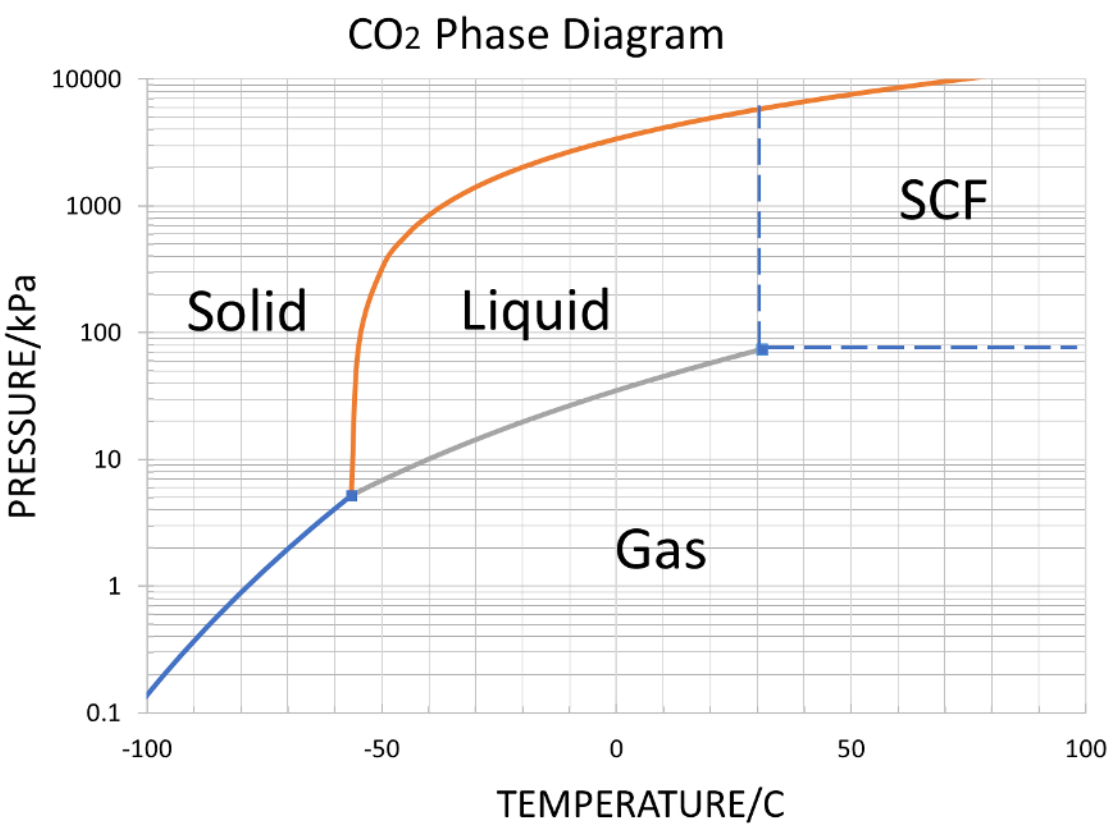
Answer

−50 °C: gas to liquid to solid

−40 °C: gas to liquid to solid

20 °C: gas to liquid to solid

PROBLEM 5.5.1.8



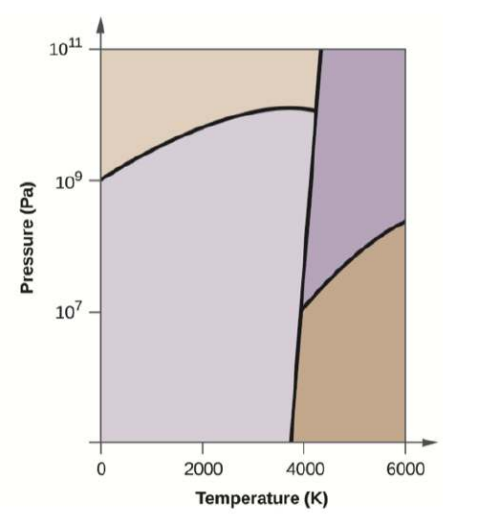
Dry ice, $CO_2(s)$, does not melt at atmospheric pressure. It sublimes at a temperature of −78 °C. What is the lowest pressure at which $CO_2(s)$ will melt to give $CO_2(l)$? At approximately what temperature will this occur?

Answer

Dry ice, $CO_2(s)$, will melt to give $CO_2(l)$ at 5.11 atm at −56.6 °C, the triple point of carbon dioxide.

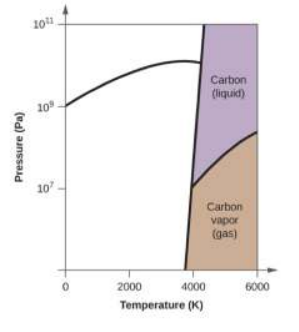
PROBLEM 5.5.1.9

Elemental carbon has one gas phase, one liquid phase, and three different solid phases, as shown in the phase diagram:

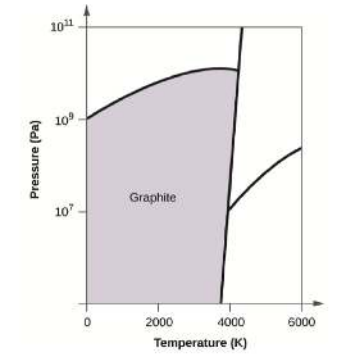


a. On the phase diagram, label the gas and liquid regions.
b. Graphite is the most stable phase of carbon at normal conditions. On the phase diagram, label the graphite phase.
c. If graphite at normal conditions is heated to 2500 K while the pressure is increased to 10^{10} Pa, it is converted into diamond. Label the diamond phase.
d. Circle each triple point on the phase diagram.
e. In what phase does carbon exist at 5000 K and 10^{8} Pa?
f. If the temperature of a sample of carbon increases from 3000 K to 5000 K at a constant pressure of 10^{6} Pa, which phase transition occurs, if any?

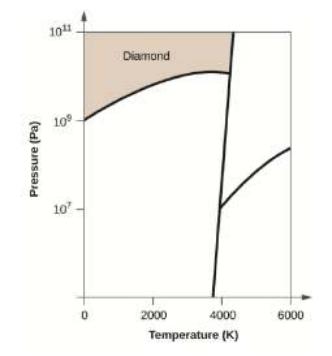
Answer a



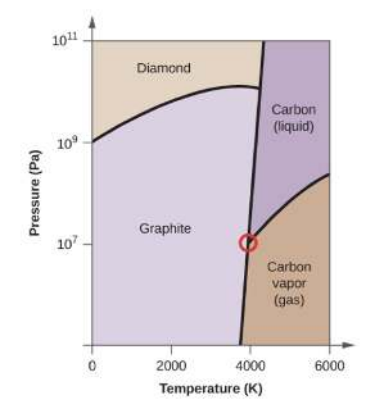
Answer b



Answer c



Answer d



Answer e

liquid

Answer f

sublimation

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- Adelaide Clark, Oregon Institute of Technology

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CHAPTER OVERVIEW

6: Applications of Bonding and Modern Materials

6.1: Lattice Energies

6.1.1: Lattice Energies (Problems)

6.2: The Solid State of Matter

6.2.1: The Solid State of Matter (Problems)

6.3: Unit Cells

6.3.1: Unit Cells (Problems)

6.4: Structure and General Properties of the Metalloids

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6.1: Lattice Energies

Skills to Develop

- Explain the formation of cations, anions, and ionic compounds
- Describe the energetics of ionic bond formation and breakage
- Use the Born-Haber cycle to compute lattice energies for ionic compounds

A bond's strength describes how strongly each atom is joined to another atom, and therefore how much energy is required to break the bond between the two atoms. In a previous section, you learned about the bond strength of covalent bonds. Now we will compare that to the strength of ionic bonds, which is related to the lattice energy of a compound. But first, let's explore how ionic bonds form.

The Formation of Ionic Compounds



***Video* 6.1.1**: *Why do atoms bond?*



***Video* 6.1.2**: *And how do atoms bond?*

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

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

dissolve readily in water. Once dissolved or melted, ionic compounds are excellent conductors of electricity and heat because the ions can move about freely.

Neutral atoms and their associated ions have very different physical and chemical properties. Sodium *atoms* form sodium metal, a soft, silvery-white metal that burns vigorously in air and reacts explosively with water. Chlorine *atoms* form chlorine gas, Cl_2, a yellow-green gas that is extremely corrosive to most metals and very poisonous to animals and plants. The vigorous reaction between the elements sodium and chlorine forms the white, crystalline compound sodium chloride, common table salt, which contains sodium *cations* and chloride *anions* (Figure Figure **6.1.1**). The compound composed of these ions exhibits properties entirely different from the properties of the elements sodium and chlorine. Chlorine is poisonous, but sodium chloride is essential to life; sodium atoms react vigorously with water, but sodium chloride simply dissolves in water.



***Figure* 6.1.1**: *(a) Sodium is a soft metal that must be stored in mineral oil to prevent reaction with air or water. (b) Chlorine is a pale yellow-green gas. (c) When combined, they form white crystals of sodium chloride (table salt). (credit a: modification of work by "Jurii"/Wikimedia Commons)*

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

As all substances must be electrically neutral, the total number of positive charges on the cations of an ionic compound must equal the total number of negative charges on its anions. The formula of an ionic compound represents the simplest ratio of the numbers of ions necessary to give identical numbers of positive and negative charges. For example, the formula for aluminum oxide, Al_2O_3, indicates that this ionic compound contains two aluminum cations, Al^{3+}, for every three oxide anions, O^{2-} [thus, $(2 \times +3) + (3 \times -2) = 0$].

It is important to note, however, that the formula for an ionic compound does *not* represent the physical arrangement of its ions. It is incorrect to refer to a sodium chloride (NaCl) "molecule" because there is not a single ionic bond, per se, between any specific pair of sodium and chloride ions. The attractive forces between ions are isotropic—the same in all directions—meaning that any particular ion is equally attracted to all of the nearby ions of opposite charge. This results in the ions arranging themselves into a tightly bound, three-dimensional lattice structure. Sodium chloride, for example, consists of a regular arrangement of equal numbers of Na^+ cations and Cl^- anions (Figure Figure **6.1.2**).

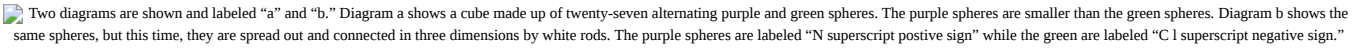

Two diagrams are shown and labeled "a" and "b." Diagram a shows a cube made up of twenty-seven alternating purple and green spheres. The purple spheres are smaller than the green spheres. Diagram b shows the same spheres, but this time, they are spread out and connected in three dimensions by white rods. The purple spheres are labeled "N superscript postive sign" while the green are labeled "C l superscript negative sign."

***Figure* 6.1.2**: *The atoms in sodium chloride (common table salt) are arranged to (a) maximize opposite charges interacting. The smaller spheres represent sodium ions, the larger ones represent chloride ions. In the expanded view (b), the geometry can be seen more clearly. Note that each ion is "bonded" to all of the surrounding ions—six in this case.*

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

$$\mathrm{NaCl}(s) \longrightarrow \mathrm{Na}^+(g) + \mathrm{Cl}^-(g) \quad \Delta H = 769\ \mathrm{kJ} \tag{6.1.1}$$



***Video* 6.1.3**: *A review of ionic bonds from last term.*

Ionic Bond Strength and Lattice Energy

An ionic compound is stable because of the electrostatic attraction between its positive and negative ions. The lattice energy of a compound is a measure of the strength of this attraction. The lattice energy ($\Delta H_{lattice}$) of an ionic compound is defined as the energy required to separate one mole of the solid into its component gaseous ions. For the ionic solid MX, the lattice energy is the enthalpy change of the process:

$$MX_{(s)} \longrightarrow Mn^{+}_{(g)} + X^{n-}_{(g)} \quad \Delta H_{lattice} \tag{6.1.2}$$

Note that we are using the convention where the ionic solid is separated into ions, so our lattice energies will be endothermic (positive values). Some texts use the equivalent but opposite convention, defining lattice energy as the energy released when separate ions combine to form a lattice and giving negative (exothermic) values. Thus, if you are looking up lattice energies in another reference, be certain to check which definition is being used. In both cases, a larger magnitude for lattice energy indicates a more stable ionic compound. For sodium chloride, $\Delta H_{\text{lattice}}$ = 769 kJ. Thus, it requires 769 kJ to separate one mole of solid NaCl into gaseous Na^+ and Cl^- ions. When one mole each of gaseous Na^+ and Cl^- ions form solid NaCl, 769 kJ of heat is released.

The lattice energy $\Delta H_{lattice}$ of an ionic crystal can be expressed by the following equation (derived from Coulomb's law, governing the forces between electric charges):

$$\Delta H_{lattice} = \frac{C(Z^+)(Z^-)}{R_o} \tag{6.1.3}$$

in which

- C is a constant that depends on the type of crystal structure;
- Z^+ and Z^- are the charges on the ions; and
- R_o is the interionic distance (the sum of the radii of the positive and negative ions).

Thus, the lattice energy of an ionic crystal increases rapidly as the charges of the ions increase and the sizes of the ions decrease. When all other parameters are kept constant, doubling the charge of both the cation and anion quadruples the lattice energy. For example, the lattice energy of LiF (Z^+ and Z^- = 1) is 1023 kJ/mol, whereas that of MgO (Z^+ and Z^- = 2) is 3900 kJ/mol (R_o is nearly the same—about 200 pm for both compounds).

Different interatomic distances produce different lattice energies. For example, we can compare the lattice energy of MgF_2 (2957 kJ/mol) to that of MgI_2 (2327 kJ/mol) to observe the effect on lattice energy of the smaller ionic size of F^- as compared to I^-.

Example 6.1.2: Lattice Energy Comparisons

The precious gem ruby is aluminum oxide, Al_2O_3, containing traces of Cr^{3+}. The compound Al_2Se_3 is used in the fabrication of some semiconductor devices. Which has the larger lattice energy, Al_2O_3 or Al_2Se_3?

Solution

In these two ionic compounds, the charges Z^+ and Z^- are the same, so the difference in lattice energy will mainly depend upon R_o. The O^{2-} ion is smaller than the Se^{2-} ion. Thus, Al_2O_3 would have a shorter interionic distance than Al_2Se_3, and Al_2O_3 would have the larger lattice energy.

Exercise 6.1.2

Zinc oxide, ZnO, is a very effective sunscreen. How would the lattice energy of ZnO compare to that of NaCl?

Answer

ZnO would have the larger lattice energy because the Z values of both the cation and the anion in ZnO are greater, and the interionic distance of ZnO is smaller than that of NaCl.

The Born-Haber Cycle

It is not possible to measure lattice energies directly. However, the lattice energy can be calculated using the equation given in the previous section or by using a thermochemical cycle. The Born-Haber cycle is an application of Hess's law that breaks down the formation of an ionic solid into a series of individual steps:

- ΔH_f°, the standard enthalpy of formation of the compound
- IE, the ionization energy of the metal
- EA, the electron affinity of the nonmetal
- ΔH_s°, the enthalpy of sublimation of the metal
- D, the bond dissociation energy of the nonmetal
- $\Delta H_{lattice}$, the lattice energy of the compound

Figure 6.1.3 diagrams the Born-Haber cycle for the formation of solid cesium fluoride.

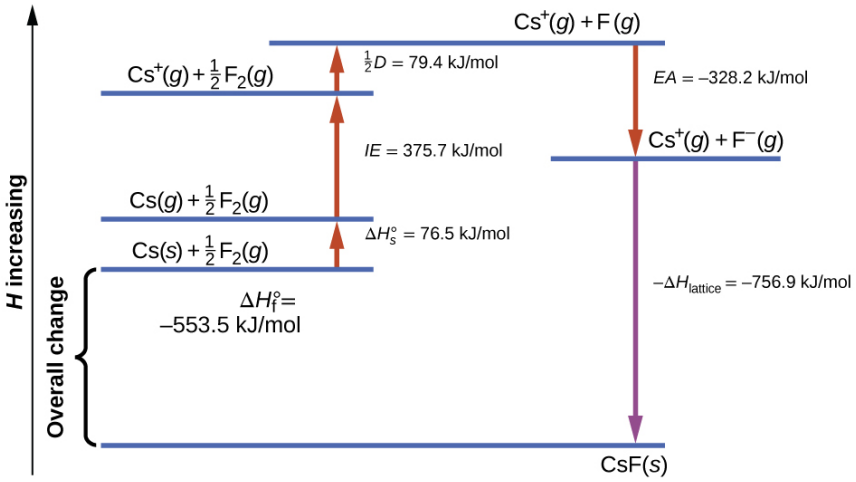


Figure* 6.1.3*: *The Born-Haber cycle shows the relative energies of each step involved in the formation of an ionic solid from the necessary elements in their reference states.*

We begin with the elements in their most common states, Cs(*s*) and $F_2(g)$. The ΔH_s° represents the conversion of solid cesium into a gas, and then the ionization energy converts the gaseous cesium atoms into cations. In the next step, we account for the energy required to break the F–F bond to produce fluorine atoms. Converting one mole of fluorine atoms into fluoride ions is an exothermic process, so this step gives off energy (the electron affinity) and is shown as decreasing along the *y*-axis. We now have one mole of Cs cations and one mole of F anions. These ions combine to produce solid cesium fluoride. The enthalpy change in this step is the negative of the lattice energy, so it is also an exothermic quantity. The total energy involved in this conversion is equal to the experimentally determined enthalpy of formation, ΔH_f°, of the compound from its elements. In this case, the overall change is exothermic.

Hess's law can also be used to show the relationship between the enthalpies of the individual steps and the enthalpy of formation. Table **6.1.1** shows this for cesium fluoride, CsF.

Table* 6.1.1*: Enthalpies of Select Transitions

Enthalpy of sublimation of Cs(s)	$\mathrm{Cs}(s) \longrightarrow \mathrm{Cs}(g) \quad \Delta H = \Delta H_s^\circ = 77\ \mathrm{kJ/mol}$
One-half of the bond energy of F_2	$\frac{1}{2}\mathrm{F_2}(g) \longrightarrow \mathrm{F}(g) \quad \Delta H = \frac{1}{2}D = 79\ \mathrm{kJ/mol}$
Ionization energy of Cs(g)	$\mathrm{Cs}(g) \longrightarrow \mathrm{Cs^+}(g) + \mathrm{e^-} \quad \Delta H = IE = 376\ k\mathrm{J/mol}$
Negative of the electron affinity of F	$\mathrm{F}(g) + \mathrm{e^-} \longrightarrow \mathrm{F^-}(g) \quad \Delta H = -EA = -328\ k\mathrm{J/mol}$
Negative of the lattice energy of CsF(s)	$\mathrm{Cs^+}(g) + \mathrm{F^-}(g) \longrightarrow \mathrm{CsF}(s) \quad \Delta H = -\Delta H_{\text{lattice}} = ?$
Enthalpy of formation of CsF(s), add steps 1–5	$\Delta H = \Delta H_f^\circ = \Delta H_s^\circ + \frac{1}{2}D + IE + (-EA) + (-\Delta H_{\text{lattice}})$ $\mathrm{Cs}(s) + \frac{1}{2}\mathrm{F_2}(g) \longrightarrow \mathrm{CsF}(s) = -554\ k\mathrm{J/mol}$

Thus, the lattice energy can be calculated from other values. For cesium chloride, using this data, the lattice energy is:

$$\Delta H_{\text{lattice}} = (411 + 109 + 122 + 496 + 368)\ \mathrm{kJ} = 770\ \mathrm{kJ} \tag{6.1.4}$$

The Born-Haber cycle may also be used to calculate any one of the other quantities in the equation for lattice energy, provided that the remainder is known. For example, if the relevant enthalpy of sublimation ΔH_s°, ionization energy (IE), bond dissociation enthalpy (D), lattice energy $\Delta H_{\text{lattice}}$, and standard enthalpy of formation ΔH_f° are known, the Born-Haber cycle can be used to determine the electron affinity of an atom.

Lattice energies calculated for ionic compounds are typically much larger than bond dissociation energies measured for covalent bonds. Whereas lattice energies typically fall in the range of 600–4000 kJ/mol (some even higher), covalent bond dissociation energies are typically between 150–400 kJ/mol for single bonds. Keep in mind, however, that these are not directly comparable values. For ionic compounds, lattice energies are associated with many interactions, as cations and anions pack together in an extended lattice. For covalent bonds, the bond dissociation energy is associated with the interaction of just two atoms.

Summary

The strength of a covalent bond is measured by its bond dissociation energy, that is, the amount of energy required to break that particular bond in a mole of molecules. Multiple bonds are stronger than single bonds between the same atoms. The enthalpy of a reaction can be estimated based on the energy input required to break bonds and the energy released when new bonds are formed. For ionic bonds, the lattice energy is the energy required to separate one mole of a compound into its gas phase ions. Lattice energy increases for ions with higher charges and shorter distances between ions. Lattice energies are often calculated using the Born-Haber cycle, a thermochemical cycle including all of the energetic steps involved in converting elements into an ionic compound.

Key Equations

- Lattice energy for a solid MX: $\mathrm{MX}(s) \longrightarrow \mathrm{M^{n+}}(g) + \mathrm{X^{n-}}(g) \quad \Delta H_{\text{lattice}}$
- Lattice energy for an ionic crystal: $\Delta H_{\text{lattice}} = \dfrac{\mathrm{C(Z^+)(Z^-)}}{\mathrm{R_o}}$

Footnotes

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

Glossary

Born-Haber cycle

thermochemical cycle relating the various energetic steps involved in the formation of an ionic solid from the relevant elements

lattice energy ($\Delta H_{lattice}$)

energy required to separate one mole of an ionic solid into its component gaseous ions

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6.1.1: Lattice Energies (Problems)

PROBLEM 6.1.1.1

Using the bond energies in Table 7.3.1, determine the approximate enthalpy change for each of the following reactions:

a. $\mathrm{H_2}(g) + \mathrm{Br_2}(g) \longrightarrow 2\,\mathrm{HBr}(g)$
b. $\mathrm{CH_4}(g) + \mathrm{I_2}(g) \longrightarrow \mathrm{CH_3I}(g) + \mathrm{HI}(g)$
c. $\mathrm{C_2H_4}(g) + 3\,\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{CO_2}(g) + 2\,\mathrm{H_2O}(g)$

Answer a

−114 kJ

Answer b

30 kJ

Answer c

−1055 kJ

PROBLEM 6.1.1.2

Using the bond energies in Table 7.3.1, determine the approximate enthalpy change for each of the following reactions:

a. $\mathrm{H_2C{=}CH_2}(g) + \mathrm{H_2}(g) \longrightarrow \mathrm{H_3CCH_3}(g)$
b. $2\,\mathrm{C_2H_6}(g) + 7\,\mathrm{O_2}(g) \longrightarrow 4\,\mathrm{CO_2}(g) + 6\,\mathrm{H_2O}(g)$

Answer a

-128 kJ

Answer b

-5175 kJ

Click here to see a video of the solution



PROBLEM 6.1.1.3

How does the bond energy of HCl differ from the standard enthalpy of formation of HCl(g)?

Answer

The enthalpy of formation is -431.6 kJ, while the bond energy of H-Cl is -432 kJ. They are practically the same.

PROBLEM 6.1.1.4

Using the standard enthalpy of formation data in Appendix G, show how the standard enthalpy of formation of HCl(g) can be used to determine the bond energy.

Answer

$$\begin{array}{rl} \mathrm{HCl}(g) \longrightarrow \frac{1}{2}\mathrm{H_2}(g) + \frac{1}{2}\mathrm{Cl_2}(g) & \Delta H_1^\circ = -\Delta H_{f[\mathrm{HCl}(g)]}^\circ \\ \frac{1}{2}\mathrm{H_2}(g) \longrightarrow \mathrm{H}(g) & \Delta H_2^\circ = \Delta H_{f[\mathrm{H}(g)]}^\circ \\ \frac{1}{2}\mathrm{Cl_2}(g) \longrightarrow \mathrm{Cl}(g) & \Delta H_3^\circ = \Delta H_{f[\mathrm{Cl}(g)]}^\circ \\ \hline \mathrm{HCl}(g) \longrightarrow \mathrm{H}(g) + \mathrm{Cl}(g) & \Delta H_{298}^\circ = \Delta H_1^\circ + \Delta H_2^\circ + \Delta H_3^\circ \end{array}$$

$$\begin{aligned} D_{\mathrm{HCl}} = \Delta H_{298}^\circ &= \Delta H_{f[\mathrm{HCl}(g)]}^\circ + \Delta H_{f[\mathrm{H}(g)]}^\circ + \Delta H_{f[\mathrm{Cl}(g)]}^\circ && (6.1.1.1) \\ &= -(-92.307\ \mathrm{kJ}) + 217.97\ \mathrm{kJ} + 121.3\ \mathrm{kJ} && (6.1.1.2) \\ &= 431.6\ \mathrm{kJ} && (6.1.1.3) \end{aligned}$$

PROBLEM 6.1.1.5

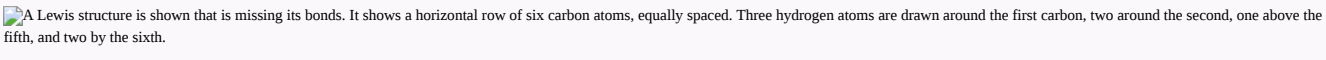
Using the standard enthalpy of formation data in Appendix G, determine which bond is stronger: the S–F bond in $SF_4(g)$ or in $SF_6(g)$?

Answer

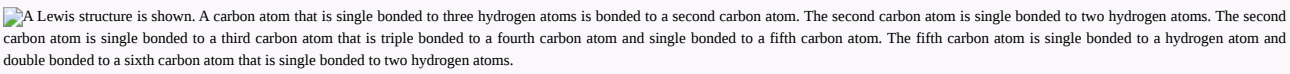
The S–F bond in SF_4 is stronger.

PROBLEM 6.1.1.6

Complete the following Lewis structure by adding bonds (not atoms), and then indicate the longest bond:


A Lewis structure is shown that is missing its bonds. It shows a horizontal row of six carbon atoms, equally spaced. Three hydrogen atoms are drawn around the first carbon, two around the second, one above the fifth, and two by the sixth.

Answer


A Lewis structure is shown. A carbon atom that is single bonded to three hydrogen atoms is bonded to a second carbon atom. The second carbon atom is single bonded to two hydrogen atoms. The second carbon atom is single bonded to a third carbon atom that is triple bonded to a fourth carbon atom and single bonded to a fifth carbon atom. The fifth carbon atom is single bonded to a hydrogen atom and double bonded to a sixth carbon atom that is single bonded to two hydrogen atoms.

The C–C single bonds are longest.

PROBLEM 6.1.1.7

Use principles of atomic structure to answer each of the following:[1]

a. The radius of the Ca atom is 197 pm; the radius of the Ca^{2+} ion is 99 pm. Account for the difference.
b. The lattice energy of CaO(s) is –3460 kJ/mol; the lattice energy of K_2O is –2240 kJ/mol. Account for the difference.
c. Given these ionization values, explain the difference between Ca and K with regard to their first and second ionization energies.

Element	First Ionization Energy (kJ/mol)	Second Ionization Energy (kJ/mol)
K	419	3050
Ca	590	1140

d. The first ionization energy of Mg is 738 kJ/mol and that of Al is 578 kJ/mol. Account for this difference.

Answer a

When two electrons are removed from the valence shell, the Ca radius loses the outermost energy level and reverts to the lower $n = 3$ level, which is much smaller in radius.

Answer b

The +2 charge on calcium pulls the oxygen much closer compared with K, thereby increasing the lattice energy relative to a less charged ion.

Answer c

Removal of the 4*s* electron in Ca requires more energy than removal of the 4*s* electron in K because of the stronger attraction of the nucleus and the extra energy required to break the pairing of the electrons. The second ionization energy for K requires that an electron be removed from a lower energy level, where the attraction is much stronger from the nucleus for the electron. In addition, energy is required to unpair two electrons in a full orbital. For Ca, the second ionization potential requires removing only a lone electron in the exposed outer energy level.

Answer d

In Al, the removed electron is relatively unprotected and unpaired in a *p* orbital. The higher energy for Mg mainly reflects the unpairing of the 2*s* electron.

Contributors

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6.2: The Solid State of Matter

Skills to Develop

- Define and describe the bonding and properties of ionic, molecular, metallic, and covalent network crystalline solids
- Describe the main types of crystalline solids: ionic solids, metallic solids, covalent network solids, and molecular solids
- Explain the ways in which crystal defects can occur in a solid

When most liquids are cooled, they eventually freeze and form crystalline solids, solids in which the atoms, ions, or molecules are arranged in a definite repeating pattern. It is also possible for a liquid to freeze before its molecules become arranged in an orderly pattern. The resulting materials are called amorphous solids or noncrystalline solids (or, sometimes, glasses). The particles of such solids lack an ordered internal structure and are randomly arranged (Figure **6.2.1**).

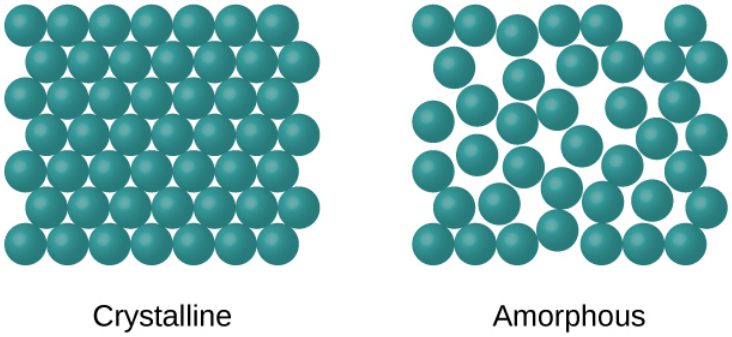


Figure* 6.2.1*: *The entities of a solid phase may be arranged in a regular, repeating pattern (crystalline solids) or randomly (amorphous).*

Metals and ionic compounds typically form ordered, crystalline solids. Substances that consist of large molecules, or a mixture of molecules whose movements are more restricted, often form amorphous solids. For examples, candle waxes are amorphous solids composed of large hydrocarbon molecules. Some substances, such as silicon dioxide (Figure **6.2.2**), can form either crystalline or amorphous solids, depending on the conditions under which it is produced. Also, amorphous solids may undergo a transition to the crystalline state under appropriate conditions.

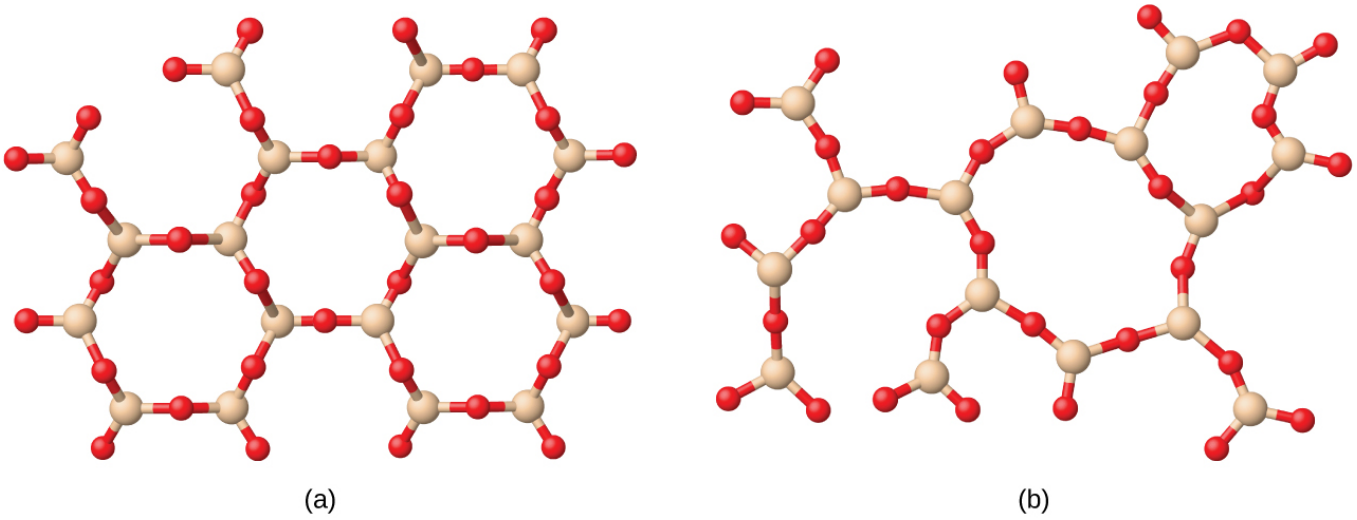


Figure* 6.2.2*: *(a) Silicon dioxide, SiO_2, is abundant in nature as one of several crystalline forms of the mineral quartz. (b) Rapid cooling of molten SiO_2 yields an amorphous solid known as "fused silica".*

Crystalline solids are generally classified according the nature of the forces that hold its particles together. These forces are primarily responsible for the physical properties exhibited by the bulk solids. The following sections provide descriptions of the major types of crystalline solids: ionic, metallic, covalent network, and molecular.

Ionic Solids

Ionic solids, such as sodium chloride and nickel oxide, are composed of positive and negative ions that are held together by electrostatic attractions, which can be quite strong (Figure **6.2.3**). Many ionic crystals also have high melting points. This is due to the very strong attractions between the ions—in ionic compounds, the attractions between full charges are (much) larger than those between the partial charges in polar molecular compounds. This will be looked at in more detail in a later discussion of lattice energies. Although they are hard, they also tend to be brittle, and they shatter rather than bend. Ionic solids do not conduct electricity; however, they do conduct when molten or dissolved because their ions are free to move. Many simple compounds formed by the reaction of a metallic element with a nonmetallic element are ionic.

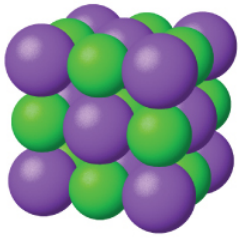


Figure* 6.2.3*: *Sodium chloride is an ionic solid.*

Metallic Bonding

In the early 1900's, Paul Drüde came up with the "sea of electrons" metallic bonding theory by modeling metals as a mixture of atomic cores (atomic cores = positive nuclei + inner shell of electrons) and valence electrons. Metallic bonds occur among metal atoms. Whereas ionic bonds join metals to non-metals, *metallic bonding joins a bulk of metal atoms*. A sheet of aluminum foil and a copper wire are both places where you can see metallic bonding in action.

Metals tend to have high melting points and boiling points suggesting strong bonds between the atoms. Even a soft metal like sodium (melting point 97.8°C) melts at a considerably higher temperature than the element (neon) which precedes it in the Periodic Table. Sodium has the electronic structure $1s^2 2s^2 2p^6 3s^1$. When sodium atoms come together, the electron in the 3s atomic orbital of one sodium atom shares space with the corresponding electron on a neighboring atom to form a molecular orbital - in much the same sort of way that a covalent bond is formed.

The difference, however, is that each sodium atom is being touched by eight other sodium atoms - and the sharing occurs between the central atom and the 3s orbitals on all of the eight other atoms. Each of these eight is in turn being touched by eight sodium atoms, which in turn are touched by eight atoms - and so on and so on, until you have taken in all the atoms in that lump of sodium. *All* of the 3s orbitals on all of the atoms overlap to give a vast number of molecular orbitals that extend over the whole piece of metal. There have to be huge numbers of molecular orbitals, of course, because any orbital can only hold two electrons.

The electrons can move freely within these molecular orbitals, and so each electron becomes detached from its parent atom. The electrons are said to be delocalized. The metal is held together by the strong forces of attraction between the positive nuclei and the delocalized electrons (Figure **6.2.4**).

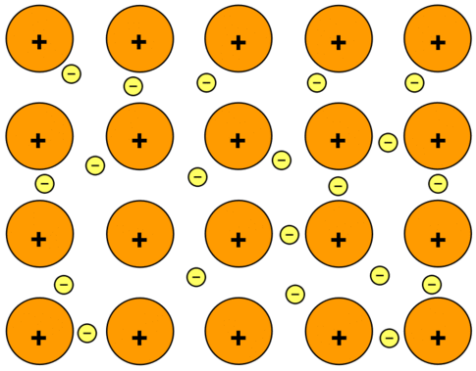


Figure **6.2.4**: Metallic Bonding: The Electron Sea Model: Positive atomic nuclei (orange circles) surrounded by a sea of delocalized electrons (yellow circles).

This is sometimes described as "an array of positive ions in a sea of electrons". If you are going to use this view, beware! Is a metal made up of atoms or ions? It is made of atoms**.** Each positive center in the diagram represents all the rest of the atom apart from the outer electron, but that electron has not been lost - it may no longer have an attachment to a particular atom, but it's still there in the structure. Sodium metal is therefore written as **Na**, not $\mathbf{Na^+}$.

Example 6.2.1: Metallic bonding in magnesium

Use the sea of electrons model to explain why Magnesium has a higher melting point (650 °C) than sodium (97.79 °C).

Solution

If you work through the same argument above for sodium with magnesium, you end up with stronger bonds and hence a higher melting point.

Magnesium has the outer electronic structure $3s^2$. Both of these electrons become delocalized, so the "sea" has twice the electron density as it does in sodium. The remaining "ions" also have twice the charge (if you are going to use this particular view of the metal bond) and so there will be more attraction between "ions" and "sea".

More realistically, each magnesium atom has 12 protons in the nucleus compared with sodium's 11. In both cases, the nucleus is screened from the delocalized electrons by the same number of inner electrons - the 10 electrons in the $1s^2$ $2s^2$ $2p^6$ orbitals. That means that there will be a net pull from the magnesium nucleus of 2+, but only 1+ from the sodium nucleus.

So not only will there be a greater number of delocalized electrons in magnesium, but there will also be a greater attraction for them from the magnesium nuclei. Magnesium atoms also have a slightly smaller radius than sodium atoms, and so the delocalized electrons are closer to the nuclei. Each magnesium atom also has twelve near neighbors rather than sodium's eight. Both of these factors increase the strength of the bond still further.

Note: Transition metals tend to have particularly high melting points and boiling points. The reason is that they can involve the 3d electrons in the delocalization as well as the 4s. The more electrons you can involve, the stronger the attractions tend to be.

Bulk properties of metals

Metals have several qualities that are unique, such as the ability to conduct electricity and heat, a low ionization energy, and a low electronegativity (so they will give up electrons easily to form cations). Their physical properties include a lustrous (shiny) appearance, and they are malleable and ductile. Metals have a crystal structure but can be easily deformed. In this model, the valence electrons are free, delocalized, mobile, and not associated with any particular atom. This model may account for:

- **Conductivity**: Since the electrons are free, if electrons from an outside source were pushed into a metal wire at one end (Figure **6.2.5**), the electrons would move through the wire and come out at the other end at the same rate (conductivity is the movement of charge).

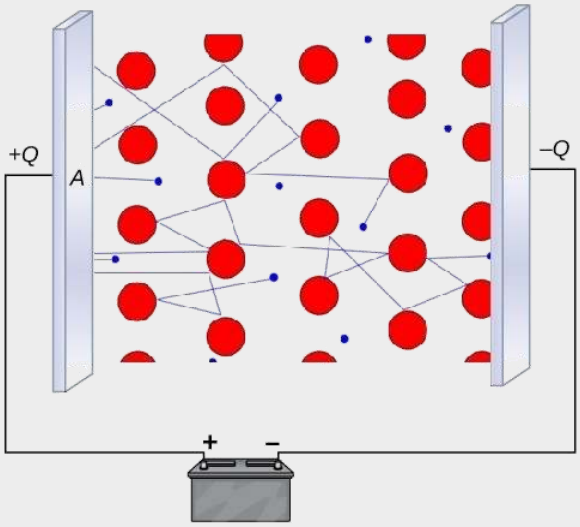


Figure **6.2.5**: The "sea of electrons" is free to flow about the crystal of positive metal ions. These flowing electron can conduct electrical change when an electric field is applied (e.g., a battery). (CC-BY-SA; OpenStax and Rafaelgarcia).

- **Malleability** and **Ductility**: The electron-sea model of metals not only explains their electrical properties but their malleability and ductility as well. The sea of electrons surrounding the protons acts like a cushion, and so when the metal is hammered on, for instance, the overall composition of the structure of the metal is not harmed or changed. The protons may be rearranged but the sea of electrons with adjust to the new formation of protons and keep the metal intact. When one layer of ions in an electron sea moves along one space with respect to the layer below it, the crystal structure does not fracture but is only deformed (Figure **6.2.6**).



Figure **6.2.6**: Malleability of metals originate from each of moving layer of atoms with respect to each other. The final situation is much the same as the initial. Thus if we hit a metal with a hammer, the crystals do not shatter, but merely change their shape, This is very different from the behavior of ionic crystals.

- **Heat capacity**: This is explained by the ability of free electrons to move about the solid.
- **Luster**: The free electrons can absorb photons in the "sea," so metals are opaque-looking. Electrons on the surface can bounce back light at the same frequency that the light hits the surface, therefore the metal appears to be shiny.

However, these observations are only qualitative, and not quantitative, so they cannot be tested. The "Sea of Electrons" theory stands today only as an oversimplified model of how metallic bonding works.

In a molten metal, the metallic bond is still present, although the ordered structure has been broken down. The metallic bond is not fully broken until the metal boils. That means that boiling point is actually a better guide to the strength of the metallic bond than melting point is. On melting, the bond is loosened, not broken. The strength of a metallic bond depends on three things:

1. The number of electrons that become delocalized from the metal
2. The charge of the cation (metal).
3. The size of the cation.

A **strong** metallic bond will be the result of more delocalized electrons, which causes the effective nuclear charge on electrons on the cation to increase, in effect making the size of the cation smaller. Metallic bonds are strong and require a great deal of energy to break, and therefore **metals have high melting and boiling points.** A metallic bonding theory must explain how so much bonding can occur with such few electrons (since metals are located on the left side of the periodic table and do not have many electrons in their valence shells). The theory must also account for all of a metal's unique chemical and physical properties.

Expanding the Range of Bonding Possible

Previously, we argued that bonding between atoms can classified as range of possible bonding between **ionic bonds** (fully charge transfer) and **covalent bonds** (fully shared electrons). When two atoms of slightly differing electronegativities come together to

form a covalent bond, one atom attracts the electrons more than the other; this is called a polar covalent bond. However, simple "ionic" and "covalent" bonding are idealized concepts and most bonds exist on a two-dimensional continuum described by the van Arkel-Ketelaar Triangle (Figure **6.2.7**).

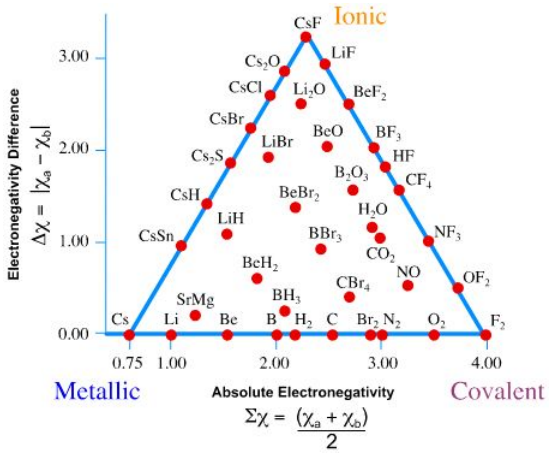


Figure **6.2.7**: van Arkel-Ketelaar Triangle plots the difference in electronegativity ($\Delta\chi$) and the average electronegativity in a bond ($\sum\chi$). the top region is where bonds are mostly ionic, the lower left region is where bonding is metallic, and the lower right region is where the bonding is covalent.

Bond triangles or **van Arkel–Ketelaar** triangles (named after Anton Eduard van Arkel and J. A. A. Ketelaar) are triangles used for showing different compounds in varying degrees of ionic, metallic and covalent bonding. In 1941 van Arkel recognized three extreme materials and associated bonding types. Using 36 main group elements, such as metals, metalloids and non-metals, he placed ionic, metallic and covalent bonds on the corners of an equilateral triangle, as well as suggested intermediate species. The bond triangle shows that chemical bonds are not just particular bonds of a specific type. Rather, bond types are interconnected and different compounds have varying degrees of different bonding character (for example, polar covalent bonds).



Video **6.2.1**: What is the van Arkel-Ketelaar Triangle of Bonding?

Using electronegativity - two compound average electronegativity on x-axis of Figure **6.2.7**.

$$\sum\chi = \frac{\chi_A + \chi_B}{2} \tag{6.2.1}$$

and electronegativity difference on y-axis,

$$\Delta\chi = |\chi_A - \chi_B| \tag{6.2.2}$$

we can rate the dominant bond between the compounds. On the right side of Figure **6.2.7** (from ionic to covalent) should be compounds with varying difference in electronegativity. The compounds with equal electronegativity, such as Cl_2 (chlorine) are placed in the covalent corner, while the ionic corner has compounds with large electronegativity difference, such as NaCl (table salt). The bottom side (from metallic to covalent) contains compounds with varying degree of directionality in the bond. At one

extreme is metallic bonds with delocalized bonding and at the other are covalent bonds in which the orbitals overlap in a particular direction. The left side (from ionic to metallic) is meant for delocalized bonds with varying electronegativity difference.

The Three Extremes in bonding

In general:

- Metallic bonds have low $\Delta\chi$ **and** low average $\sum\chi$.
- Ionic bonds have moderate-to-high $\Delta\chi$ and moderate values of average $\sum\chi$.
- Covalent bonds have moderate to high average $\sum\chi$ and can exist with moderately low $\Delta\chi$.

Example 6.2.2

Use the tables of electronegativities (Table A2) and Figure **6.2.7** to estimate the following values

- difference in electronegativity ($\Delta\chi$)
- average electronegativity in a bond ($\sum\chi$)
- percent ionic character
- likely bond type

for the selected compounds:

a. **AsH** (e.g., in arsine ***AsH***)
b. **SrLi**
c. **KF**.

Solution

a: **AsH**

- The electronegativity of **As** is 2.18
- The electronegativity of **H** is 2.22

Using Equations 6.2.1 and 6.2.2:

$$\begin{aligned}\sum\chi &= \frac{\chi_A + \chi_B}{2} \\ &= \frac{2.18 + 2.22}{2} \\ &= 2.2\end{aligned}$$

$$\begin{aligned}\Delta\chi &= \chi_A - \chi_B \\ &= 2.18 - 2.22 \\ &= 0.04\end{aligned}$$

- From Figure **6.2.4**, the bond is fairly nonpolar and has a low ionic character (10% or less)
- The bonding is in the middle of a covalent bond and a metallic bond

b: **SrLi**

- The electronegativity of **Sr** is 0.95
- The electronegativity of **Li** is 0.98

Using Equations 6.2.1 and 6.2.2:

$$\begin{aligned}\sum\chi &= \frac{\chi_A + \chi_B}{2} \\ &= \frac{0.95 + 0.98}{2} \\ &= 0.965\end{aligned}$$

$$\begin{aligned}\Delta\chi &= \chi_A - \chi_B \\ &= 0.98 - 0.95 \\ &= 0.025\end{aligned}$$

- From Figure 6.2.4, the bond is fairly nonpolar and has a low ionic character (~3% or less)
- The bonding is likely metallic.

c: **KF**

- The electronegativity of **K** is 0.82
- The electronegativity of **F** is 3.98

Using Equations 6.2.1 and 6.2.2:

$$\begin{aligned}\sum\chi &= \frac{\chi_A + \chi_B}{2} \\ &= \frac{0.82 + 3.98}{2} \\ &= 2.4\end{aligned}$$

$$\begin{aligned}\Delta\chi &= \chi_A - \chi_B \\ &= |0.82 - 3.98| \\ &= 3.16\end{aligned}$$

- From Figure 6.2.4, the bond is fairly polar and has a high ionic character (~75%)
- The bonding is likely ionic.

Exercise 6.2.2

Contrast the bonding of **NaCl** and silicon tetrafluoride.

Answer

NaCl is an ionic crystal structure, and an electrolyte when dissolved in water; $\Delta\chi = 1.58$, average $\sum\chi = 1.79$, while silicon tetrafluoride is covalent (molecular, non-polar gas; $\Delta\chi = 2.08$, average $\sum\chi = 2.94$.

Metallic Solids

Metallic solids such as crystals of copper, aluminum, and iron are formed by metal atoms Figure 6.2.8. The structure of metallic crystals is often described as a uniform distribution of atomic nuclei within a “sea” of delocalized electrons. The atoms within such a metallic solid are held together by a unique force known as *metallic bonding* that gives rise to many useful and varied bulk properties. All exhibit high thermal and electrical conductivity, metallic luster, and malleability. Many are very hard and quite strong. Because of their malleability (the ability to deform under pressure or hammering), they do not shatter and, therefore, make useful construction materials. The melting points of the metals vary widely. Mercury is a liquid at room temperature, and the alkali metals melt below 200 °C. Several post-transition metals also have low melting points, whereas the transition metals melt at temperatures above 1000 °C. These differences reflect differences in strengths of metallic bonding among the metals.

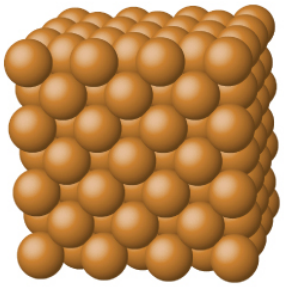


Figure 6.2.8: *Copper is a metallic solid.*

Covalent Network Solids

Covalent network solids include crystals of diamond, silicon, some other nonmetals, and some covalent compounds such as silicon dioxide (sand) and silicon carbide (carborundum, the abrasive on sandpaper). Many minerals have networks of covalent bonds. The atoms in these solids are held together by a network of covalent bonds, as shown in Figure **6.2.9**. To break or to melt a covalent network solid, covalent bonds must be broken. Because covalent bonds are relatively strong, covalent network solids are typically characterized by hardness, strength, and high melting points. For example, diamond is one of the hardest substances known and melts above 3500 °C.

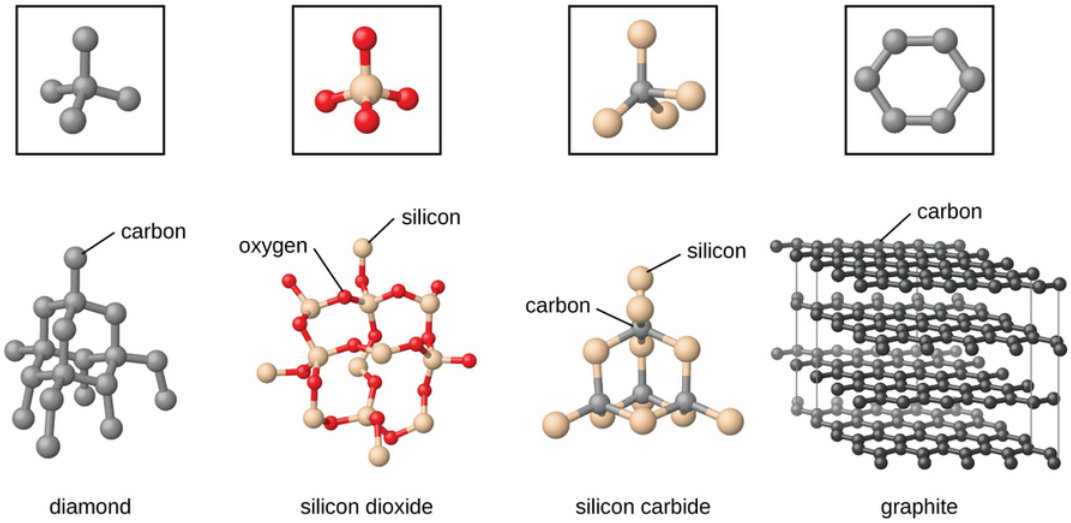


***Figure* 6.2.9**. *A covalent crystal contains a three-dimensional network of covalent bonds, as illustrated by the structures of diamond, silicon dioxide, silicon carbide, and graphite. Graphite is an exceptional example, composed of planar sheets of covalent crystals that are held together in layers by noncovalent forces. Unlike typical covalent solids, graphite is very soft and electrically conductive.*

Molecular Solids

Molecular solids, such as ice, sucrose (table sugar), and iodine, as shown in Figure **6.2.10**, are composed of neutral molecules. The strengths of the attractive forces between the units present in different crystals vary widely, as indicated by the melting points of the crystals. Small symmetrical molecules (nonpolar molecules), such as H_2, N_2, O_2, and F_2, have weak attractive forces and form molecular solids with very low melting points (below −200 °C). Substances consisting of larger, nonpolar molecules have larger attractive forces and melt at higher temperatures. Molecular solids composed of molecules with permanent dipole moments (polar molecules) melt at still higher temperatures. Examples include ice (melting point, 0 °C) and table sugar (melting point, 185 °C).

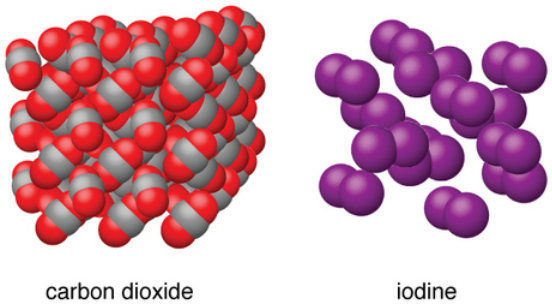


Figure* 6.2.10*: *Carbon dioxide (CO_2) consists of small, nonpolar molecules and forms a molecular solid with a melting point of −78 °C. Iodine (I_2) consists of larger, nonpolar molecules and forms a molecular solid that melts at 114 °C.*

Properties of Solids

A crystalline solid, like those listed in Table 6.2.1 has a precise melting temperature because each atom or molecule of the same type is held in place with the same forces or energy. Thus, the attractions between the units that make up the crystal all have the same strength and all require the same amount of energy to be broken. The gradual softening of an amorphous material differs dramatically from the distinct melting of a crystalline solid. This results from the structural nonequivalence of the molecules in the amorphous solid. Some forces are weaker than others, and when an amorphous material is heated, the weakest intermolecular attractions break first. As the temperature is increased further, the stronger attractions are broken. Thus amorphous materials soften over a range of temperatures.

Table* 6.2.1*: *Types of Crystalline Solids and Their Properties*

Type of Solid	Type of Particles	Type of Attractions	Properties	Examples
ionic	ions	ionic bonds	hard, brittle, conducts electricity as a liquid but not as a solid, high to very high melting points	NaCl, Al_2O_3
metallic	atoms of electropositive elements	metallic bonds	shiny, malleable, ductile, conducts heat and electricity well, variable hardness and melting temperature	Cu, Fe, Ti, Pb, U
covalent network	atoms of electronegative elements	covalent bonds	very hard, not conductive, very high melting points	C (diamond), SiO_2, SiC
molecular	molecules (or atoms)	IMFs	variable hardness, variable brittleness, not conductive, low melting points	H_2O, CO_2, I_2, $C_{12}H_{22}O_{11}$

Graphene: Material of the Future

Carbon is an essential element in our world. The unique properties of carbon atoms allow the existence of carbon-based life forms such as ourselves. Carbon forms a huge variety of substances that we use on a daily basis, including those shown in Figure 6.2.11. You may be familiar with diamond and graphite, the two most common *allotropes* of carbon. (Allotropes are different structural forms of the same element.) Diamond is one of the hardest-known substances, whereas graphite is soft enough to be used as pencil lead. These very different properties stem from the different arrangements of the carbon atoms in the different allotropes.

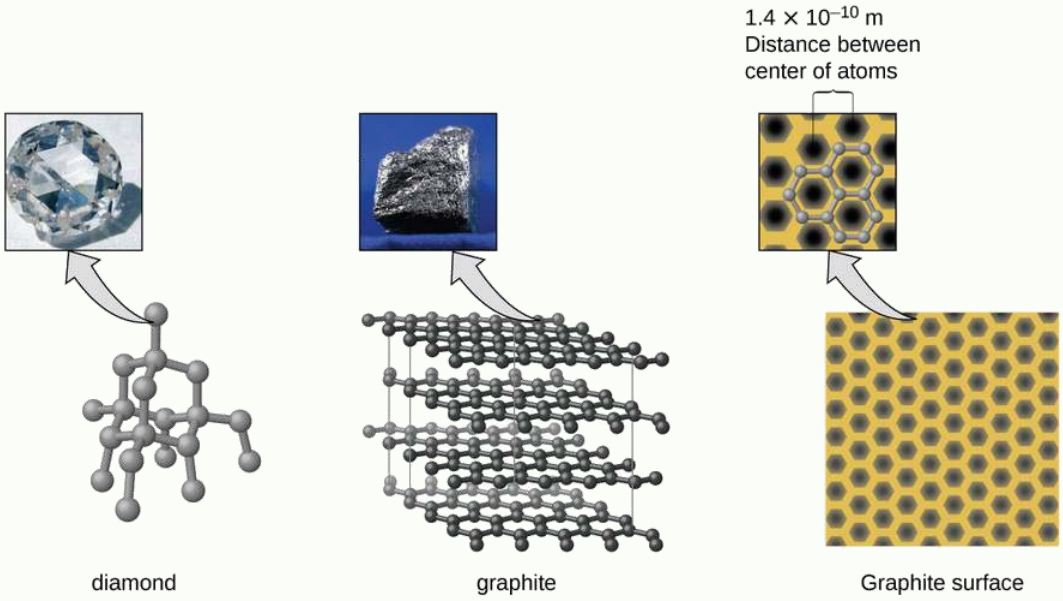


Figure* 6.2.11*: *Diamond is extremely hard because of the strong bonding between carbon atoms in all directions. Graphite (in pencil lead) rubs off onto paper due to the weak attractions between the carbon layers. An image of a graphite surface shows the distance between the centers of adjacent carbon atoms. (credit left photo: modification of work by Steve Jurvetson; credit middle photo: modification of work by United States Geological Survey)*

You may be less familiar with a recently discovered form of carbon: graphene. Graphene was first isolated in 2004 by using tape to peel off thinner and thinner layers from graphite. It is essentially a single sheet (one atom thick) of graphite. Graphene, illustrated in Figure **6.2.12**, is not only strong and lightweight, but it is also an excellent conductor of electricity and heat. These properties may prove very useful in a wide range of applications, such as vastly improved computer chips and circuits, better batteries and solar cells, and stronger and lighter structural materials. The 2010 Nobel Prize in Physics was awarded to Andre Geim and Konstantin Novoselov for their pioneering work with graphene.

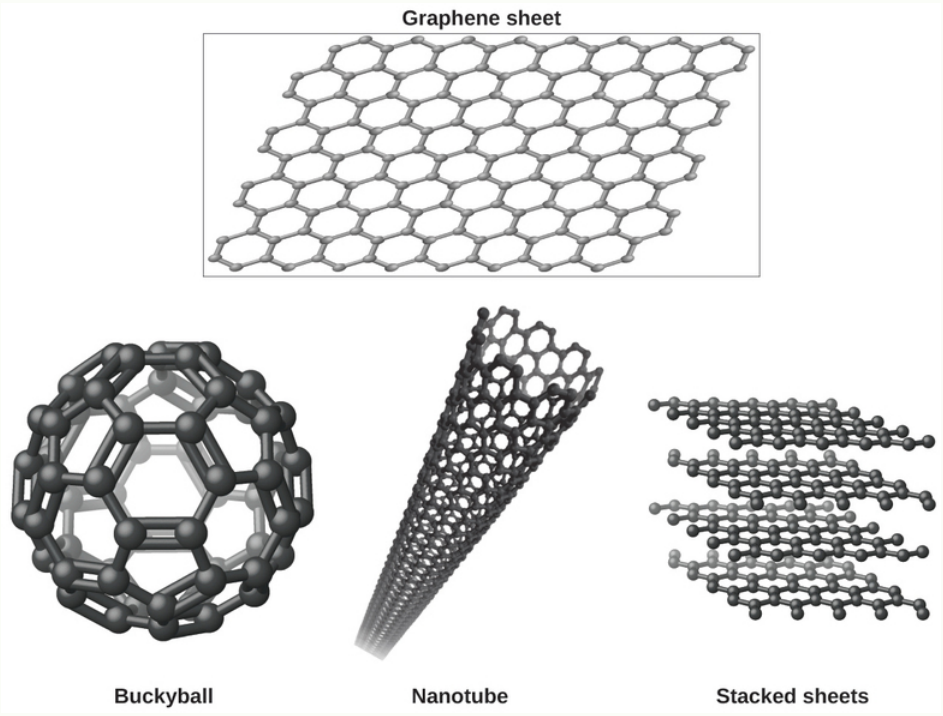


Figure* 6.2.12*: *Graphene sheets can be formed into buckyballs, nanotubes, and stacked layers.*

Crystal Defects

In a crystalline solid, the atoms, ions, or molecules are arranged in a definite repeating pattern, but occasional defects may occur in the pattern. Several types of defects are known, as illustrated in Figure **6.2.13**. Vacancies are defects that occur when positions that should contain atoms or ions are vacant. Less commonly, some atoms or ions in a crystal may occupy positions, called interstitial sites, located between the regular positions for atoms. Other distortions are found in impure crystals, as, for example, when the cations, anions, or molecules of the impurity are too large to fit into the regular positions without distorting the structure. Trace amounts of impurities are sometimes added to a crystal (a process known as *doping)* in order to create defects in the structure that yield desirable changes in its properties. For example, silicon crystals are doped with varying amounts of different elements to yield suitable electrical properties for their use in the manufacture of semiconductors and computer chips.

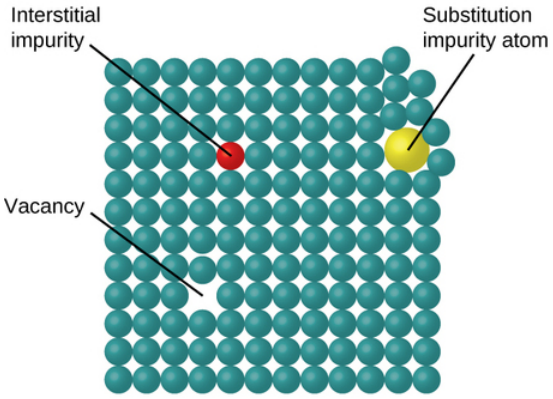


Figure* 6.2.13*: *Types of crystal defects include vacancies, interstitial atoms, and substitutions impurities.*

Summary



Video* 6.2.2*: *An overview of solids.*

Some substances form crystalline solids consisting of particles in a very organized structure; others form amorphous (noncrystalline) solids with an internal structure that is not ordered. The main types of crystalline solids are ionic solids, metallic solids, covalent network solids, and molecular solids. The properties of the different kinds of crystalline solids are due to the types of particles of which they consist, the arrangements of the particles, and the strengths of the attractions between them. Because their particles experience identical attractions, crystalline solids have distinct melting temperatures; the particles in amorphous solids experience a range of interactions, so they soften gradually and melt over a range of temperatures. Some crystalline solids have defects in the definite repeating pattern of their particles. These defects (which include vacancies, atoms or ions not in the regular positions, and impurities) change physical properties such as electrical conductivity, which is exploited in the silicon crystals used to manufacture computer chips.

Glossary

amorphous solid
(also, noncrystalline solid) solid in which the particles lack an ordered internal structure

covalent network solid
solid whose particles are held together by covalent bonds

crystalline solid
solid in which the particles are arranged in a definite repeating pattern

interstitial sites
spaces between the regular particle positions in any array of atoms or ions

ionic solid
solid composed of positive and negative ions held together by strong electrostatic attractions

metallic solid
solid composed of metal atoms

molecular solid
solid composed of neutral molecules held together by intermolecular forces of attraction

vacancy
defect that occurs when a position that should contain an atom or ion is vacant

Contributors

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6.2.1: The Solid State of Matter (Problems)

PROBLEM 6.2.1.1

At very low temperatures oxygen, O_2, freezes and forms a crystalline solid. Which best describes these crystals?

a. ionic
b. covalent network
c. metallic
d. amorphous
e. molecular crystals

Answer

(e) molecular crystals

PROBLEM 6.2.1.2

As it cools, olive oil slowly solidifies and forms a solid over a range of temperatures. Which best describes the solid?

a. ionic
b. covalent network
c. metallic
d. amorphous
e. molecular crystals

Answer

(d) amorphous

PROBLEM 6.2.1.3

Explain why ice, which is a crystalline solid, has a melting temperature of 0 °C, whereas butter, which is an amorphous solid, softens over a range of temperatures.

Answer

Ice has a crystalline structure stabilized by hydrogen bonding. These intermolecular forces are of comparable strength and thus require the same amount of energy to overcome. As a result, ice melts at a single temperature and not over a range of temperatures. The various, very large molecules that compose butter experience varied van der Waals attractions of various strengths that are overcome at various temperatures, and so the melting process occurs over a wide temperature range.

PROBLEM 6.2.1.4

Identify the type of crystalline solid (metallic, network covalent, ionic, or molecular) formed by each of the following substances:

a. SiO_2
b. KCl
c. Cu
d. CO_2
e. C (diamond)
f. $BaSO_4$
g. NH_3
h. NH_4F
i. C_2H_5OH

Answer a

covalent network

Answer b

ionic

Answer c

metallic

Answer d

molecular

Answer e

covalent network

Answer f

ionic

Answer g

molecular

Answer h

ionic

Answer i

molecular

PROBLEM 6.2.1.5

Identify the type of crystalline solid (metallic, network covalent, ionic, or molecular) formed by each of the following substances:

a. $CaCl_2$
b. SiC
c. N_2
d. Fe
e. C (graphite)
f. $CH_3CH_2CH_2CH_3$
g. HCl
h. NH_4NO_3
i. K_3PO_4

Answer a

ionic

Answer b

Covalent network

Answer c

molecular

Answer d

metallic

Answer e

covalent network

Answer f

molecular

Answer g

molecular

Answer h

ionic

Answer i

ionic

PROBLEM 6.2.1.6

Classify each substance in the table as either a metallic, ionic, molecular, or covalent network solid:

Substance	Appearance	Melting Point	Electrical Conductivity	Solubility in Water
X	lustrous, malleable	1500 °C	high	insoluble
Y	soft, yellow	113 °C	none	insoluble
Z	hard, white	800 °C	only if melted/dissolved	soluble

Answer

X = metallic; Y = covalent network; Z = ionic

PROBLEM 6.2.1.7

Classify each substance in the table as either a metallic, ionic, molecular, or covalent network solid:

Substance	Appearance	Melting Point	Electrical Conductivity	Solubility in Water
X	brittle, white	800 °C	only if melted/dissolved	soluble
Y	shiny, malleable	1100 °C	high	insoluble
Z	hard, colorless	3550 °C	none	insoluble

Answer

X = ionic; Y = metallic; Z = covalent network

PROBLEM 6.2.1.8

Substance A is shiny, conducts electricity well, and melts at 975 °C. Substance A is likely a(n):

a. ionic solid
b. metallic solid
c. molecular solid

d. covalent network solid

Answer

(b) metallic solid

PROBLEM 6.2.1.9

Substance B is hard, does not conduct electricity, and melts at 1200 °C. Substance B is likely a(n):

a. ionic solid
b. metallic solid
c. molecular solid
d. covalent network solid

Answer

(d) covalent network solid

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Let your professors know here.

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Contributors

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- Adelaide Clark, Oregon Institute of Technology

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6.3: Unit Cells

Skills to Develop

- Describe the arrangement of atoms and ions in crystalline structures



Video* 6.3.1*: *A preview of giant ionic solids and crystalline structures.*

Over 90% of naturally occurring and man-made solids are crystalline. Most solids form with a regular arrangement of their particles because the overall attractive interactions between particles are maximized, and the total intermolecular energy is minimized, when the particles pack in the most efficient manner. The regular arrangement at an atomic level is often reflected at a macroscopic level. In this module, we will explore some of the details about the structures of metallic and ionic crystalline solids, and learn how these structures are determined experimentally.

The Structures of Metals

We will begin our discussion of crystalline solids by considering elemental metals, which are relatively simple because each contains only one type of atom. A pure metal is a crystalline solid with metal atoms packed closely together in a repeating pattern. Some of the properties of metals in general, such as their malleability and ductility, are largely due to having identical atoms arranged in a regular pattern. The different properties of one metal compared to another partially depend on the sizes of their atoms and the specifics of their spatial arrangements. We will explore the similarities and differences of four of the most common metal crystal geometries in the sections that follow.

Unit Cells of Metals

The structure of a crystalline solid, whether a metal or not, is best described by considering its simplest repeating unit, which is referred to as its unit cell. The unit cell consists of lattice points that represent the locations of atoms or ions. The entire structure then consists of this unit cell repeating in three dimensions, as illustrated in Figure 6.3.1.

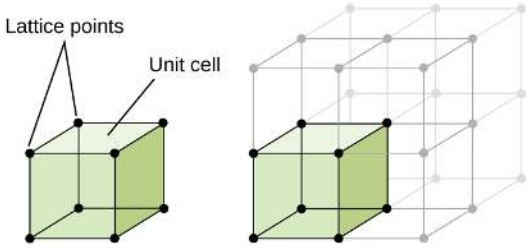


Figure* 6.3.1*: *A unit cell shows the locations of lattice points repeating in all directions.*

Let us begin our investigation of crystal lattice structure and unit cells with the most straightforward structure and the most basic unit cell. To visualize this, imagine taking a large number of identical spheres, such as tennis balls, and arranging them uniformly in a container. The simplest way to do this would be to make layers in which the spheres in one layer are directly above those in the

layer below, as illustrated in Figure **6.3.2**. This arrangement is called simple cubic structure, and the unit cell is called the simple cubic unit cell or primitive cubic unit cell.

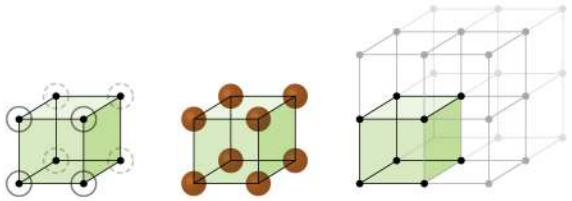


Figure* 6.3.2*: .*When metal atoms are arranged with spheres in one layer directly above or below spheres in another layer, the lattice structure is called simple cubic. Note that the spheres are in contact.*

In a simple cubic structure, the spheres are not packed as closely as they could be, and they only "fill" about 52% of the volume of the container. This is a relatively inefficient arrangement, and only one metal (polonium, Po) crystallizes in a simple cubic structure. As shown in Figure **6.3.3**, a solid with this type of arrangement consists of planes (or layers) in which each atom contacts only the four nearest neighbors in its layer; one atom directly above it in the layer above; and one atom directly below it in the layer below. The number of other particles that each particle in a crystalline solid contacts is known as its coordination number. For a polonium atom in a simple cubic array, the coordination number is, therefore, six.

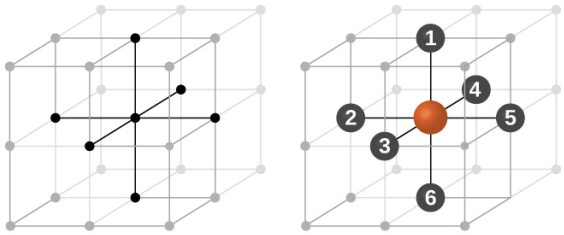


Figure* 6.3.3**:*** *An atom in a simple cubic lattice structure contacts six other atoms, so it has a coordination number of six.*

In a simple cubic lattice, the unit cell that repeats in all directions is a cube defined by the centers of eight atoms, as shown in Figure **6.3.4**. Atoms at adjacent corners of this unit cell contact each other, so the edge length of this cell is equal to two atomic radii, or one atomic diameter. A cubic unit cell contains only the parts of these atoms that are within it. Since an atom at a corner of a simple cubic unit cell is contained by a total of eight unit cells, only one-eighth of that atom is within a specific unit cell. And since each simple cubic unit cell has one atom at each of its eight "corners," there is $8 \times \frac{1}{8} = 1$ atom within one simple cubic unit cell.

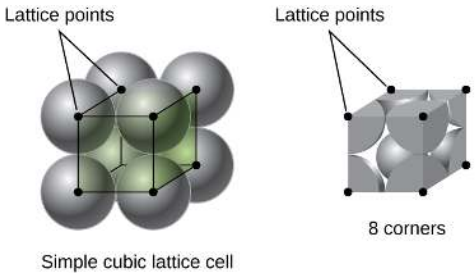


Figure* 6.3.4**:*** *A simple cubic lattice unit cell contains one-eighth of an atom at each of its eight corners, so it contains one atom total.*

Most metal crystals are one of the four major types of unit cells. For now, we will focus on the three cubic unit cells: simple cubic (which we have already seen), body-centered cubic unit cell, and face-centered cubic unit cell—all of which are illustrated in Figure **6.3.5**. (Note that there are actually seven different lattice systems, some of which have more than one type of lattice, for a total of 14 different types of unit cells. We leave the more complicated geometries for later in this module.)

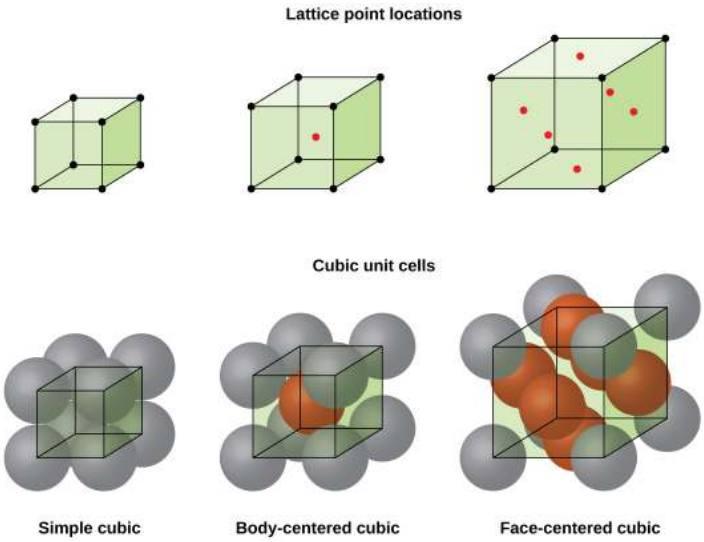


Figure* 6.3.5*: *Cubic unit cells of metals show (in the upper figures) the locations of lattice points and (in the lower figures) metal atoms located in the unit cell.*

Some metals crystallize in an arrangement that has a cubic unit cell with atoms at all of the corners and an atom in the center, as shown in Figure **6.3.6**. This is called a body-centered cubic (BCC) solid. Atoms in the corners of a BCC unit cell do not contact each other but contact the atom in the center. A BCC unit cell contains two atoms: one-eighth of an atom at each of the eight corners ($8 \times \frac{1}{8} = 1$ atom from the corners) plus one atom from the center. Any atom in this structure touches four atoms in the layer above it and four atoms in the layer below it. Thus, an atom in a BCC structure has a coordination number of eight.

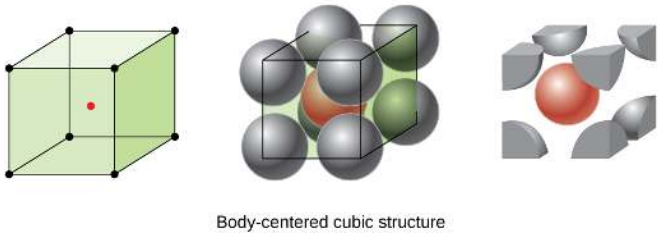


Figure* 6.3.6*: *In a body-centered cubic structure, atoms in a specific layer do not touch each other. Each atom touches four atoms in the layer above it and four atoms in the layer below it.*

Atoms in BCC arrangements are much more efficiently packed than in a simple cubic structure, occupying about 68% of the total volume. Isomorphous metals with a BCC structure include K, Ba, Cr, Mo, W, and Fe at room temperature. (Elements or compounds that crystallize with the same structure are said to be isomorphous.)

Many other metals, such as aluminum, copper, and lead, crystallize in an arrangement that has a cubic unit cell with atoms at all of the corners and at the centers of each face, as illustrated in Figure **6.3.7**. This arrangement is called a face-centered cubic (FCC) solid. A FCC unit cell contains four atoms: one-eighth of an atom at each of the eight corners ($8 \times \frac{1}{8} = 1$ atom from the corners) and one-half of an atom on each of the six faces ($6 \times \frac{1}{2} = 3$ atoms from the faces). The atoms at the corners touch the atoms in the centers of the adjacent faces along the face diagonals of the cube. Because the atoms are on identical lattice points, they have identical environments.

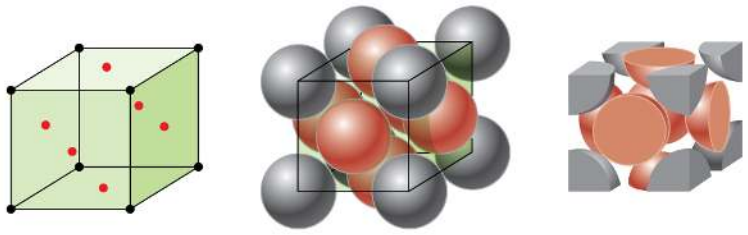


***Figure* 6.3.7**:*A face-centered cubic solid has atoms at the corners and, as the name implies, at the centers of the faces of its unit cells.*

Atoms in an FCC arrangement are packed as closely together as possible, with atoms occupying 74% of the volume. This structure is also called cubic closest packing (CCP). In CCP, there are three repeating layers of hexagonally arranged atoms. Each atom contacts six atoms in its own layer, three in the layer above, and three in the layer below. In this arrangement, each atom touches 12 near neighbors, and therefore has a coordination number of 12. The fact that FCC and CCP arrangements are equivalent may not be immediately obvious, but why they are actually the same structure is illustrated in Figure **6.3.8**. Table **6.3.1** summarizes the important characteristics of the three major unit cell types.

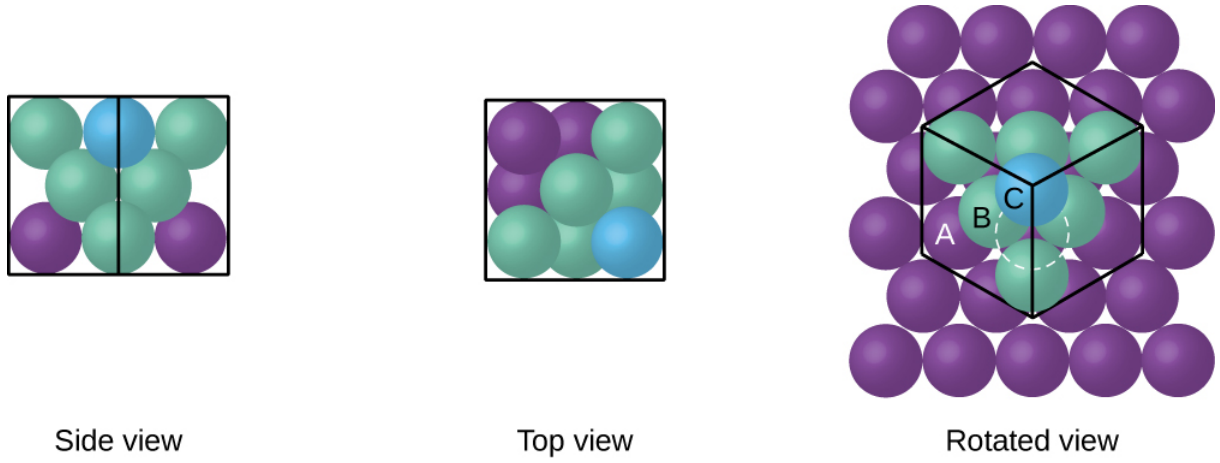


Figure* 6.3.8*: *A CCP arrangement consists of three repeating layers (ABCABC…) of hexagonally arranged atoms. Atoms in a CCP structure have a coordination number of 12 because they contact six atoms in their layer, plus three atoms in the layer above and three atoms in the layer below. By rotating our perspective, we can see that a CCP structure has a unit cell with a face containing*

an atom from layer A at one corner, atoms from layer B across a diagonal (at two corners and in the middle of the face), and an atom from layer C at the remaining corner. This is the same as a face-centered cubic arrangement.

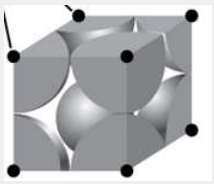
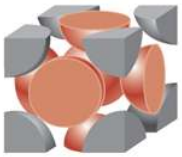
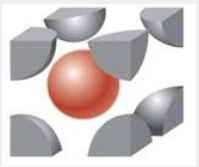
Cubic Cell Name	Atoms per Unit Cell	Structure	Coordination Number
simple cubic (sc)	1		6
face-centered cubic	4		12
body-centered cubic	2		8

Table* 6.3.1*: *A summary of the important characteristics of the three main types of unit cells.*

Because closer packing maximizes the overall attractions between atoms and minimizes the total intermolecular energy, the atoms in most metals pack in this manner. We find two types of closest packing in simple metallic crystalline structures: CCP, which we have already encountered, and hexagonal closest packing (HCP) shown in Figure **6.3.9**. Both consist of repeating layers of hexagonally arranged atoms. In both types, a second layer (B) is placed on the first layer (A) so that each atom in the second layer is in contact with three atoms in the first layer. The third layer is positioned in one of two ways. In HCP, atoms in the third layer are directly above atoms in the first layer (i.e., the third layer is also type A), and the stacking consists of alternating type A and type B close-packed layers (i.e., ABABAB⋯). In CCP, atoms in the third layer are not above atoms in either of the first two layers (i.e., the third layer is type C), and the stacking consists of alternating type A, type B, and type C close-packed layers (i.e., ABCABCABC⋯). About two–thirds of all metals crystallize in closest-packed arrays with coordination numbers of 12. Metals that crystallize in an HCP structure include Cd, Co, Li, Mg, Na, and Zn, and metals that crystallize in a CCP structure include Ag, Al, Ca, Cu, Ni, Pb, and Pt.

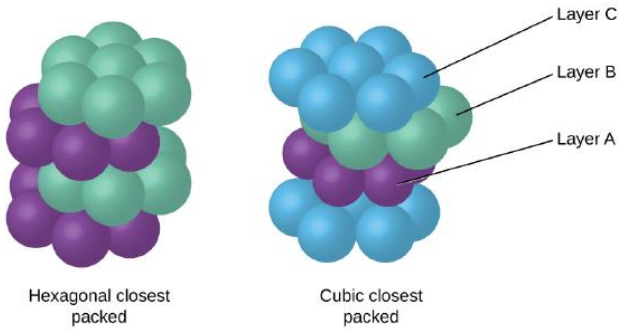


Figure* 6.3.9*: *In both types of closest packing, atoms are packed as compactly as possible. Hexagonal closest packing consists of two alternating layers (ABABAB…). Cubic closest packing consists of three alternating layers (ABCABCABC…).*

In general, a unit cell is defined by the lengths of three axes (*a*, *b*, and *c*) and the angles (*α*, *β*, and *γ*) between them, as illustrated in Figure **6.3.10**. The axes are defined as being the lengths between points in the space lattice. Consequently, unit cell axes join points with identical environments.

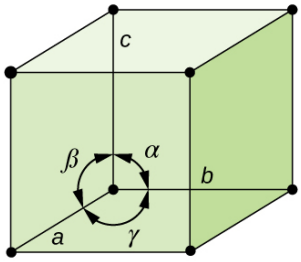


Figure* 6.3.10*: *A unit cell is defined by the lengths of its three axes (a, b, and c) and the angles (α, β, and γ) between the axes.*

There are seven different lattice systems, some of which have more than one type of lattice, for a total of fourteen different unit cells, which have the shapes shown in Figure **6.3.11**.

System/Axes/Angles	Unit Cells
Cubic $a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	Simple, Face-centered, Body-centered
Tetragonal $a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	Simple, Body-centered
Orthorhombic $a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	Simple, Body-centered, Base-centered, Face-centered
Monoclinic $a \neq b \neq c$ $\alpha = \gamma = 90^\circ; \beta \neq 90^\circ$	Simple, Base-centered
Triclinic $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$	
Hexagonal $a = b \neq c$ $\alpha = \beta = 90^\circ; \gamma = 120^\circ$	
Rhombohedral $a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$	

Figure* 6.3.11*:*There are seven different lattice systems and 14 different unit cells.*

Unit Cells of Ionic Compounds

Many ionic compounds crystallize with cubic unit cells, and we will use these compounds to describe the general features of ionic structures. When an ionic compound is composed of cations and anions of similar size in a 1:1 ratio, it typically forms a simple cubic structure. Cesium chloride, CsCl, (Figure **6.3.12**) is an example of this, with Cs^+ and Cl^- having radii of 174 pm and 181 pm,

respectively. We can think of this as chloride ions forming a simple cubic unit cell, with a cesium ion in the center; or as cesium ions forming a unit cell with a chloride ion in the center; or as simple cubic unit cells formed by Cs^+ ions overlapping unit cells formed by Cl^- ions. Cesium ions and chloride ions touch along the body diagonals of the unit cells. One cesium ion and one chloride ion are present per unit cell, giving the l:l stoichiometry required by the formula for cesium chloride. Note that there is no lattice point in the center of the cell, and CsCl is not a BCC structure because a cesium ion is not identical to a chloride ion.

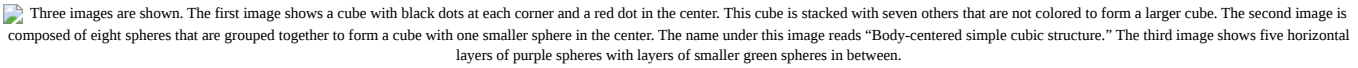


Figure* 6.3.12*: *Ionic compounds with similar-sized cations and anions, such as CsCl, usually form a simple cubic structure. They can be described by unit cells with either cations at the corners or anions at the corners.*

We have said that the location of lattice points is arbitrary. This is illustrated by an alternate description of the CsCl structure in which the lattice points are located in the centers of the cesium ions. In this description, the cesium ions are located on the lattice points at the corners of the cell, and the chloride ion is located at the center of the cell. The two unit cells are different, but they describe identical structures.

When an ionic compound is composed of a 1:1 ratio of cations and anions that differ significantly in size, it typically crystallizes with an FCC unit cell, like that shown in Figure **6.3.13**. Sodium chloride, NaCl, is an example of this, with Na^+ and Cl^- having radii of 102 pm and 181 pm, respectively. We can think of this as chloride ions forming an FCC cell, with sodium ions located in the octahedral holes in the middle of the cell edges and in the center of the cell. The sodium and chloride ions touch each other along the cell edges. The unit cell contains four sodium ions and four chloride ions, giving the 1:1 stoichiometry required by the formula, NaCl.

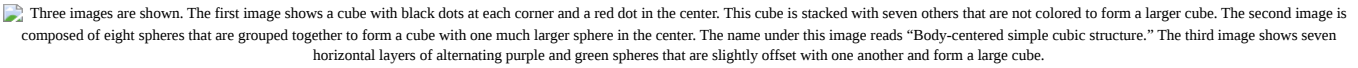


Figure* 6.3.13: Ionic compounds with anions that are much larger than cations, such as NaCl, usually form an FCC structure. They can be described by FCC unit cells with cations in the octahedral holes.*

The cubic form of zinc sulfide, zinc blende, also crystallizes in an FCC unit cell, as illustrated in Figure **6.3.14**. This structure contains sulfide ions on the lattice points of an FCC lattice. (The arrangement of sulfide ions is identical to the arrangement of chloride ions in sodium chloride.) The radius of a zinc ion is only about 40% of the radius of a sulfide ion, so these small Zn^{2+} ions are located in alternating tetrahedral holes, that is, in one half of the tetrahedral holes. There are four zinc ions and four sulfide ions in the unit cell, giving the empirical formula ZnS.

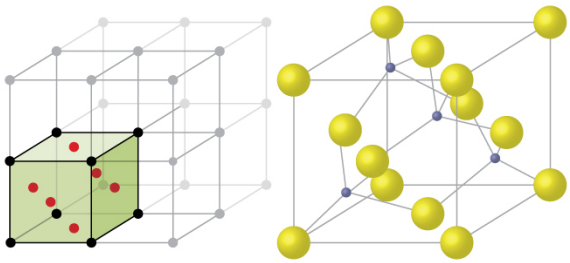
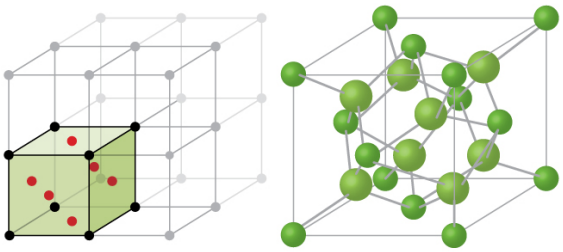


Figure* 6.3.14*: *ZnS, zinc sulfide (or zinc blende) forms an FCC unit cell with sulfide ions at the lattice points and much smaller zinc ions occupying half of the tetrahedral holes in the structure.*

A calcium fluoride unit cell, like that shown in Figure **6.3.15**, is also an FCC unit cell, but in this case, the cations are located on the lattice points; equivalent calcium ions are located on the lattice points of an FCC lattice. All of the tetrahedral sites in the FCC array of calcium ions are occupied by fluoride ions. There are four calcium ions and eight fluoride ions in a unit cell, giving a calcium:fluorine ratio of 1:2, as required by the chemical formula, CaF_2. Close examination of Figure **6.3.17** will reveal a simple cubic array of fluoride ions with calcium ions in one half of the cubic holes. The structure cannot be described in terms of a space lattice of points on the fluoride ions because the fluoride ions do not all have identical environments. The orientation of the four calcium ions about the fluoride ions differs.



CaF_2 face-centered unit cell

Figure 6.3.15: Calcium fluoride, CaF_2, forms an FCC unit cell with calcium ions (green) at the lattice points and fluoride ions (red) occupying all of the tetrahedral sites between them.

Summary

The structures of crystalline metals and simple ionic compounds can be described in terms of packing of spheres. Metal atoms can pack in hexagonal closest-packed structures, cubic closest-packed structures, body-centered structures, and simple cubic structures. The anions in simple ionic structures commonly adopt one of these structures, and the cations occupy the spaces remaining between the anions. Small cations usually occupy tetrahedral holes in a closest-packed array of anions. Larger cations usually occupy octahedral holes. Still larger cations can occupy cubic holes in a simple cubic array of anions. The structure of a solid can be described by indicating the size and shape of a unit cell and the contents of the cell.

Glossary

body-centered cubic (BCC) solid
: crystalline structure that has a cubic unit cell with lattice points at the corners and in the center of the cell

body-centered cubic unit cell
: simplest repeating unit of a body-centered cubic crystal; it is a cube containing lattice points at each corner and in the center of the cube

coordination number
: number of atoms closest to any given atom in a crystal or to the central metal atom in a complex

cubic closest packing (CCP)
: crystalline structure in which planes of closely packed atoms or ions are stacked as a series of three alternating layers of different relative orientations (ABC)

face-centered cubic (FCC) solid
: crystalline structure consisting of a cubic unit cell with lattice points on the corners and in the center of each face

face-centered cubic unit cell
: simplest repeating unit of a face-centered cubic crystal; it is a cube containing lattice points at each corner and in the center of each face

hexagonal closest packing (HCP)
: crystalline structure in which close packed layers of atoms or ions are stacked as a series of two alternating layers of different relative orientations (AB)

hole
: (also, interstice) space between atoms within a crystal

isomorphous
: possessing the same crystalline structure

octahedral hole

open space in a crystal at the center of six particles located at the corners of an octahedron

simple cubic unit cell

(also, primitive cubic unit cell) unit cell in the simple cubic structure

simple cubic structure

crystalline structure with a cubic unit cell with lattice points only at the corners

space lattice

all points within a crystal that have identical environments

tetrahedral hole

tetrahedral space formed by four atoms or ions in a crystal

unit cell

smallest portion of a space lattice that is repeated in three dimensions to form the entire lattice

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6.3.1: Unit Cells (Problems)

PROBLEM 6.3.1.1

Describe the crystal structure of iron, which crystallizes with two equivalent metal atoms in a cubic unit cell.

Answer

The structure of this low-temperature form of iron (below 910 °C) is body-centered cubic. There is one-eighth atom at each of the eight corners of the cube and one atom in the center of the cube.

PROBLEM 6.3.1.2

Describe the crystal structure of Pt, which crystallizes with four equivalent metal atoms in a cubic unit cell.

Answer

This structure of platinum is a face-centered cubic. There is one-eighth atom at each of the eight corners of the cube and one-half atom on each of the six faces of the cube.

PROBLEM 6.3.1.3

What is the coordination number of a chromium atom in the body-centered cubic structure of chromium?

Answer

eight

PROBLEM 6.3.1.4

What is the coordination number of an aluminum atom in the face-centered cubic structure of aluminum?

Answer

12

Contributors

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- Adelaide Clark, Oregon Institute of Technology

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6.4: Structure and General Properties of the Metalloids

Skills to Develop

- Describe the general preparation, properties, and uses of the metalloids
- Describe the preparation, properties, and compounds of boron and silicon
- Explain the properties of some covalent-network solids
- Describe semiconductors and some of their properties

A series of six elements called the metalloids separate the metals from the nonmetals in the periodic table. The metalloids are boron, silicon, germanium, arsenic, antimony, and tellurium. These elements look metallic; however, they do not conduct electricity as well as metals so they are semiconductors. They are semiconductors because their electrons are more tightly bound to their nuclei than are those of metallic conductors. Their chemical behavior falls between that of metals and nonmetals. For example, the pure metalloids form covalent crystals like the nonmetals, but like the metals, they generally do not form monatomic anions. This intermediate behavior is in part due to their intermediate electronegativity values. In this section, we will briefly discuss the chemical behavior of metalloids and deal with two of these elements—boron and silicon—in more detail.

The metalloid boron exhibits many similarities to its neighbor carbon and its diagonal neighbor silicon. All three elements form covalent compounds. However, boron has one distinct difference in that its $2s^2 2p^1$ outer electron structure gives it one less valence electron than it has valence orbitals. Although boron exhibits an oxidation state of 3+ in most of its stable compounds, this electron deficiency provides boron with the ability to form other, sometimes fractional, oxidation states, which occur, for example, in the boron hydrides.

Silicon has the valence shell electron configuration $3s^2 3p^2$, and it commonly forms tetrahedral structures in which it is sp^3 hybridized with a formal oxidation state of 4+. The major differences between the chemistry of carbon and silicon result from the relative strength of the carbon-carbon bond, carbon's ability to form stable bonds to itself, and the presence of the empty 3*d* valence-shell orbitals in silicon. Silicon's empty *d* orbitals and boron's empty *p* orbital enable tetrahedral silicon compounds and trigonal planar boron compounds to act as Lewis acids. Carbon, on the other hand, has no available valence shell orbitals; tetrahedral carbon compounds cannot act as Lewis acids. Germanium is very similar to silicon in its chemical behavior.

Arsenic and antimony generally form compounds in which an oxidation state of 3+ or 5+ is exhibited; however, arsenic can form arsenides with an oxidation state of 3−. These elements tarnish only slightly in dry air but readily oxidize when warmed.

Tellurium combines directly with most elements. The most stable tellurium compounds are the tellurides—salts of Te^{2-} formed with active metals and lanthanides—and compounds with oxygen, fluorine, and chlorine, in which tellurium normally exhibits an oxidation state 2+ or 4+. Although tellurium(VI) compounds are known (for example, TeF_6), there is a marked resistance to oxidation to this maximum group oxidation state.

Structures of the Metalloids

Covalent bonding is the key to the crystal structures of the metalloids. In this regard, these elements resemble nonmetals in their behavior.

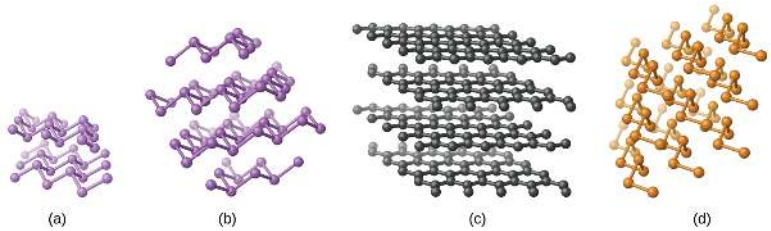
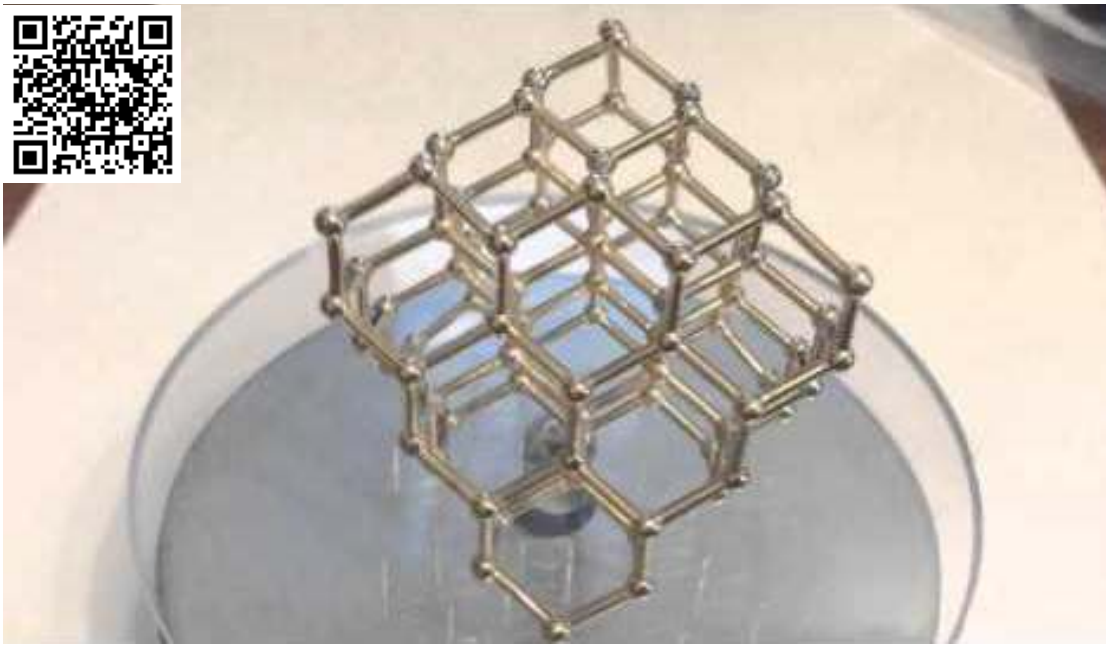


Figure* 6.4.1*: *(a) Arsenic and (b) antimony have a layered structure similar to that of (c) graphite, except that the layers are puckered rather than planar. (d) Elemental tellurium forms spiral chains.*

Elemental silicon, germanium, arsenic, antimony, and tellurium are lustrous, metallic-looking solids. Silicon and germanium crystallize with a diamond structure. Each atom within the crystal has covalent bonds to four neighboring atoms at the corners of a regular tetrahedron. Single crystals of silicon and germanium are giant, three-dimensional molecules. There are several allotropes of arsenic with the most stable being layer like and containing puckered sheets of arsenic atoms. Each arsenic atom forms covalent bonds to three other atoms within the sheet. The crystal structure of antimony is similar to that of arsenic, both shown in Figure 6.4.1. The structures of arsenic and antimony are similar to the structure of graphite, covered later in this chapter. Tellurium forms crystals that contain infinite spiral chains of tellurium atoms. Each atom in the chain bonds to two other atoms.



Video 6.4.1: Explore a cubic diamond crystal structure.

Pure crystalline boron is transparent. The crystals consist of icosahedra, as shown in Figure **6.4.2**, with a boron atom at each corner. In the most common form of boron, the icosahedra pack together in a manner similar to the cubic closest packing of spheres. All boron-boron bonds within each icosahedron are identical and are approximately 176 pm in length. In the different forms of boron, there are different arrangements and connections between the icosahedra.

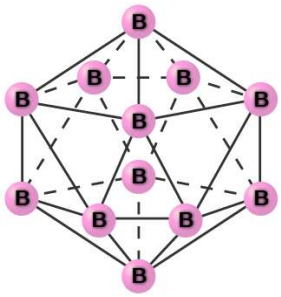


***Figure* 6.4.2:** *An icosahedron is a symmetrical, solid shape with 20 faces, each of which is an equilateral triangle. The faces meet at 12 corners.*

The name silicon is derived from the Latin word for flint, *silex*. The metalloid silicon readily forms compounds containing Si-O-Si bonds, which are of prime importance in the mineral world. This bonding capability is in contrast to the nonmetal carbon, whose ability to form carbon-carbon bonds gives it prime importance in the plant and animal worlds.

Occurrence, Preparation, and Compounds of Boron and Silicon

Boron constitutes less than 0.001% by weight of the earth's crust. In nature, it only occurs in compounds with oxygen. Boron is widely distributed in volcanic regions as boric acid, $B(OH)_3$, and in dry lake regions, including the desert areas of California, as borates and salts of boron oxyacids, such as borax, $Na_2B_4O_7{\cdot}10H_2O$.

Elemental boron is chemically inert at room temperature, reacting with only fluorine and oxygen to form boron trifluoride, BF_3, and boric oxide, B_2O_3, respectively. At higher temperatures, boron reacts with all nonmetals, except tellurium and the noble gases, and with nearly all metals; it oxidizes to B_2O_3 when heated with concentrated nitric or sulfuric acid. Boron does not react with nonoxidizing acids. Many boron compounds react readily with water to give boric acid, $B(OH)_3$ (sometimes written as H_3BO_3).

Reduction of boric oxide with magnesium powder forms boron (95–98.5% pure) as a brown, amorphous powder:

$$B_2O_3(s) + 3\,Mg(s) \longrightarrow 2\,B(s) + 3\,MgO(s) \tag{6.4.1}$$

An amorphous substance is a material that appears to be a solid, but does not have a long-range order like a true solid. Treatment with hydrochloric acid removes the magnesium oxide. Further purification of the boron begins with conversion of the impure boron into boron trichloride. The next step is to heat a mixture of boron trichloride and hydrogen:

$$2\,BCl_3(g) + 3\,H_2(g) \xrightarrow{1500\ ^\circ C} 2\,B(s) + 6\,HCl(g) \quad \Delta H^\circ = 253.7\ kJ \tag{6.4.2}$$

Silicon makes up nearly one-fourth of the mass of the earth's crust—second in abundance only to oxygen. The crust is composed almost entirely of minerals in which the silicon atoms are at the center of the silicon-oxygen tetrahedron, which connect in a variety of ways to produce, among other things, chains, layers, and three-dimensional frameworks. These minerals constitute the bulk of most common rocks, soil, and clays. In addition, materials such as bricks, ceramics, and glasses contain silicon compounds.

It is possible to produce silicon by the high-temperature reduction of silicon dioxide with strong reducing agents, such as carbon and magnesium:

$$SiO_2(s) + 2\,C(s) \xrightarrow{\Delta} Si(s) + 2\,CO(g) \tag{6.4.3}$$

$$SiO_2(s) + 2\,Mg(s) \xrightarrow{\Delta} Si(s) + 2\,MgO(s) \tag{6.4.4}$$

Extremely pure silicon is necessary for the manufacture of semiconductor electronic devices. This process begins with the conversion of impure silicon into silicon tetrahalides, or silane (SiH_4), followed by decomposition at high temperatures. Zone refining, illustrated in Figure **6.4.3**, completes the purification. In this method, a rod of silicon is heated at one end by a heat source that produces a thin cross-section of molten silicon. Slowly lowering the rod through the heat source moves the molten zone from one end of the rod to other. As this thin, molten region moves, impurities in the silicon dissolve in the liquid silicon and move with the molten region. Ultimately, the impurities move to one end of the rod, which is then cut off.

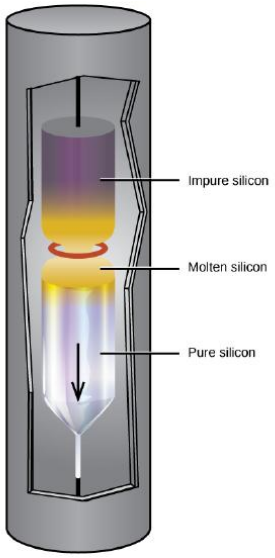


***Figure* 6.4.3:** *A zone-refining apparatus used to purify silicon.*

This highly purified silicon, containing no more than one part impurity per million parts of silicon, is the most important element in the computer industry. Pure silicon is necessary in semiconductor electronic devices such as transistors, computer chips, and solar cells.

Like some metals, passivation of silicon occurs due the formation of a very thin film of oxide (primarily silicon dioxide, SiO_2). Silicon dioxide is soluble in hot aqueous base; thus, strong bases destroy the passivation. Removal of the passivation layer allows the base to dissolve the silicon, forming hydrogen gas and silicate anions. For example:

$$Si(s) + 4\,OH^-(aq) \longrightarrow SiO_4^{4-}(aq) + 2\,H_2(g) \tag{6.4.5}$$

Silicon reacts with halogens at high temperatures, forming volatile tetrahalides, such as SiF_4.

Unlike carbon, silicon does not readily form double or triple bonds. Silicon compounds of the general formula SiX_4, where X is a highly electronegative group, can act as Lewis acids to form six-coordinate silicon. For example, silicon tetrafluoride, SiF_4, reacts with sodium fluoride to yield $Na_2[SiF_6]$, which contains the octahedral $[SiF_6]^{2-}$ ion in which silicon is sp^3d^2 hybridized:

$$2\,NaF(s) + SiF_4(g) \longrightarrow Na_2SiF_6(s) \tag{6.4.6}$$

Antimony reacts readily with stoichiometric amounts of fluorine, chlorine, bromine, or iodine, yielding trihalides or, with excess fluorine or chlorine, forming the pentahalides SbF_5 and $SbCl_5$. Depending on the stoichiometry, it forms antimony(III) sulfide, Sb_2S_3, or antimony(V) sulfide when heated with sulfur. As expected, the metallic nature of the element is greater than that of arsenic, which lies immediately above it in group 15.

Boron and Silicon Halides

Boron trihalides—BF_3, BCl_3, BBr_3, and BI_3—can be prepared by the direct reaction of the elements. These nonpolar molecules contain boron with sp^2 hybridization and a trigonal planar molecular geometry. The fluoride and chloride compounds are colorless gasses, the bromide is a liquid, and the iodide is a white crystalline solid.

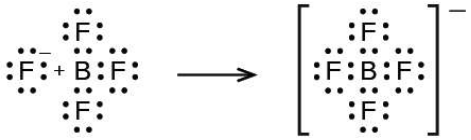
Except for boron trifluoride, the boron trihalides readily hydrolyze in water to form boric acid and the corresponding hydrohalic acid. Boron trichloride reacts according to the equation:

$$\mathrm{BCl_3}(g) + 3\,\mathrm{H_2O}(l) \longrightarrow \mathrm{B(OH)_3}(aq) + 3\,\mathrm{HCl}(aq) \tag{6.4.7}$$

Boron trifluoride reacts with hydrofluoric acid, to yield a solution of fluoroboric acid, HBF_4:

$$\mathrm{BF_3}(aq) + \mathrm{HF}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{H_3O^+}(aq) + \mathrm{BF_4^-}(aq) \tag{6.4.8}$$

In this reaction, the BF_3 molecule acts as the Lewis acid (electron pair acceptor) and accepts a pair of electrons from a fluoride ion:



All the tetrahalides of silicon, SiX_4, have been prepared. Silicon tetrachloride can be prepared by direct chlorination at elevated temperatures or by heating silicon dioxide with chlorine and carbon:

$$\mathrm{SiO_2}(s) + 2\,\mathrm{C}(s) + 2\,\mathrm{Cl_2}(g) \xrightarrow{\Delta} \mathrm{SiCl_4}(g) + 2\,\mathrm{CO}(g) \tag{6.4.9}$$

Silicon tetrachloride is a covalent tetrahedral molecule, which is a nonpolar, low-boiling (57 °C), colorless liquid. It is possible to prepare silicon tetrafluoride by the reaction of silicon dioxide with hydrofluoric acid:

$$\mathrm{SiO_2}(s) + 4\,\mathrm{HF}(g) \longrightarrow \mathrm{SiF_4}(g) + 2\,\mathrm{H_2O}(l) \quad \Delta H° = -191.2\,\mathrm{kJ} \tag{6.4.10}$$

Hydrofluoric acid is the only common acid that will react with silicon dioxide or silicates. This reaction occurs because the silicon-fluorine bond is the only bond that silicon forms that is stronger than the silicon-oxygen bond. For this reason, it is possible to store all common acids, other than hydrofluoric acid, in glass containers.

Except for silicon tetrafluoride, silicon halides are extremely sensitive to water. Upon exposure to water, $SiCl_4$ reacts rapidly with hydroxide groups, replacing all four chlorine atoms to produce unstable orthosilicic acid, $Si(OH)_4$ or H_4SiO_4, which slowly decomposes into SiO_2.

Boron and Silicon Oxides and Derivatives

Boron burns at 700 °C in oxygen, forming boric oxide, B_2O_3. Boric oxide is necessary for the production of heat-resistant borosilicate glass, like that shown in Figure **6.4.4** and certain optical glasses. Boric oxide dissolves in hot water to form boric acid, $B(OH)_3$:

$$\mathrm{B_2O_3}(s) + 3\,\mathrm{H_2O}(l) \longrightarrow 2\,\mathrm{B(OH)_3}(aq) \tag{6.4.11}$$



***Figure* 6.4.4**: *Laboratory glassware, such as Pyrex and Kimax, is made of borosilicate glass because it does not break when heated. The inclusion of borates in the glass helps to mediate the effects of thermal expansion and contraction. This reduces the likelihood of thermal shock, which causes silicate glass to crack upon rapid heating or cooling. (credit: "Tweenk"/Wikimedia Commons)*

The boron atom in $B(OH)_3$ is sp^2 hybridized and is located at the center of an equilateral triangle with oxygen atoms at the corners. In solid $B(OH)_3$, hydrogen bonding holds these triangular units together. Boric acid, shown in Figure **6.4.5**, is a very weak acid that does not act as a proton donor but rather as a Lewis acid, accepting an unshared pair of electrons from the Lewis base OH^-:

$$B(OH)_3(aq) + 2H_2O(l) \rightleftharpoons B(OH)_4^-(aq) + H_3O^+(aq) \quad K_a = 5.8 \times 10^{-10} \tag{6.4.12}$$

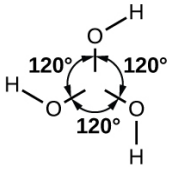


Figure* 6.4.5*: *Boric acid has a planar structure with three –OH groups spread out equally at 120° angles from each other.*

Heating boric acid to 100 °C causes molecules of water to split out between pairs of adjacent –OH groups to form metaboric acid, HBO_2. At about 150 °C, additional B-O-B linkages form, connecting the BO_3 groups together with shared oxygen atoms to form tetraboric acid, $H_2B_4O_7$. Complete water loss, at still higher temperatures, results in boric oxide.

Borates are salts of the oxyacids of boron. Borates result from the reactions of a base with an oxyacid or from the fusion of boric acid or boric oxide with a metal oxide or hydroxide. Borate anions range from the simple trigonal planar $\mathbf{BO_3^{3-}}$ ion to complex species containing chains and rings of three- and four-coordinated boron atoms. The structures of the anions found in CaB_2O_4, $K[B_5O_6(OH)_4]\cdot 2H_2O$ (commonly written $KB_5O_8\cdot 4H_2O$) and $Na_2[B_4O_5(OH)_4]\cdot 8H_2O$ (commonly written $Na_2B_4O_7\cdot 10H_2O$) are shown in Figure **6.4.6**. Commercially, the most important borate is borax, $Na_2[B_4O_5(OH)_4]\cdot 8H_2O$, which is an important component of some laundry detergents. Most of the supply of borax comes directly from dry lakes, such as Searles Lake in California, or is prepared from kernite, $Na_2B_4O_7\cdot 4H_2O$.

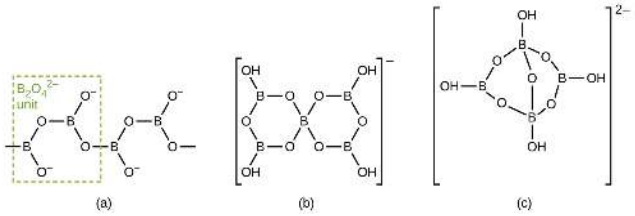


Figure* 6.4.6*: *The borate anions are (a) CaB_2O_4, (b) $KB_5O_8\cdot 4H_2O$, and (c) $Na_2B_4O_7\cdot 10H_2O$. The anion in CaB_2O_4 is an "infinite" chain.*

Silicon dioxide, silica, occurs in both crystalline and amorphous forms. The usual crystalline form of silicon dioxide is quartz, a hard, brittle, clear, colorless solid. It is useful in many ways—for architectural decorations, semiprecious jewels, and frequency control in radio transmitters. Silica takes many crystalline forms, or polymorphs, in nature. Trace amounts of Fe^{3+} in quartz give amethyst its characteristic purple color. The term *quartz* is also used for articles such as tubing and lenses that are manufactured from amorphous silica. Opal is a naturally occurring form of amorphous silica.

The contrast in structure and physical properties between silicon dioxide and carbon dioxide is interesting, as illustrated in Figure **6.4.7**. Solid carbon dioxide (dry ice) contains single CO_2 molecules with each of the two oxygen atoms attached to the carbon atom by double bonds. Very weak intermolecular forces hold the molecules together in the crystal. The volatility of dry ice reflect these weak forces between molecules. In contrast, silicon dioxide is a covalent network solid. In silicon dioxide, each silicon atom links to four oxygen atoms by single bonds directed toward the corners of a regular tetrahedron, and SiO_4 tetrahedra share oxygen atoms. This arrangement gives a three dimensional, continuous, silicon-oxygen network. A quartz crystal is a macromolecule of silicon dioxide. The difference between these two compounds is the ability of the group 14 elements to form strong π bonds. Second-period elements, such as carbon, form very strong π bonds, which is why carbon dioxide forms small molecules with strong double bonds. Elements below the second period, such as silicon, do not form π bonds as readily as second-period elements, and when they do form, the π bonds are weaker than those formed by second-period elements. For this reason, silicon dioxide does not contain π bonds but only σ bonds.

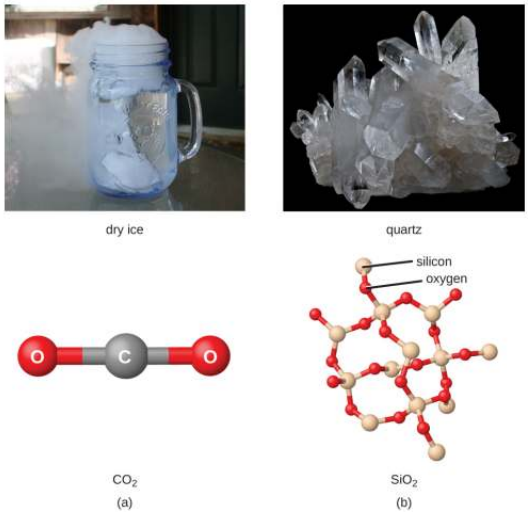


***Figure* 6.4.7:** *Because carbon tends to form double and triple bonds and silicon does not, (a) carbon dioxide is a discrete molecule with two C=O double bonds and (b) silicon dioxide is an infinite network of oxygen atoms bridging between silicon atoms with each silicon atom possessing four Si-O single bonds. (credit a photo: modification of work by Erica Gerdes; credit b photo: modification of work by Didier Descouens)*

At 1600 °C, quartz melts to yield a viscous liquid. When the liquid cools, it does not crystallize readily but usually supercools and forms a glass, also called silica. The SiO_4 tetrahedra in glassy silica have a random arrangement characteristic of supercooled liquids, and the glass has some very useful properties. Silica is highly transparent to both visible and ultraviolet light. For this reason, it is important in the manufacture of lamps that give radiation rich in ultraviolet light and in certain optical instruments that operate with ultraviolet light. The coefficient of expansion of silica glass is very low; therefore, rapid temperature changes do not cause it to fracture. CorningWare and other ceramic cookware contain amorphous silica.

Silicates are salts containing anions composed of silicon and oxygen. In nearly all silicates, sp^3-hybridized silicon atoms occur at the centers of tetrahedra with oxygen at the corners. There is a variation in the silicon-to-oxygen ratio that occurs because silicon-oxygen tetrahedra may exist as discrete, independent units or may share oxygen atoms at corners in a variety of ways. In addition, the presence of a variety of cations gives rise to the large number of silicate minerals. Many ceramics are composed of silicates. By including small amounts of other compounds, it is possible to modify the physical properties of the silicate materials to produce ceramics with useful characteristics.



***Video* 6.4.2:** *A closer look at silicon and its chemistry as a network solid.*

Graphite

Carbon has 2 **allotropes**, or pure elemental forms. The more stable form is graphite, a dark, slippery material used in pencils and lubricants. Remember that carbon typically makes 4 bonds. The structure of graphite is flat hexagonal sheets; a single sheet is called **graphene**. Each carbon atom makes 3 σ bonds and the leftover p orbitals form a delocalized π-bond network over the whole sheet, very similar to the π-bonding in benzene. The π-bond system actually forms bands, like in a metal, allowing graphite to conduct electricity along the sheets. Weak interactions, like London dispersion forces, (called π-stacking in this case) hold the sheets loosely together. Because they can slide past each other (especially when impurity atoms are trapped in between) graphite is a good lubricant.

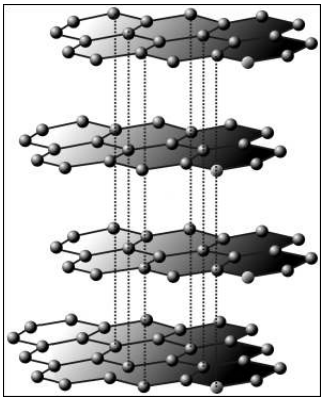


***Figure* 6.4.9**:*Graphite structure via Wikimedia Commons*

Diamond Structure

The other bulk allotrope of carbon is diamond. In diamond, each carbon makes 4 bonds in tetrahedral directions to other carbon atoms. The structure is like the zinc blende ionic structure, except that all the atoms are the same. The properties of diamond (insulator, hard) come from the strong covalent bonds. Remember that C-C bonds are some of the strongest covalent bonds. It's easiest to think about diamond as forming with sp^3 hybrid orbitals on each atom. It's hard to imagine the MO interactions, but the main thing we can know is that because there is good energy match and good overlap between the atoms, the splitting (energy difference) between bonding and anti-bonding MOs will be big (and there won't be any non-bonding MOs, because each atom has 4 orbitals and makes 4 bonds). There will still be bands like in metals, but now there are 2 bands with a big energy gap in the middle. The low-energy, bonding band is called the **valence band**, and there are exactly enough electrons to fill it. The high-energy, anti-bonding band is called the **conduction band**, and it is empty.

If it was hard to understand the previous paragraph, let's just imagine making 1 bond between 2 atoms. We use one sp^3 hybrid on each atom. These point right at each other, have exactly the same energy, and have good overlap. We can imagine drawing an MO diagram just like for H_2, with a big energy gap between the bonding and anti-bonding orbitals. Each atom has 4 electrons total, and makes 4 bonds just like this, so each bond gets 1 electron from each atom: just enough to fill up the bonding MO. When we multiply this over all the bonds in the diamond, we get the full valence band and the empty conduction band. The energy gap between them is called the **band gap**. In diamond, the band gap is big, and so diamond is an insulator.

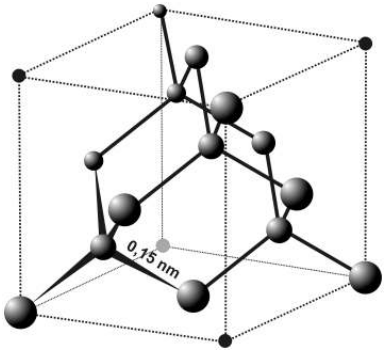


***Figure* 6.4.10**:*Diamond unit cell, by Anton via Wikimedia Commons*



***Video* 6.4.3:** *A closer look at carbon and its chemistry as a network solid.*

Semiconductors

Silicon has a structure just like diamond. (It doesn't make graphite, because mostly π-bonds are weak for the second-row elements.) However, silicon has a smaller band gap than diamond. Germanium, which is below silicon in the periodic table, has the same structure, and an even lower band gap. Generally, as we go down the periodic table, covalent bond strengths get smaller, which is the same as saying that the splitting between bonding and antibonding orbitals gets smaller. It's hard to say why, but if you assume that heavier atoms have worse orbital overlap, you will usually make good predictions.

Semiconductors are materials that conduct electricity just a little bit. They are the basis for all computing and electronics. Semiconductivity comes from having a not-quite-full valence band, a not-quite-empty conduction band, or both. If there are a few electrons in the conduction band, they can conduct electricity just like in a metal (except less, because there aren't very many of them!). If there are a few electrons missing from the valence band, the empty spots are called holes and they can move around, also conducting electricity. If the band gap of a material is not too big compared to the thermal energy, then a few electrons can be in the conduction band even though there is room for them in the valence band (because of thermal energy). For this reason, semiconductors conduct better at higher temperature, because more electrons will be in the conduction band.

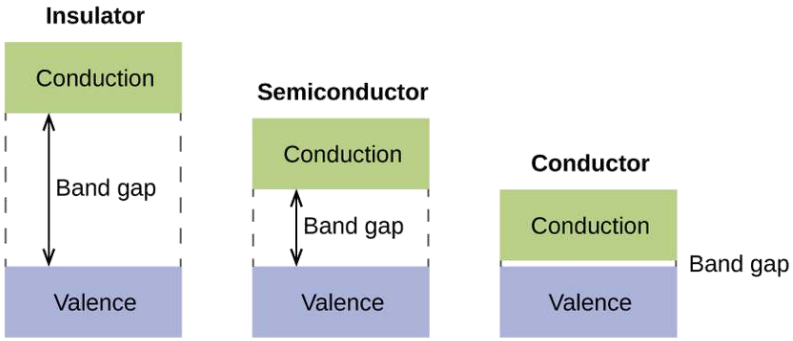


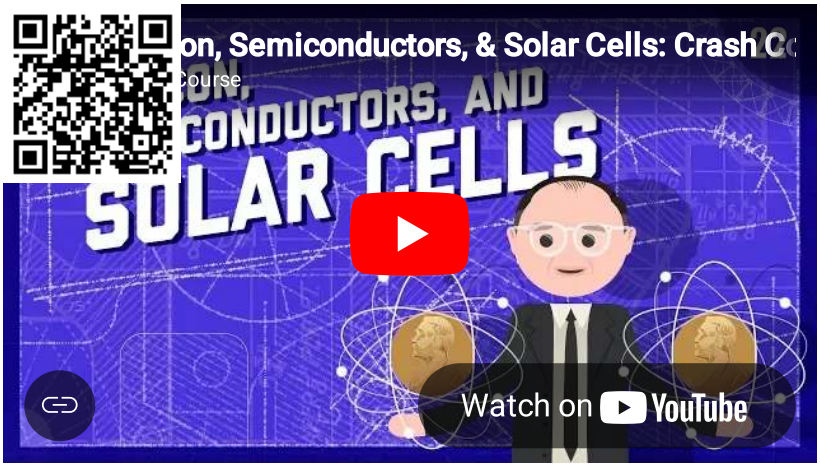
***Figure* 6.4.11**: *Diagram showing the difference between bands in metals, semiconductors and insulators. E_F, the Fermi energy, represents roughly the cutoff between full and empty MOs: the energy of a state that has a 50% chance of being full at equilibrium. The intrinsic semiconductor has electrons in the conduction band due to thermal energy.*

Doping Semiconductors

The other way to make a semiconductor, with a material whose band gap is too big at room temperature, is by adding some impurity atoms with different numbers of electrons, which is called **doping**. Imagine that you have silicon with just a few nitrogen atoms replacing silicon atoms. Each N has an extra electron. Now there will be a few electrons in the conduction band, so it's a semiconductor! And we can control the conductivity by controlling how much N we add. We can do the same thing if we add a little bit of boron, which has 3 electrons. In this case, there would be a few holes in the valence band. These are called p-type (positive, less electrons, like with B) or n-type (negative, extra electrons, like with N) semiconductors. Lots of important devices, like LEDs, solar cells and transistors (the basis of computer chips) are made of layers of p-type and n-type semiconductors.

Compound Semiconductors

We can also make semiconductors that are compounds, like gallium arsenide (formula GaAs). These have an AB formula, and there are always 8 valence electrons in the formula. For example, Ga has 3 and As has 5, so GaAs has 8. Another example is ZnSe, (Zn has 2 valence electrons in 4s, Se has 6 valence electrons just like O). Thus, they have the same number of valence electrons as C or Si. They also have the same structure (zinc blende, just like diamond except that that atoms alternate types). By combining many different elements, we can change various properties, like band gap, to be exactly what we want. Generally, the band gap increases as the 2 elements are farther apart (the bonding becomes more ionic, and ionic solids aren't conductive). We can even mix 3 or more elements, like in CdZnTe (the actual formula would probably be written (Cd,Zn)Te, meaning that the number of Cd + Zn = Te). To make semiconductors with the right properties, we can use different combinations of elements and also dope with many different elements.



***Video* 6.4.4:** *A closer look at the role of semiconductors in solar cells.*

Summary

The elements boron, silicon, germanium, arsenic, antimony, and tellurium separate the metals from the nonmetals in the periodic table. These elements, called metalloids or sometimes semimetals, exhibit properties characteristic of both metals and nonmetals. The structures of these elements are similar in many ways to those of nonmetals, but the elements are electrical semiconductors.

Glossary

amorphous
: solid material such as a glass that does not have a regular repeating component to its three-dimensional structure; a solid but not a crystal

borate
: compound containing boron-oxygen bonds, typically with clusters or chains as a part of the chemical structure

polymorph
: variation in crystalline structure that results in different physical properties for the resulting compound

silicate
: compound containing silicon-oxygen bonds, with silicate tetrahedra connected in rings, sheets, or three-dimensional networks, depending on the other elements involved in the formation of the compounds

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CHAPTER OVERVIEW

7: Solutions

7.1: The Dissolution Process

7.2: Concentrations of Solutions

7.2.1: Concentrations of Solutions (Problems)

7.3: Solubility and Intermolecular Forces

7.3.1: Solubility and Intermolecular Forces (Problems)

7.4: Colligative Properties

7.4.1: Concentrations of Solutions (Problems)

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7.1: The Dissolution Process

Learning Objectives

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

An earlier chapter of this text introduced *solutions*, defined as homogeneous mixtures of two or more substances. Often, one component of a solution is present at a significantly greater concentration, in which case it is called the solvent. The other components of the solution present in relatively lesser concentrations are called solutes. Sugar is a covalent solid composed of sucrose molecules, $C_{12}H_{22}O_{11}$. When this compound dissolves in water, its molecules become uniformly distributed among the molecules of water:

$$C_{12}H_{22}O_{11}\,(s) \longrightarrow C_{12}H_{22}O_{11}\,(aq) \tag{7.1.1}$$

The subscript "aq" in the equation signifies that the sucrose molecules are solutes and are therefore *individually dispersed* throughout the *aqueous solution* (water is the solvent). Although sucrose molecules are heavier than water molecules, they remain dispersed throughout the solution; gravity does not cause them to "settle out" over time.

Potassium dichromate, $K_2Cr_2O_7$, is an ionic compound composed of colorless potassium ions, K^+, and orange dichromate ions, $Cr_2O_7^{2-}$. When a small amount of solid potassium dichromate is added to water, the compound dissolves and dissociates to yield potassium ions and dichromate ions uniformly distributed throughout the mixture (Figure 7.1.1), as indicated in this equation:

$$K_2Cr_2O_7\,(s) \longrightarrow 2\,K^+\,(aq) + Cr_2O_7^{2-}\,(aq) \tag{7.1.2}$$

As with the mixture of sugar and water, this mixture is also an aqueous solution. Its solutes, potassium and dichromate ions, remain individually dispersed among the solvent (water) molecules.



Figure 7.1.1: When potassium dichromate ($K_2Cr_2O_7$) is mixed with water, it forms a homogeneous orange solution. (credit: modification of work by Mark Ott).

The first photo shows a small mound of an orange crystalline solid. There is a right-facing arrow. The second photo shows a translucent, colorless liquid in a clear container. There is a right-facing arrow. The third photo shows a translucent orange liquid in a clear, covered container.

Water is used so often as a solvent that the word solution has come to imply an aqueous solution to many people. However, almost any gas, liquid, or solid can act as a solvent. Many alloys are solid solutions of one metal dissolved in another; for example, US five-cent coins contain nickel dissolved in copper. Air is a gaseous solution, a homogeneous mixture of nitrogen, oxygen, and several other gases. Oxygen (a gas), alcohol (a liquid), and sugar (a solid) all dissolve in water (a liquid) to form liquid solutions. Table 7.1.1 gives examples of several different solutions and the phases of the solutes and solvents.

Table 7.1.1: Different Types of Solutions

Solution	Solute	Solvent
air	$O_2(g)$	$N_2(g)$
soft drinks	$CO_2(g)$	$H_2O(l)$
hydrogen in palladium	$H_2(g)$	$Pd(s)$
rubbing alcohol	$H_2O(l)$	$C_3H_8O(l)$ (2-propanol)
saltwater	$NaCl(s)$	$H_2O(l)$
brass	$Zn(s)$	$Cu(s)$

Solutions exhibit these defining traits:

- They are homogeneous; that is, after a solution is mixed, it has the same composition at all points throughout (its composition is uniform).
- The physical state of a solution—solid, liquid, or gas—is typically the same as that of the solvent, as demonstrated by the examples in Table **7.1.1**.
- The components of a solution are dispersed on a molecular scale; that is, they consist of a mixture of separated molecules, atoms, and/or ions.
- The dissolved solute in a solution will not settle out or separate from the solvent.
- The composition of a solution, or the concentrations of its components, can be varied continuously, within limits.

The Formation of Solutions

The formation of a solution is an example of a spontaneous process, a process that occurs under specified conditions without the requirement of energy from some external source. Sometimes we stir a mixture to speed up the dissolution process, but this is not necessary; a homogeneous solution would form if we waited long enough. The topic of spontaneity is critically important to the study of chemical thermodynamics and is treated more thoroughly in a later chapter of this text. For purposes of this chapter's discussion, it will suffice to consider two criteria that *favor*, but do not guarantee, the spontaneous formation of a solution:

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

In the process of dissolution, an internal energy change often, but not always, occurs as heat is absorbed or evolved. An increase in disorder always results when a solution forms.

When the strengths of the intermolecular forces of attraction between solute and solvent species in a solution are no different than those present in the separated components, the solution is formed with no accompanying energy change. Such a solution is called an ideal solution. A mixture of ideal gases (or gases such as helium and argon, which closely approach ideal behavior) is an example of an ideal solution, since the entities comprising these gases experience no significant intermolecular attractions.

When containers of helium and argon are connected, the gases spontaneously mix due to diffusion and form a solution (Figure **7.1.2**). The formation of this solution clearly involves an increase in disorder, since the helium and argon atoms occupy a volume twice as large as that which each occupied before mixing.

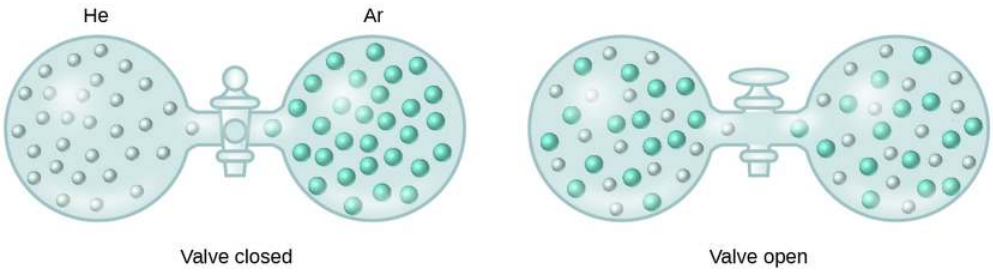


Figure **7.1.2**: Samples of helium and argon spontaneously mix to give a solution in which the disorder of the atoms of the two gases is increased.

Two figures are shown. The first contains two spherical containers joined by a closed stopcock. The container to the left is labeled H e. It holds about thirty evenly dispersed, small, light blue spheres. The container on the right is labeled A r and contains about thirty slightly larger blue-green spheres. The second, similar figure has an open stopcock between the two spherical containers. The light blue and green spheres are evenly dispersed and present in both containers.

Ideal solutions may also form when structurally similar liquids are mixed. For example, mixtures of the alcohols methanol (CH_3OH) and ethanol (C_2H_5OH) form ideal solutions, as do mixtures of the hydrocarbons pentane, $\mathbf{C_5H_{12}}$, and hexane, $\mathbf{C_6H_{14}}$. Placing methanol and ethanol, or pentane and hexane, in the bulbs shown in Figure **7.1.2** will result in the same diffusion and subsequent mixing of these liquids as is observed for the He and Ar gases (although at a much slower rate), yielding solutions with no significant change in energy. Unlike a mixture of gases, however, the components of these liquid-liquid solutions do, indeed, experience intermolecular attractive forces. But since the molecules of the two substances being mixed are structurally very similar, the intermolecular attractive forces between like and unlike molecules are essentially the same, and the dissolution process, therefore, does not entail any appreciable increase or decrease in energy. These examples illustrate how diffusion alone can provide the driving force required to cause the spontaneous formation of a solution. In some cases, however, the relative magnitudes of intermolecular forces of attraction between solute and solvent species may prevent dissolution.

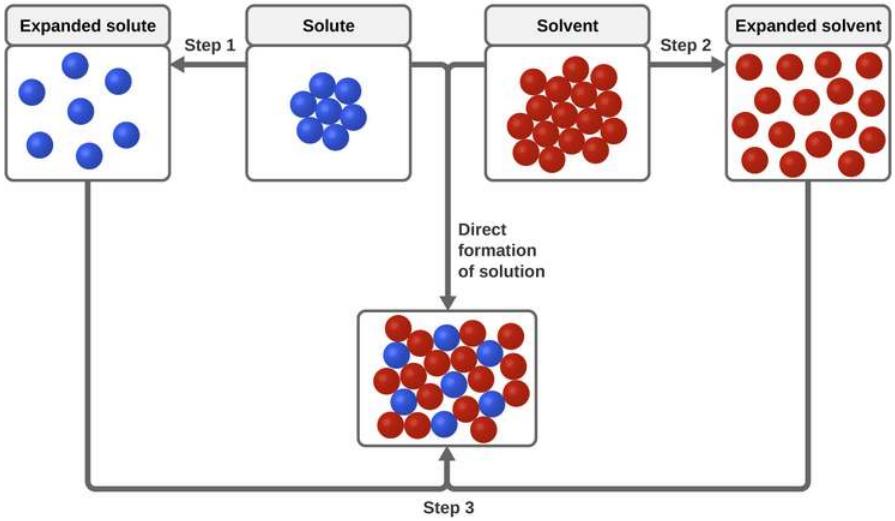


Figure **7.1.3**: This schematic representation of dissolution shows a stepwise process involving the endothermic separation of solute and solvent species (Steps 1 and 2) and exothermic solvation (Step 3).

The top, central region of the figure shows solute particles as seven blue spheres and solvent particles as 16 red spheres in separate, labeled boxes. The particles in these boxes are touching. An arrow labeled “Step 1” points left of the solute box, and shows the blue spheres no longer touching in another box labeled “expanded solute.” An arrow labeled “Step 2” points right from the solvent box and shows the red spheres no longer touching in another box labeled “expanded solvent.” Arrows proceed from the bottom of the expanded solute and expanded solvent boxes and join at the bottom of the figure where a step 3 label is shown. The joined arrows point to a box just above in which the red and blue spheres are mixed together and touching. The solute and solvent boxes are joined by another arrow labeled “direct formation of solution” which points downward at the center of the figure. This arrow also points to the box containing mixed red and blue spheres near the bottom of the figure.

Three types of intermolecular attractive forces are relevant to the dissolution process: solute-solute, solvent-solvent, and solute-solvent. As illustrated in Figure **7.1.3**, the formation of a solution may be viewed as a stepwise process in which energy is consumed to overcome solute-solute and solvent-solvent attractions (endothermic processes) and released when solute-solvent attractions are established (an exothermic process referred to as solvation). The relative magnitudes of the energy changes associated with these

stepwise processes determine whether the dissolution process overall will release or absorb energy. In some cases, solutions do not form because the energy required to separate solute and solvent species is so much greater than the energy released by solvation.



Figure **7.1.4**: A mixture of nonpolar cooking oil and polar water does not yield a solution. (credit: Gautam Dogra).

For example, cooking oils and water will not mix to any appreciable extent to yield solutions (Figure **7.1.4**). Hydrogen bonding is the dominant intermolecular attractive force present in liquid water; the nonpolar hydrocarbon molecules of cooking oils are not capable of hydrogen bonding, instead being held together by dispersion forces. Forming an oil-water solution would require overcoming the very strong hydrogen bonding in water, as well as the significantly strong dispersion forces between the relatively large oil molecules. And, since the polar water molecules and nonpolar oil molecules would not experience very strong intermolecular attraction, very little energy would be released by solvation.

On the other hand, a mixture of ethanol and water will mix in any proportions to yield a solution. In this case, both substances are capable of hydrogen bonding, and so the solvation process is sufficiently exothermic to compensate for the endothermic separations of solute and solvent molecules.

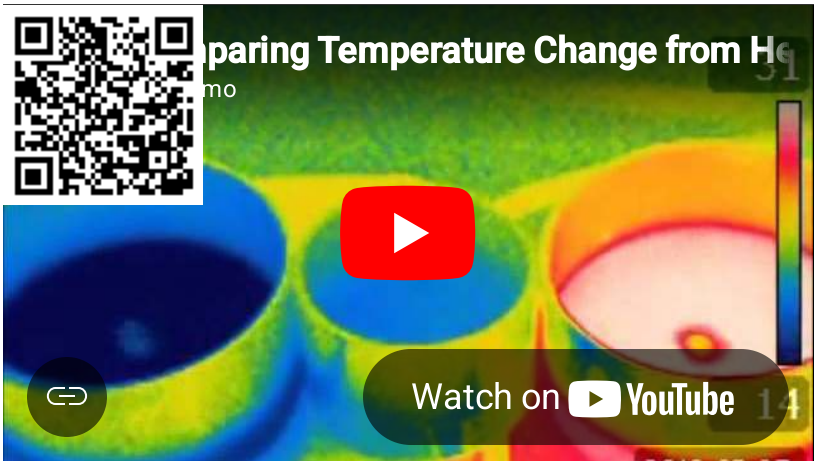


Figure **7.1.5**: An instant cold pack gets cold when certain salts, such as ammonium nitrate, dissolve in water—an endothermic process.

This figure shows a single use instant cold pack with labels indicating an inner bag of water surrounded by white particulate ammonium nitrate.

As noted at the beginning of this module, spontaneous solution formation is favored, but not guaranteed, by exothermic dissolution processes. While many soluble compounds do, indeed, dissolve with the release of heat, some dissolve endothermically. Ammonium nitrate (NH_4NO_3) is one such example and is used to make instant cold packs for treating injuries like the one pictured in Figure **7.1.5**. A thin-walled plastic bag of water is sealed inside a larger bag with solid NH_4NO_3. When the smaller bag is broken, a solution of NH_4NO_3 forms, absorbing heat from the surroundings (the injured area to which the pack is applied) and providing a cold compress that decreases swelling. Endothermic dissolutions such as this one require a greater energy input to separate the

solute species than is recovered when the solutes are solvated, but they are spontaneous nonetheless due to the increase in disorder that accompanies formation of the solution.



***Video* 7.1.1**: *Watch this brief video illustrating endothermic and exothermic dissolution processes.*

Summary

A solution forms when two or more substances combine physically to yield a mixture that is homogeneous at the molecular level. The solvent is the most concentrated component and determines the physical state of the solution. The solutes are the other components typically present at concentrations less than that of the solvent. Solutions may form endothermically or exothermically, depending upon the relative magnitudes of solute and solvent intermolecular attractive forces. Ideal solutions form with no appreciable change in energy.

Footnotes

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

Glossary

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

ideal solution
: solution that forms with no accompanying energy change

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

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

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7.2: Concentrations of Solutions

Skills to Develop

- Define the concentration units of mass percentage, volume percentage, mass-volume percentage, parts-per-million (ppm), and parts-per-billion (ppb)
- Perform computations relating a solution's concentration and its components' volumes and/or masses using these units\
- Express concentrations of solution components using mole fraction and molality
- Describe the effect of solute concentration on various solution properties (vapor pressure, boiling point, freezing point, and osmotic pressure)
- Perform calculations using the mathematical equations that describe these various colligative effects

Last term, we introduced molarity, a very useful measurement unit for evaluating the concentration of solutions. However, molarity is only one measure of concentration. In this section, we will introduce some other units of concentration that are commonly used in various applications, either for convenience or by convention.

Mass Percentage

Percentages are commonly used to express the composition of mixtures, including solutions. The mass percentage of a solution component is defined as the ratio of the component's mass to the solution's mass, expressed as a percentage:

$$\text{mass percentage} = \frac{\text{mass of component}}{\text{mass of solution}} \times 100\% \tag{7.2.1}$$

We are generally most interested in the mass percentages of solutes, but it is also possible to compute the mass percentage of solvent.

Mass percentage is also referred to by similar names such as *percent mass*, *percent weight*, *weight/weight percent*, and other variations on this theme. The most common symbol for mass percentage is simply the percent sign, %, although more detailed symbols are often used including %mass, %weight, and (w/w)%. Use of these more detailed symbols can prevent confusion of mass percentages with other types of percentages, such as volume percentages (to be discussed later in this section).

Mass percentages are popular concentration units for consumer products. The label of a typical liquid bleach bottle (Figure 7.2.1) cites the concentration of its active ingredient, sodium hypochlorite (NaOCl), as being 7.4%. A 100.0-g sample of bleach would therefore contain 7.4 g of NaOCl.



***Figure* 7.2.1:** *Liquid bleach is an aqueous solution of sodium hypochlorite (NaOCl). This brand has a concentration of 7.4% NaOCl by mass.*

Example 7.2.1: Calculation of Percent by Mass

A 5.0-g sample of spinal fluid contains 3.75 mg (0.00375 g) of glucose. What is the percent by mass of glucose in spinal fluid?

Solution

The spinal fluid sample contains roughly 4 mg of glucose in 5000 mg of fluid, so the mass fraction of glucose should be a bit less than one part in 1000, or about 0.1%. Substituting the given masses into the equation defining mass percentage yields:

$$\%\ \text{glucose} = \frac{3.75\ \text{mg glucose} \times \frac{1\ \text{g}}{1000\ \text{mg}}}{5.0\ \text{g spinal fluid}} = 0.075\% \tag{7.2.2}$$

The computed mass percentage agrees with our rough estimate (it's a bit less than 0.1%).

Note that while any mass unit may be used to compute a mass percentage (mg, g, kg, oz, and so on), the same unit must be used for both the solute and the solution so that the mass units cancel, yielding a dimensionless ratio. In this case, we converted the units of solute in the numerator from mg to g to match the units in the denominator. We could just as easily have converted the denominator from g to mg instead. As long as identical mass units are used for both solute and solution, the computed mass percentage will be correct.

Exercise 7.2.1

A bottle of a tile cleanser contains 135 g of HCl and 775 g of water. What is the percent by mass of HCl in this cleanser?

Answer

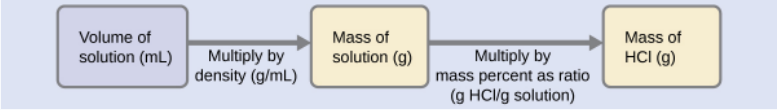
14.8%

Example 7.2.2: Calculations using Mass Percentage

"Concentrated" hydrochloric acid is an aqueous solution of 37.2% HCl that is commonly used as a laboratory reagent. The density of this solution is 1.19 g/mL. What mass of HCl is contained in 0.500 L of this solution?

Solution

The HCl concentration is near 40%, so a 100-g portion of this solution would contain about 40 g of HCl. Since the solution density isn't greatly different from that of water (1 g/mL), a reasonable estimate of the HCl mass in 500 g (0.5 L) of the solution is about five times greater than that in a 100 g portion, or $5 \times 40 = 200\ \text{g}$. To derive the mass of solute in a solution from its mass percentage, we need to know the corresponding mass of the solution. Using the solution density given, we can convert the solution's volume to mass, and then use the given mass percentage to calculate the solute mass. This mathematical approach is outlined in this flowchart:



For proper unit cancellation, the 0.500-L volume is converted into 500 mL, and the mass percentage is expressed as a ratio, 37.2 g HCl/g solution:

$$500\ \text{mL solution}\left(\frac{1.19\ \text{g solution}}{\text{mL solution}}\right)\left(\frac{37.2\ \text{g HCl}}{100\ \text{g solution}}\right) = 221\ \text{g HCl} \tag{7.2.3}$$

This mass of HCl is consistent with our rough estimate of approximately 200 g.

Exercise 7.2.2

What volume of concentrated HCl solution contains 125 g of HCl?

Answer

282 mL

Volume Percentage

Liquid volumes over a wide range of magnitudes are conveniently measured using common and relatively inexpensive laboratory equipment. The concentration of a solution formed by dissolving a liquid solute in a liquid solvent is therefore often expressed as a volume percentage, %vol or (v/v)%:

$$\text{volume percentage} = \frac{\text{volume solute}}{\text{volume solution}} \times 100\% \tag{7.2.4}$$

Example 7.2.3: Calculations using Volume Percentage

Rubbing alcohol (isopropanol) is usually sold as a 70%vol aqueous solution. If the density of isopropyl alcohol is 0.785 g/mL, how many grams of isopropyl alcohol are present in a 355 mL bottle of rubbing alcohol?

Solution

Per the definition of volume percentage, the isopropanol volume is 70% of the total solution volume. Multiplying the isopropanol volume by its density yields the requested mass:

$$\begin{aligned} &355\ \text{mL solution}\left(\frac{70\ \text{mL isopropyl alcohol}}{100\ \text{mL solution}}\right)\left(\frac{0.785\ \text{g isopropyl alcohol}}{1\ \text{mL isopropyl alcohol}}\right) \\ &= 195\ \text{g isopropyl alcohol} \end{aligned} \tag{7.2.5}$$

Exercise 7.2.3

Wine is approximately 12% ethanol (CH_3CH_2OH) by volume. Ethanol has a molar mass of 46.06 g/mol and a density 0.789 g/mL. How many moles of ethanol are present in a 750-mL bottle of wine?

Answer

1.5 mol ethanol

Mass-Volume Percentage

"Mixed" percentage units, derived from the mass of solute and the volume of solution, are popular for certain biochemical and medical applications. A mass-volume percent is a ratio of a solute's mass to the solution's volume expressed as a percentage. The specific units used for solute mass and solution volume may vary, depending on the solution. For example, physiological saline solution, used to prepare intravenous fluids, has a concentration of 0.9% mass/volume (m/v), indicating that the composition is 0.9 g of solute per 100 mL of solution. The concentration of glucose in blood (commonly referred to as "blood sugar") is also typically expressed in terms of a mass-volume ratio. Though not expressed explicitly as a percentage, its concentration is usually given in milligrams of glucose per deciliter (100 mL) of blood (Figure 7.2.2).



***Figure* 7.2.2**: *"Mixed" mass-volume units are commonly encountered in medical settings. (a) The NaCl concentration of physiological saline is 0.9% (m/v). (b) This device measures glucose levels in a sample of blood. The normal range for glucose concentration in blood (fasting) is around 70–100 mg/dL. (credit a: modification of work by "The National Guard"/Flickr; credit b: modification of work by Biswarup Ganguly).*

Parts per Million and Parts per Billion

Very low solute concentrations are often expressed using appropriately small units such as parts per million (ppm) or parts per billion (ppb). Like percentage ("part per hundred") units, ppm and ppb may be defined in terms of masses, volumes, or mixed mass-volume units. There are also ppm and ppb units defined with respect to numbers of atoms and molecules.

The mass-based definitions of ppm and ppb are given here:

$$\text{ppm} = \frac{\text{mass solute}}{\text{mass solution}} \times 10^6 \text{ ppm} \tag{7.2.6}$$

$$\text{ppb} = \frac{\text{mass solute}}{\text{mass solution}} \times 10^9 \text{ ppb} \tag{7.2.7}$$

Both ppm and ppb are convenient units for reporting the concentrations of pollutants and other trace contaminants in water. Concentrations of these contaminants are typically very low in treated and natural waters, and their levels cannot exceed relatively low concentration thresholds without causing adverse effects on health and wildlife. For example, the EPA has identified the maximum safe level of fluoride ion in tap water to be 4 ppm. Inline water filters are designed to reduce the concentration of fluoride and several other trace-level contaminants in tap water (Figure **7.2.3**).



Figure* 7.2.3*: *(a) In some areas, trace-level concentrations of contaminants can render unfiltered tap water unsafe for drinking and cooking. (b) Inline water filters reduce the concentration of solutes in tap water. (credit a: modification of work by Jenn Durfey; credit b: modification of work by "vastateparkstaff"/Wikimedia commons).*

Example 7.2.4: Parts per Million and Parts per Billion Concentrations

According to the EPA, when the concentration of lead in tap water reaches 15 ppb, certain remedial actions must be taken. What is this concentration in ppm? At this concentration, what mass of lead (μg) would be contained in a typical glass of water (300 mL)?

Solution

The definitions of the ppm and ppb units may be used to convert the given concentration from ppb to ppm. Comparing these two unit definitions shows that ppm is 1000 times greater than ppb (1 ppm = 10^3 ppb). Thus:

$$15 \cancel{\text{ ppb}} \times \frac{1 \text{ ppm}}{10^3 \cancel{\text{ ppb}}} = 0.015 \text{ ppm} \tag{7.2.8}$$

The definition of the ppb unit may be used to calculate the requested mass if the mass of the solution is provided. However, only the volume of solution (300 mL) is given, so we must use the density to derive the corresponding mass. We can assume the density of tap water to be roughly the same as that of pure water (~1.00 g/mL), since the concentrations of any dissolved substances should not be very large. Rearranging the equation defining the ppb unit and substituting the given quantities yields:

$$\text{ppb} = \frac{\text{mass solute}}{\text{mass solution}} \times 10^9 \text{ ppb} \tag{7.2.9}$$

$$\text{mass solute} = \frac{\text{ppb} \times \text{mass solution}}{10^9 \text{ ppb}} \tag{7.2.10}$$

$$\text{mass solute} = \frac{15 \text{ ppb} \times 300 \text{ mL} \times \frac{1.00 \text{ g}}{\text{mL}}}{10^9 \text{ ppb}} = 4.5 \times 10^{-6} \text{ g} \tag{7.2.11}$$

Finally, convert this mass to the requested unit of micrograms:

$$4.5 \times 10^{-6}\ \text{g} \times \frac{1\ \mu\text{g}}{10^{-6}\ \text{g}} = 4.5\ \mu\text{g} \tag{7.2.12}$$

Exercise 7.2.4

A 50.0-g sample of industrial wastewater was determined to contain 0.48 mg of mercury. Express the mercury concentration of the wastewater in ppm and ppb units.

Answer

9.6 ppm, 9600 ppb

The properties of a solution are different from those of either the pure solute(s) or solvent. Many solution properties are dependent upon the chemical identity of the solute. Compared to pure water, a solution of hydrogen chloride is more acidic, a solution of ammonia is more basic, a solution of sodium chloride is more dense, and a solution of sucrose is more viscous. There are a few solution properties, however, that depend *only* upon the total concentration of solute species, regardless of their identities. These colligative properties include vapor pressure lowering, boiling point elevation, freezing point depression, and osmotic pressure. This small set of properties is of central importance to many natural phenomena and technological applications, as will be described in this module.

Mole Fraction and Molality

Several units commonly used to express the concentrations of solution components were introduced in an earlier chapter of this text, each providing certain benefits for use in different applications. For example, molarity (M) is a convenient unit for use in stoichiometric calculations, since it is defined in terms of the molar amounts of solute species:

$$M = \frac{\text{mol solute}}{\text{L solution}} \tag{7.2.13}$$

Because solution volumes vary with temperature, molar concentrations will likewise vary. When expressed as molarity, the concentration of a solution with identical numbers of solute and solvent species will be different at different temperatures, due to the contraction/expansion of the solution. More appropriate for calculations involving many colligative properties are mole-based concentration units whose values are not dependent on temperature. Two such units are *mole fraction* (introduced in the previous chapter on gases) and *molality*.

The mole fraction, X, of a component is the ratio of its molar amount to the total number of moles of all solution components:

$$X_\text{A} = \frac{\text{mol A}}{\text{total mol of all components}} \tag{7.2.14}$$

Molality is a concentration unit defined as the ratio of the numbers of moles of solute to the mass of the solvent in kilograms:

$$m = \frac{\text{mol solute}}{\text{kg solvent}} \tag{7.2.15}$$

Since these units are computed using only masses and molar amounts, they do not vary with temperature and, thus, are better suited for applications requiring temperature-independent concentrations, including several colligative properties, as will be described in this chapter module.

Example 7.2.5: Calculating Mole Fraction and Molality

The antifreeze in most automobile radiators is a mixture of equal volumes of ethylene glycol and water, with minor amounts of other additives that prevent corrosion. What are the (a) mole fraction and (b) molality of ethylene glycol, $C_2H_4(OH)_2$, in a solution prepared from 2.22×10^3 g of ethylene glycol and 2.00×10^3 g of water (approximately 2 L of glycol and 2 L of water)?

Solution

(a) The mole fraction of ethylene glycol may be computed by first deriving molar amounts of both solution components and then substituting these amounts into the unit definition.

$$\text{mol } C_2H_4(OH)_2 = 2220 \text{ g} \times \frac{1 \text{ mol } C_2H_4(OH)_2}{62.07 \text{ g } C_2H_4(OH)_2} = 35.8 \text{ mol } C_2H_4(OH)_2$$

$$\text{mol } H_2O = 2000 \text{ g} \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 111 \text{ mol } H_2O$$

$$X_{\text{ethylene glycol}} = \frac{35.8 \text{ mol } C_2H_4(OH)_2}{(35.8 + 111) \text{ mol total}} = 0.245$$

Notice that mole fraction is a dimensionless property, being the ratio of properties with identical units (moles).

(b) To find molality, we need to know the moles of the solute and the mass of the solvent (in kg).

First, use the given mass of ethylene glycol and its molar mass to find the moles of solute:

$$2220 \text{ g } C_2H_4(OH)_2 \left(\frac{\text{mol } C_2H_2(OH)_2}{62.07 \text{ g}} \right) = 35.8 \text{ mol } C_2H_4(OH)_2 \tag{7.2.16}$$

Then, convert the mass of the water from grams to kilograms:

$$2000 \text{ g } H_2O \left(\frac{1 \text{ kg}}{1000 \text{ g}} \right) = 2 \text{ kg } H_2O \tag{7.2.17}$$

Finally, calculate molarity per its definition:

$$\text{molality} = \frac{\text{mol solute}}{\text{kg solvent}} \tag{7.2.18}$$

$$\text{molality} = \frac{35.8 \text{ mol } C_2H_4(OH)_2}{2 \text{ kg } H_2O} \tag{7.2.19}$$

$$\text{molality} = 17.9 \, m \tag{7.2.20}$$

Exercise 7.2.5

What are the mole fraction and molality of a solution that contains 0.850 g of ammonia, NH_3, dissolved in 125 g of water?

Answer

7.14×10^{-3}; 0.399 *m*

Example 7.2.6: Converting Mole Fraction and Molal Concentrations

Calculate the mole fraction of solute and solvent in a 3.0 *m* solution of sodium chloride.

Solution

Converting from one concentration unit to another is accomplished by first comparing the two unit definitions. In this case, both units have the same numerator (moles of solute) but different denominators. The provided molal concentration may be written as:

$$\frac{3.0 \text{ mol NaCl}}{1.0 \text{ kg } H_2O} \tag{7.2.21}$$

The numerator for this solution's mole fraction is, therefore, 3.0 mol NaCl. The denominator may be computed by deriving the molar amount of water corresponding to 1.0 kg

$$1.0 \text{ kg } H_2O \left(\frac{1000 \text{ g}}{1 \text{ kg}} \right) \left(\frac{\text{mol } H_2O}{18.02 \text{ g}} \right) = 55 \text{ mol } H_2O$$

and then substituting these molar amounts into the definition for mole fraction.

$$X_{H_2O} = \frac{\text{mol } H_2O}{\text{mol NaCl} + \text{mol } H_2O}$$
$$X_{H_2O} = \frac{55 \text{ mol } H_2O}{3.0 \text{ mol NaCl} + 55 \text{ mol } H_2O}$$
$$X_{H_2O} = 0.95$$
$$X_{NaCl} = \frac{\text{mol NaCl}}{\text{mol NaCl} + \text{mol } H_2O}$$
$$X_{NaCl} = \frac{3.0 \text{ mol NaCl}}{3.0 \text{ mol NaCl} + 55 \text{ mol } H_2O}$$
$$X_{NaCl} = 0.052$$

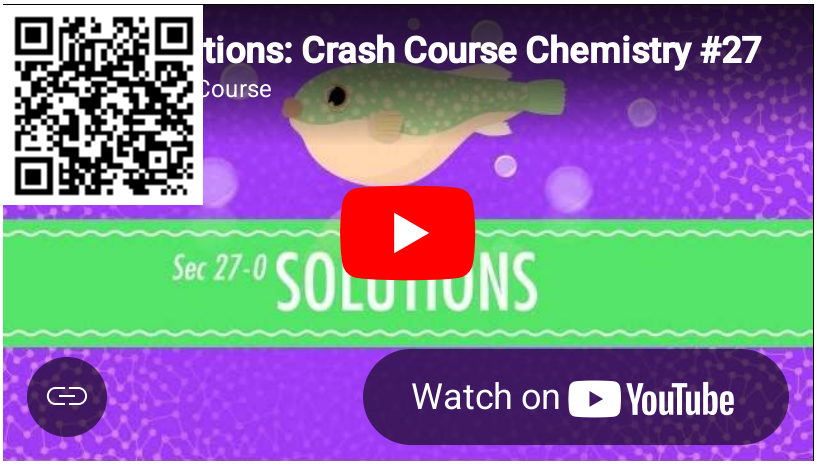
Exercise 7.2.6

The mole fraction of iodine, I_2, dissolved in dichloromethane, CH_2Cl_2, is 0.115. What is the molal concentration, *m*, of iodine in this solution?

Answer

1.50 *m*

Summary



Video* 7.2.2*: *An overview of concentration units for solutions.*

In addition to molarity, a number of other solution concentration units are used in various applications. Percentage concentrations based on the solution components' masses, volumes, or both are useful for expressing relatively high concentrations, whereas lower concentrations are conveniently expressed using ppm or ppb units. These units are popular in environmental, medical, and other fields where mole-based units such as molarity are not as commonly used.

Footnotes

1. A nonelectrolyte shown for comparison.

Glossary

mass percentage

ratio of solute-to-solution mass expressed as a percentage

mass-volume percent

ratio of solute mass to solution volume, expressed as a percentage

parts per billion (ppb)
ratio of solute-to-solution mass multiplied by 10^9

parts per million (ppm)
ratio of solute-to-solution mass multiplied by 10^6

volume percentage
ratio of solute-to-solution volume expressed as a percentage

boiling point elevation
elevation of the boiling point of a liquid by addition of a solute

boiling point elevation constant
the proportionality constant in the equation relating boiling point elevation to solute molality; also known as the ebullioscopic constant

colligative property
property of a solution that depends only on the concentration of a solute species

freezing point depression
lowering of the freezing point of a liquid by addition of a solute

freezing point depression constant
(also, cryoscopic constant) proportionality constant in the equation relating freezing point depression to solute molality

ion pair
solvated anion/cation pair held together by moderate electrostatic attraction

molality (*m*)
a concentration unit defined as the ratio of the numbers of moles of solute to the mass of the solvent in kilograms

van't Hoff factor (*i*)
the ratio of the number of moles of particles in a solution to the number of moles of formula units dissolved in the solution

Contributors

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7.2.1: Concentrations of Solutions (Problems)

PROBLEM 7.2.1.1

What mass of a concentrated solution of nitric acid (68.0% HNO_3 by mass) is needed to prepare 400.0 g of a 10.0% solution of HNO_3 by mass?

Answer

58.8 g

PROBLEM 7.2.1.2

What mass of a 4.00% NaOH solution by mass contains 15.0 g of NaOH?

Answer

375 g

Click here to see a video of the solution



PROBLEM 7.2.1.3

What mass of solid NaOH (97.0% NaOH by mass) is required to prepare 1.00 L of a 10.0% solution of NaOH by mass? The density of the 10.0% solution is 1.109 g/mL.

Answer

114 g

PROBLEM 7.2.1.4

The hardness of water (hardness count) is usually expressed in parts per million (by mass) of $\mathbf{CaCO_3}$, which is equivalent to milligrams of $\mathbf{CaCO_3}$ per liter of water. What is the molar concentration of Ca^{2+} ions in a water sample with a hardness count of 175 mg $CaCO_3$/L?

Answer

$\mathbf{1.75\times 10^{-3}}M$

PROBLEM 7.2.1.5

A throat spray is 1.40% by mass phenol, $\mathbf{C_6H_5OH}$, in water. If the solution has a density of 0.9956 g/mL, calculate the molarity of the solution.

Answer

0.148 M

Click here to see a video of the solution



PROBLEM 7.2.1.6

Copper(I) iodide (CuI) is often added to table salt as a dietary source of iodine. How many moles of CuI are contained in 1.00 lb (454 g) of table salt containing 0.0100% CuI by mass?

Answer

2.38×10^{-4} mol

PROBLEM 7.2.1.7

What are the mole fractions of H_3PO_4 and water in a solution of 14.5 g of H_3PO_4 in 125 g of water?

Answer

$X_{H_3PO_4} = 0.021$

$X_{H_2O} = 0.979$

Click here to see a video of the solution



PROBLEM 7.2.1.8

What are the mole fractions of HNO_3 and water in a concentrated solution of nitric acid (68.0% HNO_3 by mass)?

Answer

$X_{HNO_3} = 0.378$

$X_{H_2O} = 0.622$

PROBLEM 7.2.1.9

Calculate the mole fraction of each solute and solvent:

a. 583 g of H_2SO_4 in 1.50 kg of water—the acid solution used in an automobile battery
b. 0.86 g of NaCl in 1.00×10^2 g of water—a solution of sodium chloride for intravenous injection
c. 46.85 g of codeine, $C_{18}H_{21}NO_3$, in 125.5 g of ethanol, C_2H_5OH
d. 25 g of I_2 in 125 g of ethanol, C_2H_5OH

Answer a

$X_{H_2SO_4} = 0.067$

$X_{H_2O} = 0.933$

Answer b

$X_{HCl} = 0.0026$

$X_{H_2O} = 0.9974$

Answer c

$X_{codiene} = 0.054$

$X_{EtOH} = 0.946$

Answer d

$X_{I_2} = 0.035$

$X_{EtOH} = 0.965$

Click here to see a video of the solution



PROBLEM 7.2.1.10

Calculate the mole fraction of each solute and solvent:

a. 0.710 kg of sodium carbonate (washing soda), Na_2CO_3, in 10.0 kg of water—a saturated solution at 0 °C
b. 125 g of NH_4NO_3 in 275 g of water—a mixture used to make an instant ice pack
c. 25 g of Cl_2 in 125 g of dichloromethane, CH_2Cl_2
d. 0.372 g of histamine, C_5H_9N, in 125 g of chloroform, $CHCl_3$

Answer a

$X_{Na_2CO_3} = 0.0119$

$X_{H_2O} = 0.988$

Answer b

$X_{NH_4NO_3} = 0.09927$

$X_{H_2O} = 0.907$

Answer c

$X_{Cl_2} = 0.192$

$X_{CH_2Cl_2} = 0.808$

Answer d

$X_{C_5H_9N} = 0.00426$

$X_{CHCl_3} = 0.997$

PROBLEM 7.2.1.11

What is the difference between a 1 *M* solution and a 1 *m* solution?

Answer

In a 1 *M* solution, the mole is contained in exactly 1 L of solution. In a 1 *m* solution, the mole is contained in exactly 1 kg of solvent.

PROBLEM 7.2.1.12

What is the molality of phosphoric acid, H_3PO_4, in a solution of 14.5 g of H_3PO_4 in 125 g of water?

Answer

1.18 *m*

PROBLEM 7.2.1.13

What is the molality of nitric acid in a concentrated solution of nitric acid (68.0% HNO_3 by mass)?

Answer

33.7 *m*

PROBLEM 7.2.1.14

Calculate the molality of each of the following solutions:

a. 0.710 kg of sodium carbonate (washing soda), Na_2CO_3, in 10.0 kg of water—a saturated solution at 0°C
b. 125 g of NH_4NO_3 in 275 g of water—a mixture used to make an instant ice pack
c. 25 g of Cl_2 in 125 g of dichloromethane, CH_2Cl_2
d. 0.372 g of histamine, C_5H_9N, in 125 g of chloroform, $CHCl_3$

Answer

6.70×10^{-1} *m*

Answer

5.67 *m*

Answer

2.8 *m*

Answer

0.0358 *m*

PROBLEM 7.2.1.15

A 13.0% solution of K_2CO_3 by mass has a density of 1.09 g/cm^3. Calculate the molality of the solution.

Answer

1.08 *m*

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7.3: Solubility and Intermolecular Forces

Skills to Develop

- Describe the effects of temperature and pressure on solubility
- State Henry's law and use it in calculations involving the solubility of a gas in a liquid
- Explain the degrees of solubility possible for liquid-liquid solutions

Imagine adding a small amount of salt to a glass of water, stirring until all the salt has dissolved, and then adding a bit more. You can repeat this process until the salt concentration of the solution reaches its natural limit, a limit determined primarily by the relative strengths of the solute-solute, solute-solvent, and solvent-solvent attractive forces discussed in the previous two modules of this chapter. You can be certain that you have reached this limit because, no matter how long you stir the solution, undissolved salt remains. The concentration of salt in the solution at this point is known as its solubility.

The solubility of a solute in a particular solvent is the maximum concentration that may be achieved under given conditions when the dissolution process is *at equilibrium*. Referring to the example of salt in water:

$$\mathrm{NaCl}(s) \rightleftharpoons \mathrm{Na}^+(aq) + \mathrm{Cl}^-(aq) \tag{7.3.1}$$

When a solute's concentration is equal to its solubility, the solution is said to be saturated with that solute. If the solute's concentration is less than its solubility, the solution is said to be unsaturated. A solution that contains a relatively low concentration of solute is called dilute, and one with a relatively high concentration is called concentrated.

If we add more salt to a saturated solution of salt, we see it fall to the bottom and no more seems to dissolve. In fact, the added salt does dissolve, as represented by the forward direction of the dissolution equation. Accompanying this process, dissolved salt will precipitate, as depicted by the reverse direction of the equation. The system is said to be at equilibrium when these two reciprocal processes are occurring at equal rates, and so the amount of undissolved and dissolved salt remains constant. Support for the simultaneous occurrence of the dissolution and precipitation processes is provided by noting that the number and sizes of the undissolved salt crystals will change over time, though their combined mass will remain the same.



***Video* 7.3.1:** *Watch this impressive video showing the precipitation of sodium acetate from a supersaturated solution.*

Solutions may be prepared in which a solute concentration *exceeds* its solubility. Such solutions are said to be supersaturated, and they are interesting examples of *nonequilibrium* states. For example, the carbonated beverage in an open container that has not yet "gone flat" is supersaturated with carbon dioxide gas; given time, the CO_2 concentration will decrease until it reaches its equilibrium value.

Solutions of Gases in Liquids

In an earlier module of this chapter, the effect of intermolecular attractive forces on solution formation was discussed. The chemical structures of the solute and solvent dictate the types of forces possible and, consequently, are important factors in determining solubility. For example, under similar conditions, the water solubility of oxygen is approximately three times greater than that of

helium, but 100 times less than the solubility of chloromethane, $CHCl_3$. Considering the role of the solvent's chemical structure, note that the solubility of oxygen in the liquid hydrocarbon hexane, C_6H_{14}, is approximately 20 times greater than it is in water.

Other factors also affect the solubility of a given substance in a given solvent. Temperature is one such factor, with gas solubility typically decreasing as temperature increases (Figure **7.3.1**). This is one of the major impacts resulting from the thermal pollution of natural bodies of water.

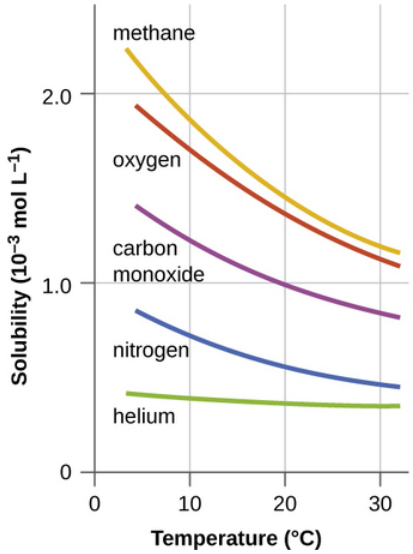


Figure* 7.3.1*: *The solubilities of these gases in water decrease as the temperature increases. All solubilities were measured with a constant pressure of 101.3 kPa (1 atm) of gas above the solutions.*

When the temperature of a river, lake, or stream is raised abnormally high, usually due to the discharge of hot water from some industrial process, the solubility of oxygen in the water is decreased. Decreased levels of dissolved oxygen may have serious consequences for the health of the water's ecosystems and, in severe cases, can result in large-scale fish kills (Figure **7.3.2**).



Figure* 7.3.2*: *(a) The small bubbles of air in this glass of chilled water formed when the water warmed to room temperature and the solubility of its dissolved air decreased. (b) The decreased solubility of oxygen in natural waters subjected to thermal pollution can result in large-scale fish kills. (credit a: modification of work by Liz West; credit b: modification of work by U.S. Fish and Wildlife Service)*

The solubility of a gaseous solute is also affected by the partial pressure of solute in the gas to which the solution is exposed. Gas solubility increases as the pressure of the gas increases. Carbonated beverages provide a nice illustration of this relationship. The carbonation process involves exposing the beverage to a relatively high pressure of carbon dioxide gas and then sealing the beverage container, thus saturating the beverage with CO_2 at this pressure. When the beverage container is opened, a familiar hiss is heard as the carbon dioxide gas pressure is released, and some of the dissolved carbon dioxide is typically seen leaving solution in the form of small bubbles (Figure **7.3.3**). At this point, the beverage is *supersaturated* with carbon dioxide and, with time, the dissolved carbon dioxide concentration will decrease to its equilibrium value and the beverage will become "flat."

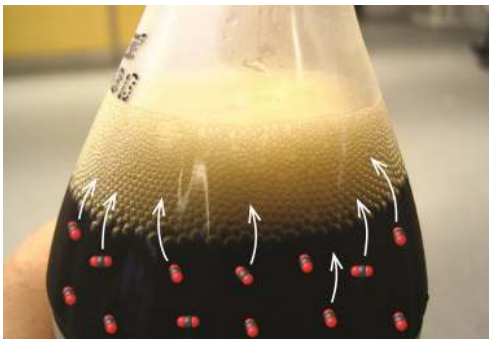


Figure 7.3.3: *Opening the bottle of carbonated beverage reduces the pressure of the gaseous carbon dioxide above the beverage. The solubility of CO_2 is thus lowered, and some dissolved carbon dioxide may be seen leaving the solution as small gas bubbles. (credit: modification of work by Derrick Coetzee)*

For many gaseous solutes, the relation between solubility, C_g, and partial pressure, P_g, is a proportional one:

$$C_g = kP_g \tag{7.3.2}$$

where k is a proportionality constant that depends on the identities of the gaseous solute and solvent, and on the solution temperature. This is a mathematical statement of Henry's law: *The quantity of an ideal gas that dissolves in a definite volume of liquid is directly proportional to the pressure of the gas.*

Example 7.3.1: Application of Henry's Law

At 20 °C, the concentration of dissolved oxygen in water exposed to gaseous oxygen at a partial pressure of 101.3 kPa (760 torr) is 1.38×10^{-3} mol L^{-1}. Use Henry's law to determine the solubility of oxygen when its partial pressure is 20.7 kPa (155 torr), the approximate pressure of oxygen in earth's atmosphere.

Solution

According to Henry's law, for an ideal solution the solubility, C_g, of a gas (1.38×10^{-3} mol L^{-1}, in this case) is directly proportional to the pressure, P_g, of the undissolved gas above the solution (101.3 kPa, or 760 torr, in this case). Because we know both C_g and P_g, we can rearrange this expression to solve for k.

$$\begin{aligned} C_g &= kP_g \\ k &= \frac{C_g}{P_g} \\ &= \frac{1.38 \times 10^{-3}\ \text{mol L}^{-1}}{101.3\ \text{kPa}} \\ &= 1.36 \times 10^{-5}\ \text{mol L}^{-1}\ \text{kPa}^{-1} \\ &\quad (1.82 \times 10^{-6}\ \text{mol L}^{-1}\ \text{torr}^{-1}) \end{aligned}$$

Now we can use k to find the solubility at the lower pressure.

$$C_g = kP_g \tag{7.3.3}$$

$$\begin{aligned} &1.36 \times 10^{-5}\ \text{mol L}^{-1}\ \text{kPa}^{-1} \times 20.7\ \text{kPa} \\ &(\text{or } 1.82 \times 10^{-6}\ \text{mol L}^{-1}\ \text{torr}^{-1} \times 155\ \text{torr}) \\ &= 2.82 \times 10^{-4}\ \text{mol L}^{-1} \end{aligned} \tag{7.3.4}$$

Note that various units may be used to express the quantities involved in these sorts of computations. Any combination of units that yield to the constraints of dimensional analysis are acceptable.

Exercise 7.3.1

Exposing a 100.0 mL sample of water at 0 °C to an atmosphere containing a gaseous solute at 20.26 kPa (152 torr) resulted in the dissolution of 1.45×10^{-3} g of the solute. Use Henry's law to determine the solubility of this gaseous solute when its

pressure is 101.3 kPa (760 torr).

Answer

7.25×10^{-3} g in 100.0 mL or 0.0725 g/L

Case Study: Decompression Sickness (“The Bends”)

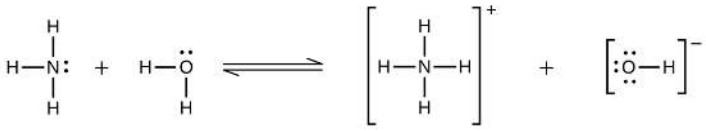
Decompression sickness (DCS), or “the bends,” is an effect of the increased pressure of the air inhaled by scuba divers when swimming underwater at considerable depths. In addition to the pressure exerted by the atmosphere, divers are subjected to additional pressure due to the water above them, experiencing an increase of approximately 1 atm for each 10 m of depth. Therefore, the air inhaled by a diver while submerged contains gases at the corresponding higher ambient pressure, and the concentrations of the gases dissolved in the diver’s blood are proportionally higher per Henry’s law.



***Figure* 7.3.4**: *(a) US Navy divers undergo training in a recompression chamber. (b) Divers receive hyperbaric oxygen therapy.*

As the diver ascends to the surface of the water, the ambient pressure decreases and the dissolved gases becomes less soluble. If the ascent is too rapid, the gases escaping from the diver’s blood may form bubbles that can cause a variety of symptoms ranging from rashes and joint pain to paralysis and death. To avoid DCS, divers must ascend from depths at relatively slow speeds (10 or 20 m/min) or otherwise make several decompression stops, pausing for several minutes at given depths during the ascent. When these preventive measures are unsuccessful, divers with DCS are often provided hyperbaric oxygen therapy in pressurized vessels called decompression (or recompression) chambers (Figure **7.3.4**).

Deviations from Henry’s law are observed when a chemical reaction takes place between the gaseous solute and the solvent. Thus, for example, the solubility of ammonia in water does not increase as rapidly with increasing pressure as predicted by the law because ammonia, being a base, reacts to some extent with water to form ammonium ions and hydroxide ions.



Gases can form supersaturated solutions. If a solution of a gas in a liquid is prepared either at low temperature or under pressure (or both), then as the solution warms or as the gas pressure is reduced, the solution may become supersaturated. In 1986, more than 1700 people in Cameroon were killed when a cloud of gas, almost certainly carbon dioxide, bubbled from Lake Nyos (Figure **7.3.5**), a deep lake in a volcanic crater. The water at the bottom of Lake Nyos is saturated with carbon dioxide by volcanic activity beneath the lake. It is believed that the lake underwent a turnover due to gradual heating from below the lake, and the warmer, less-dense water saturated with carbon dioxide reached the surface. Consequently, tremendous quantities of dissolved CO_2 were released, and the colorless gas, which is denser than air, flowed down the valley below the lake and suffocated humans and animals living in the valley.



(a) (b)

Figure* 7.3.5*: *(a) It is believed that the 1986 disaster that killed more than 1700 people near Lake Nyos in Cameroon resulted when a large volume of carbon dioxide gas was released from the lake. (b) A CO_2 vent has since been installed to help outgas the lake in a slow, controlled fashion and prevent a similar catastrophe from happening in the future. (credit a: modification of work by Jack Lockwood; credit b: modification of work by Bill Evans)*

Solutions of Liquids in Liquids

We know that some liquids mix with each other in all proportions; in other words, they have infinite mutual solubility and are said to be miscible. Ethanol, sulfuric acid, and ethylene glycol (popular for use as antifreeze, pictured in Figure **7.3.6**) are examples of liquids that are completely miscible with water. Two-cycle motor oil is miscible with gasoline.



Figure* 7.3.6**:*** *Water and antifreeze are miscible; mixtures of the two are homogeneous in all proportions. (credit: "dno1967"/Wikimedia commons)*

Liquids that mix with water in all proportions are usually polar substances or substances that form hydrogen bonds. For such liquids, the dipole-dipole attractions (or hydrogen bonding) of the solute molecules with the solvent molecules are at least as strong as those between molecules in the pure solute or in the pure solvent. Hence, the two kinds of molecules mix easily. Likewise, nonpolar liquids are miscible with each other because there is no appreciable difference in the strengths of solute-solute, solvent-solvent, and solute-solvent intermolecular attractions. The solubility of polar molecules in polar solvents and of nonpolar molecules in nonpolar solvents is, again, an illustration of the chemical axiom "like dissolves like."

Two liquids that do not mix to an appreciable extent are called immiscible. Layers are formed when we pour immiscible liquids into the same container. Gasoline, oil (Figure **7.3.7**), benzene, carbon tetrachloride, some paints, and many other nonpolar liquids are immiscible with water. The attraction between the molecules of such nonpolar liquids and polar water molecules is ineffectively weak. The only strong attractions in such a mixture are between the water molecules, so they effectively squeeze out the molecules of the nonpolar liquid. The distinction between immiscibility and miscibility is really one of degrees, so that miscible liquids are of infinite mutual solubility, while liquids said to be immiscible are of very low (though not zero) mutual solubility.



Figure* 7.3.7: Water and oil are immiscible. Mixtures of these two substances will form two separate layers with the less dense oil floating on top of the water. (credit: "Yortw"/Flickr)*

Two liquids, such as bromine and water, that are of *moderate* mutual solubility are said to be partially miscible. Two partially miscible liquids usually form two layers when mixed. In the case of the bromine and water mixture, the upper layer is water, saturated with bromine, and the lower layer is bromine saturated with water. Since bromine is nonpolar, and, thus, not very soluble in water, the water layer is only slightly discolored by the bright orange bromine dissolved in it. Since the solubility of water in bromine is very low, there is no noticeable effect on the dark color of the bromine layer (Figure **7.3.8**).



Figure* 7.3.8: Bromine (the deep orange liquid on the left) and water (the clear liquid in the middle) are partially miscible. The top layer in the mixture on the right is a saturated solution of bromine in water; the bottom layer is a saturated solution of water in bromine. (credit: Paul Flowers)*

Solutions of Solids in Liquids

The dependence of solubility on temperature for a number of inorganic solids in water is shown by the solubility curves in Figure **7.3.9**. Reviewing these data indicate a general trend of increasing solubility with temperature, although there are exceptions, as illustrated by the ionic compound cerium sulfate.

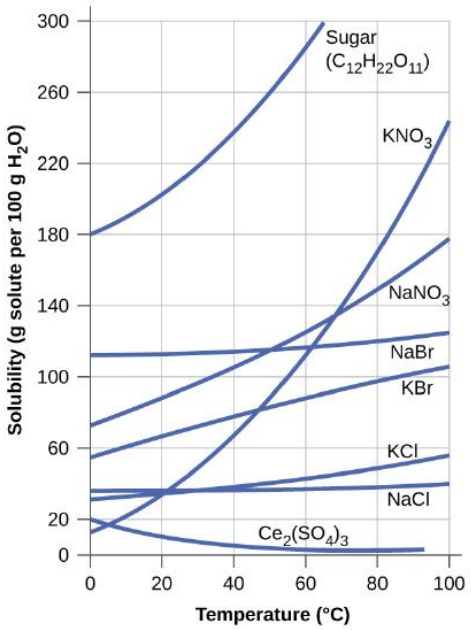


Figure 7.3.9: *This graph shows how the solubility of several solids changes with temperature.*

The temperature dependence of solubility can be exploited to prepare supersaturated solutions of certain compounds. A solution may be saturated with the compound at an elevated temperature (where the solute is more soluble) and subsequently cooled to a lower temperature without precipitating the solute. The resultant solution contains solute at a concentration greater than its equilibrium solubility at the lower temperature (i.e., it is supersaturated) and is relatively stable. Precipitation of the excess solute can be initiated by adding a seed crystal (see the video in the Link to Learning earlier in this module) or by mechanically agitating the solution. Some hand warmers, such as the one pictured in Figure **7.3.10**, take advantage of this behavior.



Figure 7.3.10: *This hand warmer produces heat when the sodium acetate in a supersaturated solution precipitates. Precipitation of the solute is initiated by a mechanical shockwave generated when the flexible metal disk within the solution is "clicked." (credit: modification of work by "Velela"/Wikimedia Commons)*



Video 7.3.2: *This video shows the crystallization process occurring in a hand warmer.*

Why Don't Oil and Water Mix?

https://chem.libretexts.org/@go/page/236762



***Video* 7.3.3:** *A look into why oil and water don't mix.*

Summary



***Video* 7.3.4:** *An overview of solubility.*

The extent to which one substance will dissolve in another is determined by several factors, including the types and relative strengths of intermolecular attractive forces that may exist between the substances' atoms, ions, or molecules. This tendency to dissolve is quantified as substance's solubility, its maximum concentration in a solution at equilibrium under specified conditions. A saturated solution contains solute at a concentration equal to its solubility. A supersaturated solution is one in which a solute's concentration exceeds its solubility—a nonequilibrium (unstable) condition that will result in solute precipitation when the solution is appropriately perturbed. Miscible liquids are soluble in all proportions, and immiscible liquids exhibit very low mutual solubility. Solubilities for gaseous solutes decrease with increasing temperature, while those for most, but not all, solid solutes increase with temperature. The concentration of a gaseous solute in a solution is proportional to the partial pressure of the gas to which the solution is exposed, a relation known as Henry's law.

Key Equations

- $C_g = kP_g$

Glossary

Henry's law

law stating the proportional relationship between the concentration of dissolved gas in a solution and the partial pressure of the gas in contact with the solution

immiscible

of negligible mutual solubility; typically refers to liquid substances

miscible
mutually soluble in all proportions; typically refers to liquid substances

partially miscible
of moderate mutual solubility; typically refers to liquid substances

saturated
of concentration equal to solubility; containing the maximum concentration of solute possible for a given temperature and pressure

solubility
extent to which a solute may be dissolved in water, or any solvent

supersaturated
of concentration that exceeds solubility; a nonequilibrium state

unsaturated
of concentration less than solubility

Contributors

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7.3.1: Solubility and Intermolecular Forces (Problems)

PROBLEM 7.3.1.1

Suggest an explanation for the observations that ethanol, C_2H_5OH, is completely miscible with water and that ethanethiol, C_2H_5SH, is soluble only to the extent of 1.5 g per 100 mL of water.

Answer

The hydrogen bonds between water and C_2H_5OH are much stronger than the intermolecular attractions between water and C_2H_5SH.

PROBLEM 7.3.1.2

Which of the following gases is expected to be most soluble in water? Explain your reasoning.

a. CH_4
b. CCl_4
c. $CHCl_3$

Answer

(c) $CHCl_3$ is expected to be most soluble in water. Of the three gases, only this one is polar and thus capable of experiencing relatively strong dipole-dipole attraction to water molecules.

Contributors

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7.4: Colligative Properties

Skills to Develop

- Describe the effect of solute concentration on various solution properties (vapor pressure, boiling point, freezing point, and osmotic pressure)
- Perform calculations using the mathematical equations that describe the various colligative effects
- Describe ion pairing and use the van't Hoff factor in calculations

Colligative Properties

The properties of a solution are different from those of either the pure solute(s) or solvent. Many solution properties are dependent upon the chemical identity of the solute. Compared to pure water, a solution of hydrogen chloride is more acidic, a solution of ammonia is more basic, a solution of sodium chloride is more dense, and a solution of sucrose is more viscous. There are a few solution properties, however, that depend *only* upon the total concentration of solute species, regardless of their identities. These colligative properties include vapor pressure lowering, boiling point elevation, freezing point depression, and osmotic pressure. This small set of properties is of central importance to many natural phenomena and technological applications, as will be described in this module.

Vapor Pressure Lowering

The equilibrium vapor pressure of a liquid is the pressure exerted by its gaseous phase when vaporization and condensation are occurring at equal rates:

$$\text{liquid} \rightleftharpoons \text{gas} \tag{7.4.1}$$

Dissolving a nonvolatile substance in a volatile liquid results in a lowering of the liquid's vapor pressure. This phenomenon can be rationalized by considering the effect of added solute molecules on the liquid's vaporization and condensation processes. To vaporize, solvent molecules must be present at the surface of the solution. The presence of solute decreases the surface area available to solvent molecules and thereby reduces the rate of solvent vaporization. Since the rate of condensation is unaffected by the presence of solute, the net result is that the vaporization-condensation equilibrium is achieved with fewer solvent molecules in the vapor phase (i.e., at a lower vapor pressure) (Figure **7.4.4**). While this kinetic interpretation is useful, it does not account for several important aspects of the colligative nature of vapor pressure lowering. A more rigorous explanation involves the property of *entropy*, a topic of discussion in a later text chapter on thermodynamics. For purposes of understanding the lowering of a liquid's vapor pressure, it is adequate to note that the greater entropy of a solution in comparison to its separate solvent and solute serves to effectively stabilize the solvent molecules and hinder their vaporization. A lower vapor pressure results, and a correspondingly higher boiling point as described in the next section of this module.

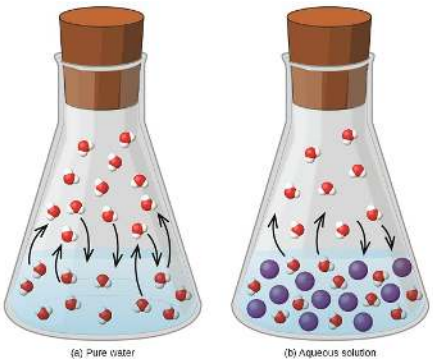


Figure* 7.4.4*: *The presence of nonvolatile solutes lowers the vapor pressure of a solution by impeding the evaporation of solvent molecules.*

The relationship between the vapor pressures of solution components and the concentrations of those components is described by Raoult's law: *The partial pressure exerted by any component of an ideal solution is equal to the vapor pressure of the pure*

component multiplied by its mole fraction in the solution.

$$P_A = X_A P_A^\circ \tag{7.4.2}$$

where P_A is the partial pressure exerted by component A in the solution, P_A° is the vapor pressure of pure A, and X_A is the mole fraction of A in the solution. (Mole fraction is a concentration unit introduced in the chapter on gases.)

Elevation of the Boiling Point of a Solvent

As described in the chapter on liquids and solids, the *boiling point* of a liquid is the temperature at which its vapor pressure is equal to ambient atmospheric pressure. Since the vapor pressure of a solution is lowered due to the presence of nonvolatile solutes, it stands to reason that the solution's boiling point will subsequently be increased. Compared to pure solvent, a solution, therefore, will require a higher temperature to achieve any given vapor pressure, including one equivalent to that of the surrounding atmosphere. The increase in boiling point observed when nonvolatile solute is dissolved in a solvent, ΔT_b, is called boiling point elevation and is directly proportional to the molal concentration of solute species:

$$\Delta T_b = K_b m \tag{7.4.3}$$

where

- K_b is the boiling point elevation constant, or the *ebullioscopic constant* and
- m is the molal concentration (molality) of all solute species.

Boiling point elevation constants are characteristic properties that depend on the identity of the solvent. Values of K_b for several solvents are listed in Table 7.4.1.

Table* 7.4.1*: *Boiling Point Elevation and Freezing Point Depression Constants for Several Solvents*

Solvent	Boiling Point (°C at 1 atm)	Kb (Cm^{-1})	Freezing Point (°C at 1 atm)	Kf (Cm−1)
water	100.0	0.512	0.0	1.86
hydrogen acetate	118.1	3.07	16.6	3.9
benzene	80.1	2.53	5.5	5.12
chloroform	61.26	3.63	−63.5	4.68
nitrobenzene	210.9	5.24	5.67	8.1

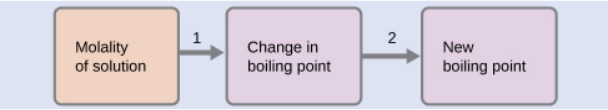
The extent to which the vapor pressure of a solvent is lowered and the boiling point is elevated depends on the total number of solute particles present in a given amount of solvent, not on the mass or size or chemical identities of the particles. A 1 *m* aqueous solution of sucrose (342 g/mol) and a 1 *m* aqueous solution of ethylene glycol (62 g/mol) will exhibit the same boiling point because each solution has one mole of solute particles (molecules) per kilogram of solvent.

Example 7.4.7: Calculating the Boiling Point of a Solution

What is the boiling point of a 0.33 *m* solution of a nonvolatile solute in benzene?

Solution

Use the equation relating boiling point elevation to solute molality to solve this problem in two steps.



1. *Calculate the change in boiling point.*

$$\Delta T_b = K_b m = 2.53\ °C\ m^{-1} \times 0.33\ m = 0.83\ °C$$

- *Add the boiling point elevation to the pure solvent's boiling point.*

$$\text{Boiling temperature} = 80.1\ ^\circ\text{C} + 0.83\ ^\circ\text{C} = 80.9\ ^\circ\text{C}$$

Exercise 7.4.7

What is the boiling point of the antifreeze described in Example **7.4.4**?

Answer

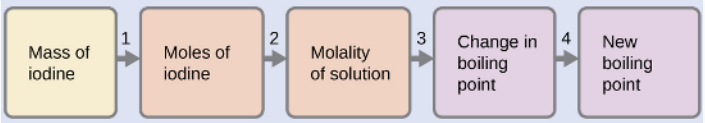
109.2 °C

Example 7.4.8: The Boiling Point of an Iodine Solution

Find the boiling point of a solution of 92.1 g of iodine, I_2, in 800.0 g of chloroform, $CHCl_3$, assuming that the iodine is nonvolatile and that the solution is ideal.

Solution

We can solve this problem using four steps.



1. *Convert from grams to moles of* I_2 *using the molar mass of* I_2 *in the unit conversion factor.*
   Result: 0.363 mol
2. *Determine the molality of the solution from the number of moles of solute and the mass of solvent, in kilograms.*
   Result: 0.454 *m*
3. *Use the direct proportionality between the change in boiling point and molal concentration to determine how much the boiling point changes.*
   Result: 1.65 °C
4. *Determine the new boiling point from the boiling point of the pure solvent and the change.*
   Result: 62.91 °C

Check each result as a self-assessment.

Exercise 7.4.8

What is the boiling point of a solution of 1.0 g of glycerin, $C_3H_5(OH)_3$, in 47.8 g of water? Assume an ideal solution.

Answer

100.12 °C

Distillation of Solutions

Distillation is a technique for separating the components of mixtures that is widely applied in both in the laboratory and in industrial settings. It is used to refine petroleum, to isolate fermentation products, and to purify water. This separation technique involves the controlled heating of a sample mixture to selectively vaporize, condense, and collect one or more components of interest. A typical apparatus for laboratory-scale distillations is shown in Figure **7.4.5**.

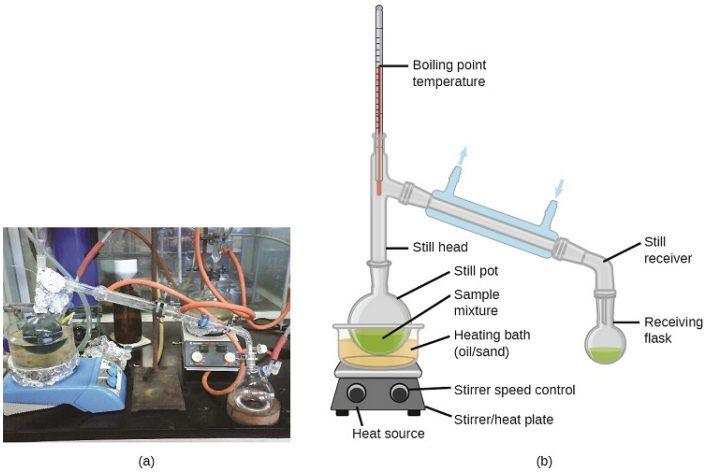


Figure* 7.4.5*: *A typical laboratory distillation unit is shown in (a) a photograph and (b) a schematic diagram of the components. (credit a: modification of work by "Rifleman82"/Wikimedia commons; credit b: modification of work by "Slashme"/Wikimedia Commons)*

Oil refineries use large-scale *fractional distillation* to separate the components of crude oil. The crude oil is heated to high temperatures at the base of a tall *fractionating column*, vaporizing many of the components that rise within the column. As vaporized components reach adequately cool zones during their ascent, they condense and are collected. The collected liquids are simpler mixtures of hydrocarbons and other petroleum compounds that are of appropriate composition for various applications (e.g., diesel fuel, kerosene, gasoline), as depicted in Figure **7.4.6**.

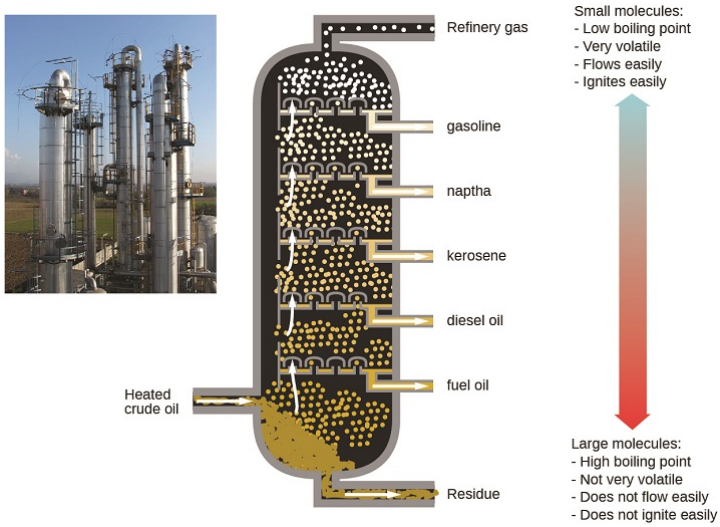


Figure* 7.4.6*: *Crude oil is a complex mixture that is separated by large-scale fractional distillation to isolate various simpler mixtures.*

Depression of the Freezing Point of a Solvent

Solutions freeze at lower temperatures than pure liquids. This phenomenon is exploited in "de-icing" schemes that use salt (Figure **7.4.7**), calcium chloride, or urea to melt ice on roads and sidewalks, and in the use of ethylene glycol as an "antifreeze" in automobile radiators. Seawater freezes at a lower temperature than fresh water, and so the Arctic and Antarctic oceans remain unfrozen even at temperatures below 0 °C (as do the body fluids of fish and other cold-blooded sea animals that live in these oceans).



***Figure* 7.4.7:** *Rock salt (NaCl), calcium chloride ($CaCl_2$), or a mixture of the two are used to melt ice. (credit: modification of work by Eddie Welker)*

The decrease in freezing point of a dilute solution compared to that of the pure solvent, ΔT_f, is called the freezing point depression and is directly proportional to the molal concentration of the solute

$$\Delta T_f = K_f m \tag{7.4.4}$$

where

- m is the *molal* concentration of the solute in the solvent and
- K_f is called the freezing point depression constant (or *cryoscopic constant*).

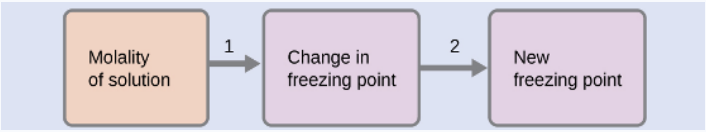
Just as for boiling point elevation constants, these are characteristic properties whose values depend on the chemical identity of the solvent. Values of K_f for several solvents are listed in Table **7.4.1**.

Example 7.4.9: Calculation of the Freezing Point of a Solution

What is the freezing point of the 0.33 *m* solution of a nonvolatile nonelectrolyte solute in benzene described in Example **7.4.4**?

Solution

Use the equation relating freezing point depression to solute molality to solve this problem in two steps.



1. *Calculate the change in freezing point.*

$$\Delta T_f = K_f m = 5.12\ ^\circ\text{C}\ m^{-1} \times 0.33\ m = 1.7\ ^\circ\text{C} \tag{7.4.5}$$

2. *Subtract the freezing point change observed from the pure solvent's freezing point.* [\mathrm{Freezing\: Temperature=5.5\: °C−1.7\:°C=3.8\:°C}\]

Exercise 7.4.9

What is the freezing point of a 1.85 *m* solution of a nonvolatile nonelectrolyte solute in nitrobenzene?

Answer

−9.3 °C

Colligative Properties and De-Icing

Sodium chloride and its group 2 analogs calcium and magnesium chloride are often used to de-ice roadways and sidewalks, due to the fact that a solution of any one of these salts will have a freezing point lower than 0 °C, the freezing point of pure water. The group 2 metal salts are frequently mixed with the cheaper and more readily available sodium chloride ("rock salt") for use on roads, since they tend to be somewhat less corrosive than the NaCl, and they provide a larger depression of the freezing point, since they dissociate to yield three particles per formula unit, rather than two particles like the sodium chloride.

Because these ionic compounds tend to hasten the corrosion of metal, they would not be a wise choice to use in antifreeze for the radiator in your car or to de-ice a plane prior to takeoff. For these applications, covalent compounds, such as ethylene or

propylene glycol, are often used. The glycols used in radiator fluid not only lower the freezing point of the liquid, but they elevate the boiling point, making the fluid useful in both winter and summer. Heated glycols are often sprayed onto the surface of airplanes prior to takeoff in inclement weather in the winter to remove ice that has already formed and prevent the formation of more ice, which would be particularly dangerous if formed on the control surfaces of the aircraft (Video **7.4.1**).



Video* 7.4.1*: *Freezing point depression is exploited to remove ice from the control surfaces of aircraft.*

Phase Diagram for an Aqueous Solution of a Nonelectrolyte

The colligative effects on vapor pressure, boiling point, and freezing point described in the previous section are conveniently summarized by comparing the phase diagrams for a pure liquid and a solution derived from that liquid. Phase diagrams for water and an aqueous solution are shown in Figure **7.4.8**.

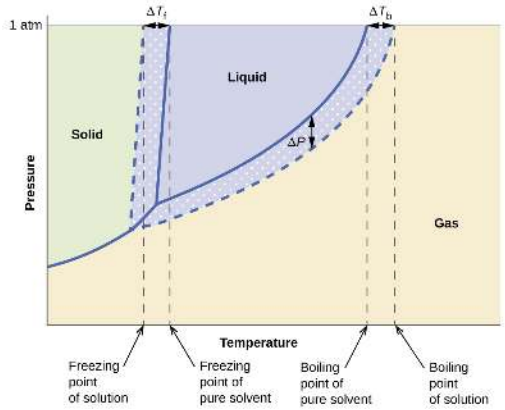


Figure* 7.4.8*: *These phase diagrams show water (solid curves) and an aqueous solution of nonelectrolyte (dashed curves).*

The liquid-vapor curve for the solution is located *beneath* the corresponding curve for the solvent, depicting the vapor pressure *lowering*, ΔP, that results from the dissolution of nonvolatile solute. Consequently, at any given pressure, the solution's boiling point is observed at a higher temperature than that for the pure solvent, reflecting the boiling point elevation, ΔT_b, associated with the presence of nonvolatile solute. The solid-liquid curve for the solution is displaced left of that for the pure solvent, representing the freezing point depression, ΔT_f, that accompanies solution formation. Finally, notice that the solid-gas curves for the solvent and its solution are identical. This is the case for many solutions comprising liquid solvents and nonvolatile solutes. Just as for vaporization, when a solution of this sort is frozen, it is actually just the *solvent* molecules that undergo the liquid-to-solid transition, forming pure solid solvent that excludes solute species. The solid and gaseous phases, therefore, are composed solvent only, and so transitions between these phases are not subject to colligative effects.

Determination of Molar Masses

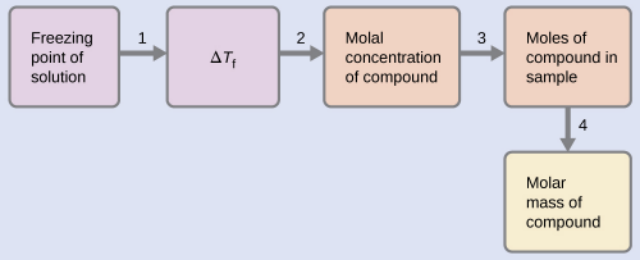
Changes in freezing point, boiling point, and vapor pressure are directly proportional to the concentration of solute present. Consequently, we can use a measurement of one of these properties to determine the molar mass of the solute from the measurements.

Example 7.4.10: Determining Molar Mass from Freezing Point Depression

A solution of 4.00 g of a nonelectrolyte dissolved in 55.0 g of benzene is found to freeze at 2.32 °C. What is the molar mass of this compound?

Solution

We can solve this problem using the following steps.



1. *Determine the change in freezing point from the observed freezing point and the freezing point of pure benzene* (Table 11.5.1).
   $\Delta T_f = 5.5\ °C - 2.32\ °C = 3.2\ °C$
2. *Determine the molal concentration from K_f, the freezing point depression constant for benzene* (Table 11.5.1), *and* ΔT_f.
   $\Delta T_f = K_f m$
   $m = \dfrac{\Delta T_f}{K_f} = \dfrac{3.2\ °C}{5.12\ °C m^{-1}} = 0.63\ m$
3. *Determine the number of moles of compound in the solution from the molal concentration and the mass of solvent used to make the solution.*
   $\text{Moles of solute} = \dfrac{0.62\ \text{mol solute}}{1.00\ \cancel{\text{kg solvent}}} \times 0.0550\ \cancel{\text{kg solvent}} = 0.035\ \text{mol}$
4. *Determine the molar mass from the mass of the solute and the number of moles in that mass.*
   $\text{Molar mass} = \dfrac{4.00\ \text{g}}{0.034\ \text{mol}} = 1.2 \times 10^2\ \text{g/mol}$

Exercise 7.4.10

A solution of 35.7 g of a nonelectrolyte in 220.0 g of chloroform has a boiling point of 64.5 °C. What is the molar mass of this compound?

Answer

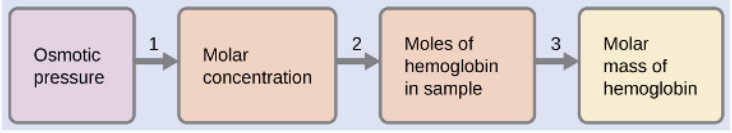
1.8×10^2 g/mol

Example 7.4.11: Determination of a Molar Mass from Osmotic Pressure

A 0.500 L sample of an aqueous solution containing 10.0 g of hemoglobin has an osmotic pressure of 5.9 torr at 22 °C. What is the molar mass of hemoglobin?

Solution

Here is one set of steps that can be used to solve the problem:



1. *Convert the osmotic pressure to atmospheres, then determine the molar concentration from the osmotic pressure.*
\[\Pi=\mathrm{\dfrac{5.9\:torr×1\:atm}{760\:torr}=7.8×10^{−3}\:atm}\]

$$\Pi = MRT \tag{7.4.6}$$

$$M = \frac{\Pi}{RT} = \frac{7.8 \times 10^{-3}\ \text{atm}}{(0.08206\ \text{L atm/mol K})(295\ \text{K})} = 3.2 \times 10^{-4}\ \text{M}$$

2. *Determine the number of moles of hemoglobin in the solution from the concentration and the volume of the solution.*

$$\text{moles of hemoglobin} = \frac{3.2 \times 10^{-4}\ \text{mol}}{1\ \cancel{\text{L solution}}} \times 0.500\ \cancel{\text{L solution}} = 1.6 \times 10^{-4}\ \text{mol}$$

3. *Determine the molar mass from the mass of hemoglobin and the number of moles in that mass.*

$$\text{molar mass} = \frac{10.0\ \text{g}}{1.6 \times 10^{-4}\ \text{mol}} = 6.2 \times 10^{4}\ \text{g/mol}$$

Exercise 7.4.11

What is the molar mass of a protein if a solution of 0.02 g of the protein in 25.0 mL of solution has an osmotic pressure of 0.56 torr at 25 °C?

Answer

2.7×10^4 g/mol

Colligative Properties of Electrolytes

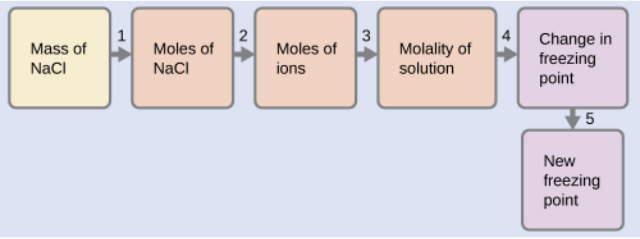
As noted previously in this module, the colligative properties of a solution depend only on the number, not on the kind, of solute species dissolved. For example, 1 mole of any nonelectrolyte dissolved in 1 kilogram of solvent produces the same lowering of the freezing point as does 1 mole of any other nonelectrolyte. However, 1 mole of sodium chloride (an electrolyte) forms *2 moles* of ions when dissolved in solution. Each individual ion produces the same effect on the freezing point as a single molecule does.

Example 7.4.13: The Freezing Point of a Solution of an Electrolyte

The concentration of ions in seawater is approximately the same as that in a solution containing 4.2 g of NaCl dissolved in 125 g of water. Assume that each of the ions in the NaCl solution has the same effect on the freezing point of water as a nonelectrolyte molecule, and determine the freezing temperature the solution (which is approximately equal to the freezing temperature of seawater).

Solution

We can solve this problem using the following series of steps.



- *Convert from grams to moles of NaCl using the molar mass of NaCl in the unit conversion factor.* Result: 0.072 mol NaCl
- *Determine the number of moles of ions present in the solution using the number of moles of ions in 1 mole of NaCl as the conversion factor (2 mol ions/1 mol NaCl).* Result: 0.14 mol ions
- *Determine the molality of the ions in the solution from the number of moles of ions and the mass of solvent, in kilograms.* Result: 1.1 *m*
- *Use the direct proportionality between the change in freezing point and molal concentration to determine how much the freezing point changes.* Result: 2.0 °C
- *Determine the new freezing point from the freezing point of the pure solvent and the change.* Result: −2.0 °C

Check each result as a self-assessment.

Exercise 7.4.13

Assume that each of the ions in calcium chloride, $CaCl_2$, has the same effect on the freezing point of water as a nonelectrolyte molecule. Calculate the freezing point of a solution of 0.724 g of $CaCl_2$ in 175 g of water.

Answer

−0.208 °C

Assuming complete dissociation, a 1.0 *m* aqueous solution of NaCl contains 2.0 mole of ions (1.0 mol Na^+ and 1.0 mol Cl^-) per each kilogram of water, and its freezing point depression is expected to be

$$\Delta T_f = 2.0 \text{ mol ions/kg water} \times 1.86 \text{ °C kg water/mol ion} = 3.7 \text{ °C}. \tag{7.4.7}$$

When this solution is actually prepared and its freezing point depression measured, however, a value of 3.4 °C is obtained. Similar discrepancies are observed for other ionic compounds, and the differences between the measured and expected colligative property values typically become more significant as solute concentrations increase. These observations suggest that the ions of sodium chloride (and other strong electrolytes) are not completely dissociated in solution.

To account for this and avoid the errors accompanying the assumption of total dissociation, an experimentally measured parameter named in honor of Nobel Prize-winning German chemist Jacobus Henricus van't Hoff is used. The van't Hoff factor (*i*) is defined as the ratio of solute particles in solution to the number of formula units dissolved:

$$i = \frac{\text{moles of particles in solution}}{\text{moles of formula units dissolved}} \tag{7.4.8}$$

Values for measured van't Hoff factors for several solutes, along with predicted values assuming complete dissociation, are shown in Table **7.4.2**.

***Table* 7.4.2**: *Expected and Observed van't Hoff Factors for Several 0.050 m Aqueous Electrolyte Solutions*

Electrolyte	Particles in Solution	*i* (Predicted)	*i* (Measured)
HCl	H^+, Cl^-	2	1.9
NaCl	Na^+, Cl^-	2	1.9
$MgSO_4$	Mg^{2+}, SO_4^{2-}	2	1.3
$MgCl_2$	Mg^{2+}, $2Cl^-$	3	2.7
$FeCl_3$	Fe^{3+}, $3Cl^-$	4	3.4
glucose (a non-electrolyte)	$C_{12}H_{22}O_{11}$	1	1.0

In 1923, the chemists Peter Debye and Erich Hückel proposed a theory to explain the apparent incomplete ionization of strong electrolytes. They suggested that although interionic attraction in an aqueous solution is very greatly reduced by solvation of the ions and the insulating action of the polar solvent, it is not completely nullified. The residual attractions prevent the ions from behaving as totally independent particles (Figure **7.4.9**). In some cases, a positive and negative ion may actually touch, giving a solvated unit called an ion pair. Thus, the activity, or the effective concentration, of any particular kind of ion is less than that indicated by the actual concentration. Ions become more and more widely separated the more dilute the solution, and the residual interionic attractions become less and less. Thus, in extremely dilute solutions, the effective concentrations of the ions (their activities) are essentially equal to the actual concentrations. Note that the van't Hoff factors for the electrolytes in Table **7.4.2** are for 0.05 *m* solutions, at which concentration the value of *i* for NaCl is 1.9, as opposed to an ideal value of 2.

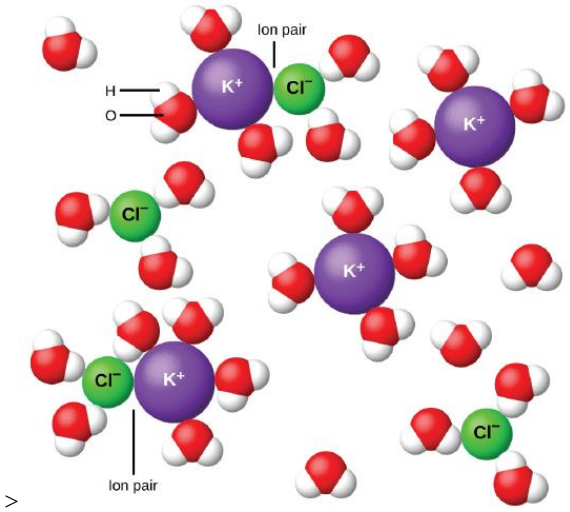


***Figure* 7.4.9:** *Ions become more and more widely separated the more dilute the solution, and the residual interionic attractions become less.*

Summary



***Video* 7.4.2:** *An overview of concentration units for solutions.*

In addition to molarity, a number of other solution concentration units are used in various applications. Percentage concentrations based on the solution components' masses, volumes, or both are useful for expressing relatively high concentrations, whereas lower concentrations are conveniently expressed using ppm or ppb units. These units are popular in environmental, medical, and other fields where mole-based units such as molarity are not as commonly used.

Properties of a solution that depend only on the concentration of solute particles are called colligative properties. They include changes in the vapor pressure, boiling point, and freezing point of the solvent in the solution. The magnitudes of these properties depend only on the total concentration of solute particles in solution, not on the type of particles. Ionic compounds may not completely dissociate in solution due to activity effects, in which case observed colligative effects may be less than predicted.

Key Equations

- $\Delta T_b = K_b m$
- $\Delta T_f = K_f m$
- $\Pi = MRT$

Footnotes

1. A nonelectrolyte shown for comparison.

Glossary

mass percentage
ratio of solute-to-solution mass expressed as a percentage

mass-volume percent
ratio of solute mass to solution volume, expressed as a percentage

parts per billion (ppb)
ratio of solute-to-solution mass multiplied by 10^9

parts per million (ppm)
ratio of solute-to-solution mass multiplied by 10^6

volume percentage
ratio of solute-to-solution volume expressed as a percentage

boiling point elevation
elevation of the boiling point of a liquid by addition of a solute

boiling point elevation constant
the proportionality constant in the equation relating boiling point elevation to solute molality; also known as the ebullioscopic constant

colligative property
property of a solution that depends only on the concentration of a solute species

freezing point depression
lowering of the freezing point of a liquid by addition of a solute

freezing point depression constant
(also, cryoscopic constant) proportionality constant in the equation relating freezing point depression to solute molality

ion pair
solvated anion/cation pair held together by moderate electrostatic attraction

molality (*m*)
a concentration unit defined as the ratio of the numbers of moles of solute to the mass of the solvent in kilograms

van't Hoff factor (*i*)
the ratio of the number of moles of particles in a solution to the number of moles of formula units dissolved in the solution

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7.4.1: Concentrations of Solutions (Problems)

PROBLEM 7.4.1.1

What mass of a concentrated solution of nitric acid (68.0% HNO_3 by mass) is needed to prepare 400.0 g of a 10.0% solution of HNO_3 by mass?

Answer

58.8 g

PROBLEM 7.4.1.2

What mass of a 4.00% NaOH solution by mass contains 15.0 g of NaOH?

Answer

375 g

Click here to see a video of the solution



PROBLEM 7.4.1.3

What mass of solid NaOH (97.0% NaOH by mass) is required to prepare 1.00 L of a 10.0% solution of NaOH by mass? The density of the 10.0% solution is 1.109 g/mL.

Answer

114 g

PROBLEM 7.4.1.4

The hardness of water (hardness count) is usually expressed in parts per million (by mass) of $\mathbf{CaCO_3}$, which is equivalent to milligrams of $\mathbf{CaCO_3}$ per liter of water. What is the molar concentration of Ca^{2+} ions in a water sample with a hardness count of 175 mg $CaCO_3$/L?

Answer

$\mathbf{1.75\times 10^{-3}}M$

PROBLEM 7.4.1.5

A throat spray is 1.40% by mass phenol, $\mathbf{C_6H_5OH}$, in water. If the solution has a density of 0.9956 g/mL, calculate the molarity of the solution.

Answer

0.148 M

Click here to see a video of the solution



PROBLEM 7.4.1.6

Copper(I) iodide (CuI) is often added to table salt as a dietary source of iodine. How many moles of CuI are contained in 1.00 lb (454 g) of table salt containing 0.0100% CuI by mass?

Answer

2.38×10^{-4} mol

PROBLEM 7.4.1.7

What are the mole fractions of H_3PO_4 and water in a solution of 14.5 g of H_3PO_4 in 125 g of water?

Answer

$X_{H_3PO_4} = 0.021$

$X_{H_2O} = 0.979$

Click here to see a video of the solution



PROBLEM 7.4.1.8

What are the mole fractions of HNO_3 and water in a concentrated solution of nitric acid (68.0% HNO_3 by mass)?

Answer

$X_{HNO_3} = 0.378$

$X_{H_2O} = 0.622$

PROBLEM 7.4.1.9

Calculate the mole fraction of each solute and solvent:

a. 583 g of H_2SO_4 in 1.50 kg of water—the acid solution used in an automobile battery
b. 0.86 g of NaCl in 1.00×10^2 g of water—a solution of sodium chloride for intravenous injection
c. 46.85 g of codeine, $C_{18}H_{21}NO_3$, in 125.5 g of ethanol, C_2H_5OH
d. 25 g of I_2 in 125 g of ethanol, C_2H_5OH

Answer a

$X_{H_2SO_4} = 0.067$

$X_{H_2O} = 0.933$

Answer b

$X_{HCl} = 0.0026$

$X_{H_2O} = 0.9974$

Answer c

$X_{codiene} = 0.054$

$X_{EtOH} = 0.946$

Answer d

$X_{I_2} = 0.035$

$X_{EtOH} = 0.965$

Click here to see a video of the solution



PROBLEM 7.4.1.10

Calculate the mole fraction of each solute and solvent:

a. 0.710 kg of sodium carbonate (washing soda), Na_2CO_3, in 10.0 kg of water—a saturated solution at 0 °C
b. 125 g of NH_4NO_3 in 275 g of water—a mixture used to make an instant ice pack
c. 25 g of Cl_2 in 125 g of dichloromethane, CH_2Cl_2
d. 0.372 g of histamine, C_5H_9N, in 125 g of chloroform, $CHCl_3$

Answer a

$X_{Na_2CO_3} = 0.0119$

$X_{H_2O} = 0.988$

Answer b

$X_{NH_4NO_3} = 0.09927$

$X_{H_2O} = 0.907$

Answer c

$X_{Cl_2} = 0.192$

$X_{CH_2Cl_2} = 0.808$

Answer d

$X_{C_5H_9N} = 0.00426$

$X_{CHCl_3} = 0.997$

PROBLEM 7.4.1.11

What is the difference between a 1 *M* solution and a 1 *m* solution?

Answer

In a 1 *M* solution, the mole is contained in exactly 1 L of solution. In a 1 *m* solution, the mole is contained in exactly 1 kg of solvent.

PROBLEM 7.4.1.12

What is the molality of phosphoric acid, H_3PO_4, in a solution of 14.5 g of H_3PO_4 in 125 g of water?

Answer

1.18 *m*

PROBLEM 7.4.1.13

What is the molality of nitric acid in a concentrated solution of nitric acid (68.0% HNO_3 by mass)?

Answer

33.7 *m*

PROBLEM 7.4.1.14

Calculate the molality of each of the following solutions:

a. 0.710 kg of sodium carbonate (washing soda), Na_2CO_3, in 10.0 kg of water—a saturated solution at 0°C
b. 125 g of NH_4NO_3 in 275 g of water—a mixture used to make an instant ice pack
c. 25 g of Cl_2 in 125 g of dichloromethane, CH_2Cl_2
d. 0.372 g of histamine, C_5H_9N, in 125 g of chloroform, $CHCl_3$

Answer

6.70×10^{-1} *m*

Answer

5.67 *m*

Answer

2.8 *m*

Answer

0.0358 *m*

PROBLEM 7.4.1.15

A 13.0% solution of K_2CO_3 by mass has a density of 1.09 g/cm^3. Calculate the molality of the solution.

Answer

1.08 *m*

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- Adelaide Clark, Oregon Institute of Technology

Feedback

Think one of the answers above is wrong? Let us know here.

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CHAPTER OVERVIEW

8: Crash Course on Kinetics, Equilibrium and Thermodynamics

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8.4: Collision Theory (Kinetics)
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8.6: Equilibrium Constants
8.7: Shifting Equilibria - Le Chatelier’s Principle
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8.1: Introduction

A Crash Course of Kinetics, Equilbrum and Thermodynamics

This unit was custom built for Oregon Tech PDX - Metro students. These three topics are central to general chemistry and are used extensively in many other fields, including engineering. Before the OT engineering students go off into their programs, it is important for them to have basic concepts of these three topics. Usually, these subjects are presented in their own unit and take a week to cover each! This crash course will cover the general concepts of kinetics, equilibrium, and thermodynamics, so that students have a basic understanding when they enter their upper division courses. Students that take General Chemistry III will learn this content in much more detail and for those students that plan to take organic chemistry next year, a strong understanding of these three subjects is imperative.

While these three topics are related, they are independent concepts and models. It is very important to distinguish between the three topics.

Kinetics (rates)

From baking a cake to determining the useful lifespan of a bridge, rates of chemical reactions play important roles in our understanding of processes that involve chemical changes. When planning to run a chemical reaction, we should ask at least two questions. The first is: “Will the reaction produce the desired products in useful quantities?” The second question is: “How rapidly will the reaction occur?” A reaction that takes 50 years to produce a product is about as useful as one that never gives a product at all. A third question is often asked when investigating reactions in greater detail: “What specific molecular-level processes take place as the reaction occurs?” Knowing the answer to this question is of practical importance when the yield or rate of a reaction needs to be controlled.

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

Equilibrium

Imagine a beach populated with sunbathers and swimmers. As those basking in the sun get too hot and want to cool off, they head into the surf to swim. As the swimmers tire, they head to the beach to rest. If these two rates of transfer (sunbathers entering the water, swimmers leaving the water) are equal, the number of sunbathers and swimmers would be constant, or at equilibrium, although the identities of the people are constantly changing from sunbather to swimmer and back. An analogous situation occurs in chemical reactions. Reactions can occur in both directions simultaneously (reactants to products and products to reactants) and eventually reach a state of balance.

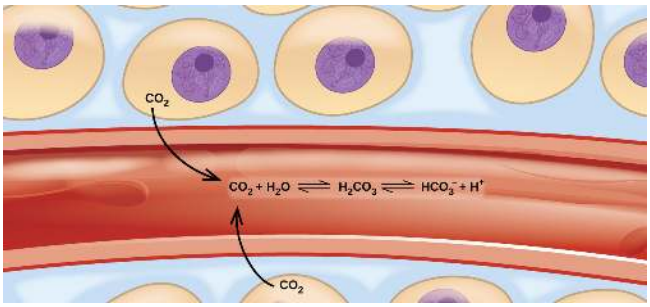


Figure **8.1.1**: Movement of carbon dioxide through tissues and blood cells involves several equilibrium reactions.

These balanced two-way reactions occur all around and even in us. For example, they occur in our blood, where the reaction between carbon dioxide and water forms carbonic acid (HCO−3)(HCO3−) (Figure 13.0.113.0.1). Human physiology is adapted to the amount of ionized products produced by this reaction (HCO−3HCO3− and H^+). In this chapter, you will learn how to predict the position of the balance and the yield of a product of a reaction under specific conditions, how to change a reaction's conditions to increase or reduce yield, and how to evaluate an equilibrium system's reaction to disturbances

Thermodynamics

Among the many capabilities of chemistry is its ability to predict if a process will occur under specified conditions. Thermodynamics, the study of relationships between the energy and work associated with chemical and physical processes, provides this predictive ability. Previous chapters in this text have described various applications of thermochemistry, an important aspect of thermodynamics concerned with the heat flow accompanying chemical reactions and phase transitions. This chapter will introduce additional thermodynamic concepts, including those that enable the prediction of any chemical or physical changes under a given set of conditions.

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8.2: Chemical Reaction Rates (Kinetics)

Learning Objectives

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

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

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

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

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

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

$$\begin{aligned}\text{rate of decomposition of } H_2O_2 &= -\frac{\text{change in concentration of reactant}}{\text{time interval}} \\ &= -\frac{[H_2O_2]_{t_2} - [H_2O_2]_{t_1}}{t_2 - t_1} \\ &= -\frac{\Delta[H_2O_2]}{\Delta t}\end{aligned}$$

This mathematical representation of the change in species concentration over time is the rate expression for the reaction. The brackets indicate molar concentrations, and the symbol delta (Δ) indicates "change in." Thus, $[H_2O_2]_{t_1}$ represents the molar concentration of hydrogen peroxide at some time t_1; likewise, $[H_2O_2]_{t_2}$ represents the molar concentration of hydrogen peroxide at a later time t_2; and $\Delta[H_2O_2]$ represents the change in molar concentration of hydrogen peroxide during the time interval Δt (that is, $t_2 - t_1$). Since the reactant concentration decreases as the reaction proceeds, $\Delta[H_2O_2]$ is a negative quantity; we place a negative sign in front of the expression because reaction rates are, by convention, positive quantities. Figure **8.2.1** provides an example of data collected during the decomposition of H_2O_2.

Time (h)	$[H_2O_2]$ (mol L^{-1})	$\Delta[H_2O_2]$ (mol L^{-1})	Δt (h)	Rate of Decomposition, (mol/L/h)
0.00	1.000			
		−0.500	6.00	−0.0833
6.00	0.500			
		−0.250	6.00	−0.0417
12.00	0.250			
		−0.125	6.00	−0.0208
18.00	0.125			
		−0.062	6.00	−0.0103
24.00	0.0625			

Figure **8.2.1**: The rate of decomposition of H_2O_2 in an aqueous solution decreases as the concentration of H_2O_2 decreases.

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

$$\frac{-\Delta[H_2O_2]}{\Delta t} = \frac{-(0.500\ \text{mol/L} - 1.000\ \text{mol/L})}{(6.00\ \text{h} - 0.00\ \text{h})} = 0.0833\ \text{mol L}^{-1}\ \text{h}^{-1} \tag{8.2.1}$$

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

$$\frac{-\Delta[H_2O_2]}{\Delta t} = \frac{-(0.0625\ \text{mol/L} - 0.125\ \text{mol/L})}{(24.00\ \text{h} - 18.00\ \text{h})} = 0.0104\ \text{mol L}^{-1}\ \text{h}^{-1} \tag{8.2.2}$$

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

The instantaneous rate of a reaction may be determined one of two ways. If experimental conditions permit the measurement of concentration changes over very short time intervals, then average rates computed as described earlier provide reasonably good approximations of instantaneous rates. Alternatively, a graphical procedure may be used that, in effect, yields the results that would be obtained if short time interval measurements were possible. If we plot the concentration of hydrogen peroxide against time, the instantaneous rate of decomposition of H_2O_2 at any time t is given by the slope of a straight line that is tangent to the curve at that time (Figure 8.2.2). We can use calculus to evaluating the slopes of such tangent lines, but the procedure for doing so is beyond the scope of this chapter.

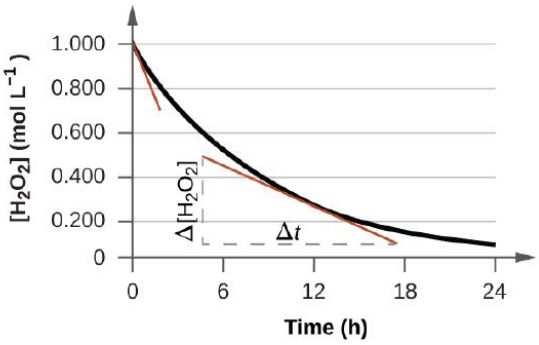


Figure 8.2.1: This graph shows a plot of concentration versus time for a 1.000 M solution of H_2O_2. The rate at any instant is equal to the opposite of the slope of a line tangential to this curve at that time. Tangents are shown at t = 0 h ("initial rate") and at t = 10 h ("instantaneous rate" at that particular time).

Reaction Rates in Analysis: Test Strips for Urinalysis

Physicians often use disposable test strips to measure the amounts of various substances in a patient's urine (Figure 8.2.2). These test strips contain various chemical reagents, embedded in small pads at various locations along the strip, which undergo changes in color upon exposure to sufficient concentrations of specific substances. The usage instructions for test strips often stress that proper read time is critical for optimal results. This emphasis on read time suggests that kinetic aspects of the chemical reactions occurring on the test strip are important considerations.

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

$$C_6H_{12}O_6 + O_2 \xrightarrow[\text{catalyst}]{} C_6H_{10}O_6 + H_2O_2 \tag{8.2.3}$$

$$2\,H_2O_2 + 2\,I^- \xrightarrow[\text{catalyst}]{} I_2 + 2\,H_2O + O_2 \tag{8.2.4}$$

Equation 8.2.3 depicts the oxidation of glucose in the urine to yield glucolactone and hydrogen peroxide. The hydrogen peroxide produced subsequently oxidizes colorless iodide ion to yield brown iodine (Equation 8.2.4), which may be visually detected. Some strips include an additional substance that reacts with iodine to produce a more distinct color change.

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



Figure 8.2.2: Test strips are commonly used to detect the presence of specific substances in a person's urine. Many test strips have several pads containing various reagents to permit the detection of multiple substances on a single strip. (credit: Iqbal Osman).

Relative Rates of Reaction

The rate of a reaction may be expressed in terms of the change in the amount of any reactant or product, and may be simply derived from the stoichiometry of the reaction. Consider the reaction represented by the following equation:

$$2\,NH_3(g) \longrightarrow N_2(g) + 3\,H_2(g) \tag{8.2.5}$$

The stoichiometric factors derived from this equation may be used to relate reaction rates in the same manner that they are used to related reactant and product amounts. The relation between the reaction rates expressed in terms of nitrogen production and ammonia consumption, for example, is:

$$-\frac{\Delta \text{mol } NH_3}{\Delta t} \times \frac{1 \text{ mol } N_2}{2 \text{ mol } NH_3} = \frac{\Delta \text{mol } N_2}{\Delta t} \tag{8.2.6}$$

We can express this more simply without showing the stoichiometric factor's units:

$$-\frac{1}{2}\frac{\Delta \text{mol } NH_3}{\Delta t} = \frac{\Delta \text{mol } N_2}{\Delta t} \tag{8.2.7}$$

Note that a negative sign has been added to account for the opposite signs of the two amount changes (the reactant amount is decreasing while the product amount is increasing). If the reactants and products are present in the same solution, the molar amounts may be replaced by concentrations:

$$-\frac{1}{2}\frac{\Delta[NH_3]}{\Delta t} = \frac{\Delta[N_2]}{\Delta t} \tag{8.2.8}$$

Similarly, the rate of formation of H_2 is three times the rate of formation of N_2 because three moles of H_2 form during the time required for the formation of one mole of N_2:

$$\frac{1}{3}\frac{\Delta[H_2]}{\Delta t} = \frac{\Delta[N_2]}{\Delta t} \tag{8.2.9}$$

Figure 8.2.3 illustrates the change in concentrations over time for the decomposition of ammonia into nitrogen and hydrogen at 1100 °C. We can see from the slopes of the tangents drawn at t = 500 seconds that the instantaneous rates of change in the concentrations of the reactants and products are related by their stoichiometric factors. The rate of hydrogen production, for example, is observed to be three times greater than that for nitrogen production:

$$\frac{2.91 \times 10^{-6}\ M/\text{s}}{9.71 \times 10^{-6}\ M/\text{s}} \approx 3 \tag{8.2.10}$$

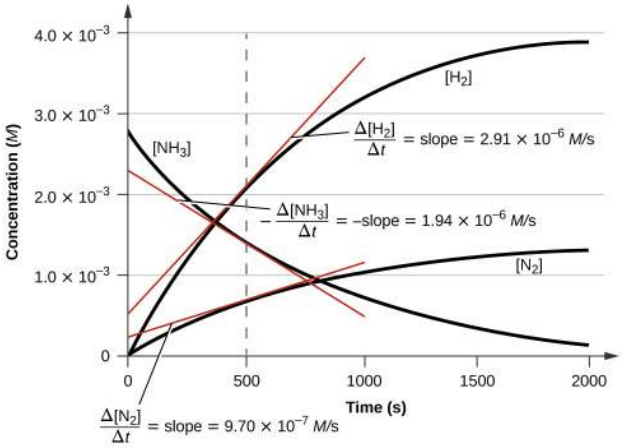


Figure 8.2.3: This graph shows the changes in concentrations of the reactants and products during the reaction $2\,NH_3 \longrightarrow N_2 + 3\,H_2$. *The rates of change of the three concentrations are related by their stoichiometric factors, as shown by the different slopes of the tangents at t = 500 s.*

Example 8.2.1: Expressions for Relative Reaction Rates

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

$$4\,NH_3(g) + 5\,O_2(g) \longrightarrow 4\,NO(g) + 6\,H_2O(g)$$

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

Solution

Considering the stoichiometry of this homogeneous reaction, the rates for the consumption of reactants and formation of products are:

$$-\frac{1}{4}\frac{\Delta[NH_3]}{\Delta t} = -\frac{1}{5}\frac{\Delta[O_2]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO]}{\Delta t} = \frac{1}{6}\frac{\Delta[H_2O]}{\Delta t}$$

Exercise 8.2.1

The rate of formation of Br_2 is 6.0×10^{-6} mol/L/s in a reaction described by the following net ionic equation:

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

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

Answer

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

Example 8.2.2: Reaction Rate Expressions for Decomposition of H_2O_2

The graph in Figure 8.2.3 shows the rate of the decomposition of H_2O_2 over time:

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

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

$$-\frac{\Delta[H_2O_2]}{\Delta t} = 3.20 \times 10^{-2}\ \text{mol}\ \text{L}^{-1}\ \text{h}^{-1}$$

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

Solution

Using the stoichiometry of the reaction, we may determine that:

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

Therefore:

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

and

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

Exercise 8.2.2

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

Answer

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

Contributors and Attributions

Summary

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

Glossary

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

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

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

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

rate expression

mathematical representation relating reaction rate to changes in amount, concentration, or pressure of reactant or product species per unit time

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8.3: Factors Affecting Reaction Rates (Kinetics)

Learning Objectives

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

The rates at which reactants are consumed and products are formed during chemical reactions vary greatly. We can identify five factors that affect the rates of chemical reactions: the chemical nature of the reacting substances, the state of subdivision (one large lump versus many small particles) of the reactants, the temperature of the reactants, the concentration of the reactants, and the presence of a catalyst.

The Chemical Nature of the Reacting Substances

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

The State of Subdivision of the Reactants

Except for substances in the gaseous state or in solution, reactions occur at the boundary, or interface, between two phases. Hence, the rate of a reaction between two phases depends to a great extent on the surface contact between them. A finely divided solid has more surface area available for reaction than does one large piece of the same substance. Thus a liquid will react more rapidly with a finely divided solid than with a large piece of the same solid. For example, large pieces of iron react slowly with acids; finely divided iron reacts much more rapidly (Figure **8.3.1**). Large pieces of wood smolder, smaller pieces burn rapidly, and saw dust burns explosively.



Figure **8.3.1**: (a) Iron powder reacts rapidly with dilute hydrochloric acid and produces bubbles of hydrogen gas because the powder has a large total area: 2Fe(s) + 6HCl(aq) ⟶ 2FeCl3(aq) + 3H2(g). (surfaceb) An iron nail reacts more slowly.

This figure shows two photos labeled (a) and (b). Photo (a) shows the bottom of a test tube. The test tube is filled with a dark gas, and there is a dark substance and bubbles in the bottom. Photo (b) shows a rod and bubbles in a test tube similar to photo (a), but the gas in the test tube is not as dark.



Video* 8.3.1: The reaction of cesium with water in slow motion and a discussion of how the state of reactants and particle size affect reaction rates.*

Temperature of the Reactants

Chemical reactions typically occur faster at higher temperatures. Food can spoil quickly when left on the kitchen counter. However, the lower temperature inside of a refrigerator slows that process so that the same food remains fresh for days. We use a burner or a hot plate in the laboratory to increase the speed of reactions that proceed slowly at ordinary temperatures. In many cases, an increase in temperature of only 10 °C will approximately double the rate of a reaction in a homogeneous system.

Concentrations of the Reactants

The rates of many reactions depend on the concentrations of the reactants. Rates usually increase when the concentration of one or more of the reactants increases. For example, calcium carbonate ($\mathbf{CaCO_3}$) deteriorates as a result of its reaction with the pollutant sulfur dioxide. The rate of this reaction depends on the amount of sulfur dioxide in the air (Figure **8.3.2**). As an acidic oxide, sulfur dioxide combines with water vapor in the air to produce sulfurous acid in the following reaction:

$$\mathbf{SO_{2(g)} + H_2O_{(g)} \longrightarrow H_2SO_{3(aq)}} \tag{8.3.1}$$

Calcium carbonate reacts with sulfurous acid as follows:

$$\mathbf{CaCO_{3(s)} + H_2SO_{3(aq)} \longrightarrow CaSO_{3(aq)} + CO_{2(g)} + H_2O_{(l)}} \tag{8.3.2}$$

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

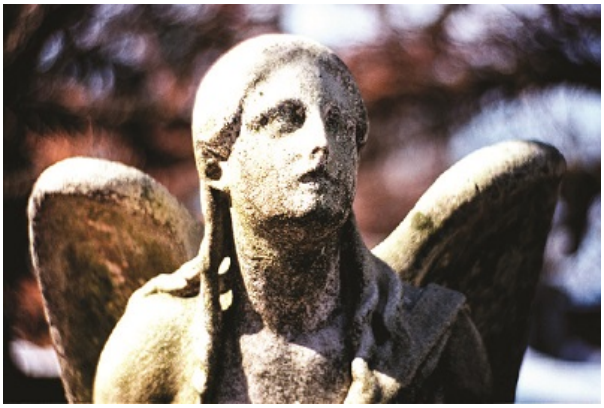


Figure **8.3.2**: Statues made from carbonate compounds such as limestone and marble typically weather slowly over time due to the actions of water, and thermal expansion and contraction. However, pollutants like sulfur dioxide can accelerate weathering. As the concentration of air pollutants increases, deterioration of limestone occurs more rapidly. (credit: James P Fisher III).

A photograph is shown of an angel statue. While some details of the statue, including facial features, are present, effects of weathering appear to be diminishing these features.



***Video* 8.3.2**: *Phosphorous burns rapidly in air, but it will burn even more rapidly if the concentration of oxygen in is higher.*

The Presence of a Catalyst

Hydrogen peroxide solutions foam when poured onto an open wound because substances in the exposed tissues act as catalysts, increasing the rate of hydrogen peroxide's decomposition. However, in the absence of these catalysts (for example, in the bottle in the medicine cabinet) complete decomposition can take months. A catalyst is a substance that increases the rate of a chemical reaction by lowering the activation energy without itself being consumed by the reaction. Activation energy is the minimum amount of energy required for a chemical reaction to proceed in the forward direction. A catalyst increases the reaction rate by providing an alternative pathway or mechanism for the reaction to follow (Figure **8.3.3**). Catalysis will be discussed in greater detail later in this chapter as it relates to mechanisms of reactions.

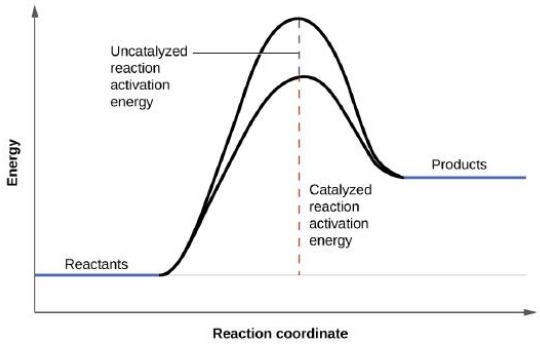


Figure **8.3.3**: The presence of a catalyst increases the rate of a reaction by lowering its activation energy.

A graph is shown with the label, "Reaction coordinate," on the x-axis. The x-axis is depicted as an arrow. The y-axis is also an arrow and is labeled, "Energy." There is a horizontal line that runs the width of the graph and appears just above the x-axis. A segment of this line is blue and is labeled, "Reactants." From the right end of this line segment, a solid black, concave down curve is shown which reaches the level just below the end of the y-axis. The curve ends at another short, blue line labeled, "Products." The "Products" line appears at a higher level than the "Reactants" line. An arrow extends from the horizontal line to the apex of the curve. The arrow is labeled, "Uncatalyzed reaction activation energy." A second, black concave down curve is shown. This curve also meets the reactants and products blue line segments, but only extends to about two-thirds the height of the initial curve. From the horizontal line is another arrow pointing to the apex of the second curve. This arrow is labeled, "Catalyzed reaction activation energy."

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

Summary

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

Glossary

catalyst

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

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8.4: Collision Theory (Kinetics)

Learning Objectives

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

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

Postulates of Collision theory

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

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

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

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

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

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

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

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

Although there are many different possible orientations the two molecules can have relative to each other, consider the two presented in Figure 8.4.1. In the first case, the oxygen side of the carbon monoxide molecule collides with the oxygen molecule. In the second case, the carbon side of the carbon monoxide molecule collides with the oxygen molecule. The second case is clearly more likely to result in the formation of carbon dioxide, which has a central carbon atom bonded to two oxygen atoms (O=C=O). This is a rather simple example of how important the orientation of the collision is in terms of creating the desired product of the reaction.

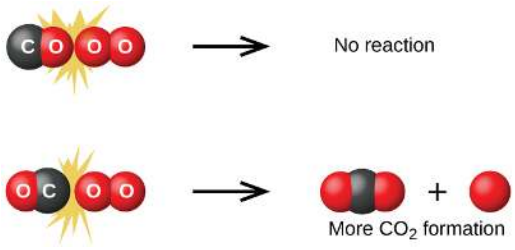


Figure 8.4.1: Illustrated are two collisions that might take place between carbon monoxide and oxygen molecules. The orientation of the colliding molecules partially determines whether a reaction between the two molecules will occur.

If the collision does take place with the correct orientation, there is still no guarantee that the reaction will proceed to form carbon dioxide. Every reaction requires a certain amount of activation energy for it to proceed in the forward direction, yielding an appropriate activated complex along the way. As Figure **8.4.2** demonstrates, even a collision with the correct orientation can fail to form the reaction product. In the study of reaction mechanisms, each of these three arrangements of atoms is called a proposed activated complex or transition state.

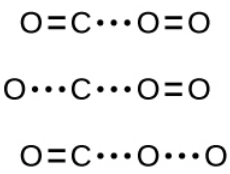


Figure **8.4.2**: Possible transition states (activated complexes) for carbon monoxide reacting with oxygen to form carbon dioxide. Solid lines represent covalent bonds, while dotted lines represent unstable orbital overlaps that may, or may not, become covalent bonds as product is formed. In the first two examples in this figure, the O=O double bond is not impacted; therefore, carbon dioxide cannot form. The third proposed transition state will result in the formation of carbon dioxide if the third "extra" oxygen atom separates from the rest of the molecule.

In most circumstances, it is impossible to isolate or identify a transition state or activated complex. In the reaction between carbon monoxide and oxygen to form carbon dioxide, activated complexes have only been observed spectroscopically in systems that utilize a heterogeneous catalyst. The gas-phase reaction occurs too rapidly to isolate any such chemical compound.

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

Activation Energy and the Arrhenius Equation

The minimum energy necessary to form a product during a collision between reactants is called the activation energy (E_a). The kinetic energy of reactant molecules plays an important role in a reaction because the energy necessary to form a product is provided by a collision of a reactant molecule with another reactant molecule. (In single-reactant reactions, activation energy may be provided by a collision of the reactant molecule with the wall of the reaction vessel or with molecules of an inert contaminant.) If the activation energy is much larger than the average kinetic energy of the molecules, the reaction will occur slowly: Only a few fast-moving molecules will have enough energy to react. If the activation energy is much smaller than the average kinetic energy of the molecules, the fraction of molecules possessing the necessary kinetic energy will be large; most collisions between molecules will result in reaction, and the reaction will occur rapidly.

Figure **8.4.3** shows the energy relationships for the general reaction of a molecule of A with a molecule of B to form molecules of C and D:

$$A + B \longrightarrow C + D$$

The figure shows that the energy of the transition state is higher than that of the reactants A and B by an amount equal to E_a, the activation energy. Thus, the sum of the kinetic energies of A and B must be **equal to or greater** than E_a to reach the transition state. After the transition state has been reached, and as C and D begin to form, the system loses energy until its total energy is lower than that of the initial mixture. This lost energy is transferred to other molecules, giving them enough energy to reach the transition state. The forward reaction (that between molecules A and B) therefore tends to take place readily once the reaction has started. In Figure **8.4.3**, ΔH represents the difference in enthalpy between the reactants (A and B) and the products (C and D). The sum of E_a and ΔH represents the activation energy for the reverse reaction:

$$C + D \longrightarrow A + B$$

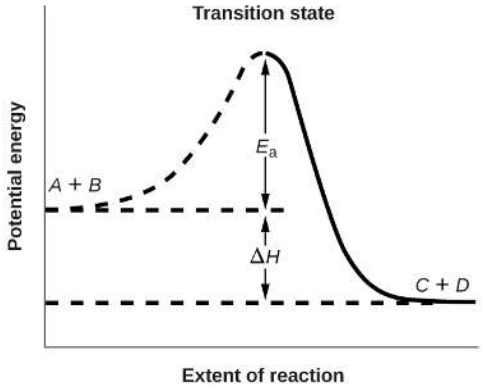


Figure **8.4.3**: This graph shows the potential energy relationships for the reaction $A + B \longrightarrow C + D$. The dashed portion of the curve represents the energy of the system with a molecule of A and a molecule of B present, and the solid portion the energy of the system with a molecule of C and a molecule of D present. The activation energy for the forward reaction is represented by E_a. The activation energy for the reverse reaction is greater than that for the forward reaction by an amount equal to ΔH. The curve's peak represents the transition state.

We can use the Arrhenius equation to relate the activation energy and the rate constant, *k*, of a given reaction:

$$k = Ae^{-E_a/RT} \tag{8.4.1}$$

In this equation,

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

Both postulates of the collision theory of reaction rates are accommodated in the Arrhenius equation. The frequency factor *A* is related to the rate at which collisions having the correct *orientation* occur. The exponential term, $e^{-E_a/RT}$, is related to the fraction of collisions providing adequate *energy* to overcome the activation barrier of the reaction.

At one extreme, the system does not contain enough energy for collisions to overcome the activation barrier. In such cases, no reaction occurs. At the other extreme, the system has so much energy that every collision with the correct orientation can overcome the activation barrier, causing the reaction to proceed. In such cases, the reaction is nearly instantaneous.

The Arrhenius equation (Equation 8.4.1) describes quantitatively much of what we have already discussed about reaction rates. For two reactions at the same temperature, the reaction with the higher activation energy has the lower rate constant and the slower rate. The larger value of E_a results in a smaller value for $e^{-E_a/RT}$, reflecting the smaller fraction of molecules with enough energy to react. Alternatively, the reaction with the smaller E_a has a larger fraction of molecules with enough energy to react. This will be reflected as a larger value of $e^{-E_a/RT}$, a larger rate constant, and a faster rate for the reaction.

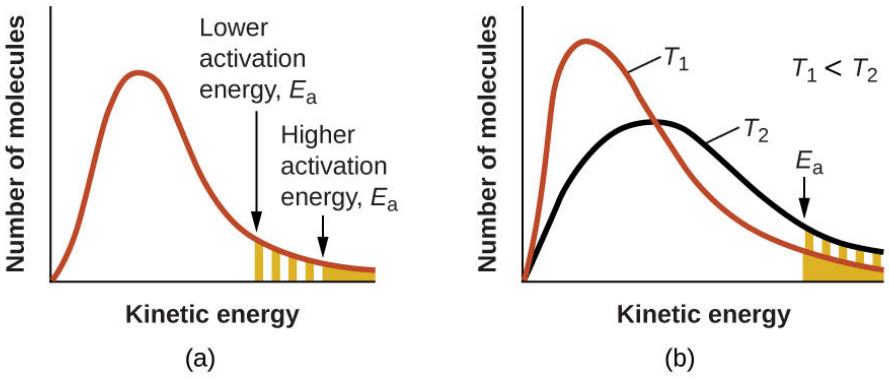


Figure 8.4.4: (a) As the activation energy of a reaction decreases, the number of molecules with at least this much energy increases, as shown by the shaded areas. (b) At a higher temperature, T2, more molecules have kinetic energies greater than Ea, as shown by the yellow shaded area.

An increase in temperature has the same effect as a decrease in activation energy. A larger fraction of molecules has the necessary energy to react (Figure 8.4.4), as indicated by an increase in the value of $e^{-E_a/RT}$. The rate constant is also directly proportional to the frequency factor, A. Hence a change in conditions or reactants that increases the number of collisions with a favorable orientation for reaction results in an increase in A and, consequently, an increase in k.

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

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

Thus, a plot of $\ln k$ versus $\frac{1}{T}$ gives a straight line with the slope $\frac{-E_a}{R}$, from which E_a may be determined. The intercept gives the value of $\ln A$. This is sometimes call an Arrhenius Plot.

Example 8.4.1

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

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

variation of the rate constant with temperature for the decomposition of HI(g) to H2(g) and I2(g)

T (K)	k (L/mol/s)
555	3.52×10^{-7}
575	1.22×10^{-6}
645	8.59×10^{-5}
700	1.16×10^{-3}
781	3.95×10^{-2}

Solution

Values of $\frac{1}{T}$ and ln k are:

Solutions to Example 12.5.1

$\frac{1}{T}$ (K^{-1})	ln k
1.80×10^{-3}	−14.860
1.74×10^{-3}	−13.617
1.55×10^{-3}	−9.362
1.43×10^{-3}	−6.759
1.28×10^{-3}	−3.231

Figure 8.4.5 is a graph of ln k versus $\frac{1}{T}$. To determine the slope of the line, we need two values of ln k, which are determined from the line at two values of $\frac{1}{T}$ (one near each end of the line is preferable). For example, the value of ln k determined from the line when $\frac{1}{T} = 1.25 \times 10^{-3}$ is −2.593; the value when $\frac{1}{T} = 1.78 \times 10^{-3}$ is −14.447.

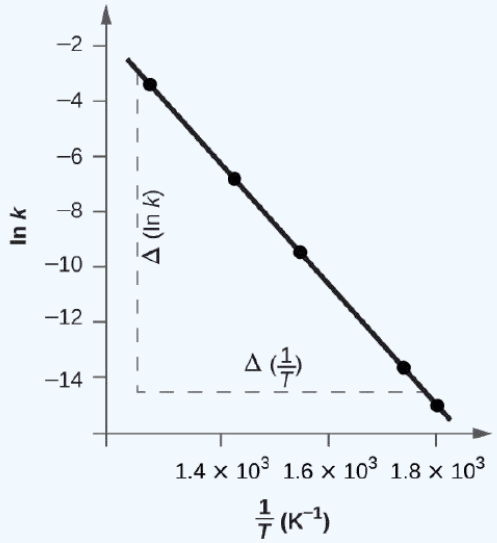


Figure 8.4.5: This graph shows the linear relationship between $\ln k$ and $\frac{1}{T}$ for the reaction $2\,HI \longrightarrow H_2 + I_2$ according to the Arrhenius equation.

The slope of this line is given by the following expression:

$$\begin{aligned} \text{Slope} &= \frac{\Delta(\ln k)}{\Delta\left(\frac{1}{T}\right)} \\ &= \frac{(-14.447) - (-2.593)}{(1.78 \times 10^{-3}\ \text{K}^{-1}) - (1.25 \times 10^{-3}\ \text{K}^{-1})} \\ &= \frac{-11.854}{0.53 \times 10^{-3}\ \text{K}^{-1}} = 2.2 \times 10^{4}\ \text{K} \\ &= -\frac{E_a}{R} \end{aligned}$$

Thus:

$$\begin{aligned} E_a &= -\text{slope} \times R = -(-2.2 \times 10^{4}\ \text{K} \times 8.314\ \text{J mol}^{-1}\ \text{K}^{-1}) \\ &= 1.8 \times 10^{5}\ \text{J mol}^{-1} \end{aligned}$$

In many situations, it is possible to obtain a reasonable estimate of the activation energy without going through the entire process of constructing the Arrhenius plot. The Arrhenius equation:

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

can be rearranged as shown to give:

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

or

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

This equation can be rearranged to give a one-step calculation to obtain an estimate for the activation energy:

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

Using the experimental data presented here, we can simply select two data entries. For this example, we select the first entry and the last entry:

First and Last Entry

T (K)	k (L/mol/s)	$\frac{1}{T}$ (K^{-1})	ln k
555	3.52×10^{-7}	1.80×10^{-3}	−14.860
781	3.95×10^{-2}	1.28×10^{-3}	−3.231

After calculating $\frac{1}{T}$ and ln *k*, we can substitute into the equation:

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

and the result is E_a = 185,900 J/mol.

This method is very effective, especially when a limited number of temperature-dependent rate constants are available for the reaction of interest.

? Exercise 8.4.1

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

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

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

Answer

113,000 J/mol

Summary

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

Key Equations

- $k = Ae^{-E_a/RT}$
- $\ln k = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A$
- $\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

Glossary

activated complex

(also, transition state) unstable combination of reactant species representing the highest energy state of a reaction system

activation energy (E_a)

energy necessary in order for a reaction to take place

Arrhenius equation

mathematical relationship between the rate constant and the activation energy of a reaction

collision theory

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

frequency factor (A)

proportionality constant in the Arrhenius equation, related to the relative number of collisions having an orientation capable of leading to product formation

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8.5: Chemical Equilibria

Learning Objectives

- Describe the nature of equilibrium systems
- Explain the dynamic nature of a chemical equilibrium

A chemical reaction is usually written in a way that suggests it proceeds in one direction, the direction in which we read, but all chemical reactions are reversible, and both the forward and reverse reaction occur to one degree or another depending on conditions. In a chemical equilibrium, the forward and reverse reactions occur at equal rates, and the concentrations of products and reactants remain constant. If we run a reaction in a closed system so that the products cannot escape, we often find the reaction does not give a 100% yield of products. Instead, some reactants remain after the concentrations stop changing. At this point, when there is no further change in concentrations of reactants and products, we say the reaction is at equilibrium. A mixture of reactants and products is found at equilibrium.

For example, when we place a sample of dinitrogen tetroxide (N_2O_4, a colorless gas) in a glass tube, it forms nitrogen dioxide (NO_2, a brown gas) by the reaction

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \tag{8.5.1}$$

The color becomes darker as N_2O_4 is converted to NO_2. When the system reaches equilibrium, both N_2O_4 and NO_2 are present (Figure 8.5.1).

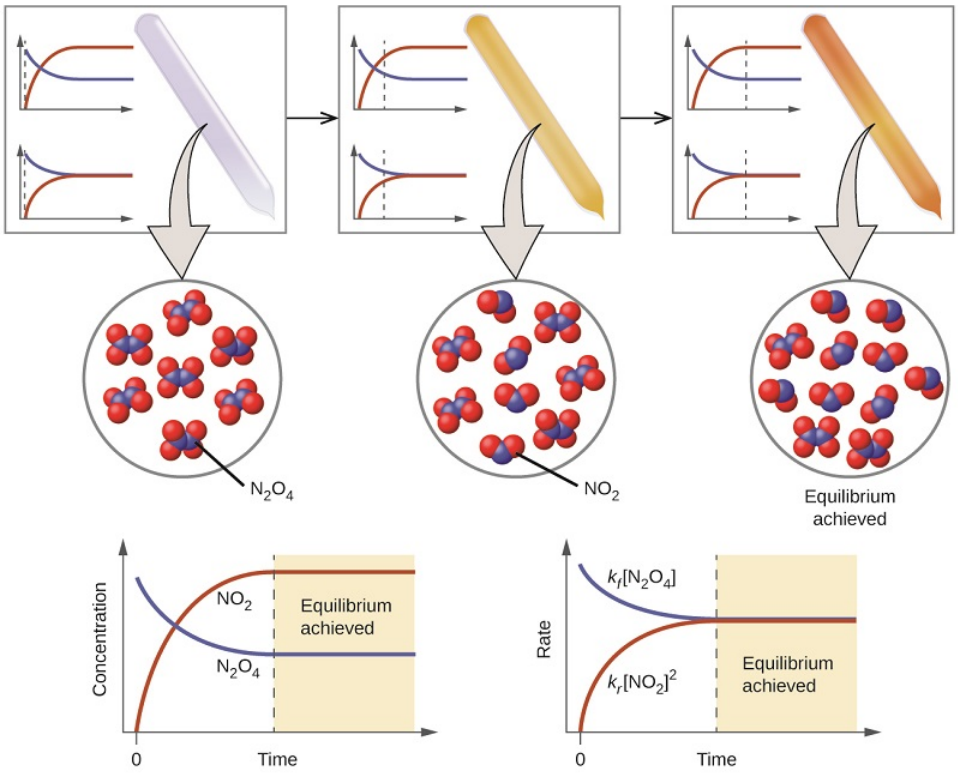


Figure 8.5.1: A mixture of NO_2 and N_2O_4 moves toward equilibrium. Colorless N_2O_4 reacts to form brown NO_2. As the reaction proceeds toward equilibrium, the color of the mixture darkens due to the increasing concentration of NO_2.

A three-part diagram is shown. At the top of the diagram, three beakers are shown, and each one contains a sealed tube. The tube in the left beaker is full of a colorless gas which is connected to a zoom-in view of the particles in the tube by a downward-facing arrow. This particle view shows seven particles, each composed of two connected blue spheres. Each blue sphere is connected to two red spheres. The tube in the middle beaker is full of a light brown gas which is connected to a zoom-in view of the particles in the tube by a downward-facing arrow. This particle view shows nine particles, five of which are composed of two connected blue spheres. Each blue sphere is connected to two red spheres. The remaining four are composed of two red spheres connected to a blue sphere. The tube in the right beaker is full of a brown gas which is connected to a zoom-in view of the particles in the tube by a downward-facing arrow. This particle view shows eleven particles, three of which are composed of two connected blue spheres. Each blue sphere is connected to two red spheres. The remaining eight are composed of two red spheres connected to a blue sphere. At the bottom of the image are two graphs. The left graph has a y-axis labeled, “Concentration,” and an x-axis labeled, “Time.” A red line labeled, “N O subscript 2,” begins in the bottom left corner of the graph at a point labeled, “0,” and rises near the highest point on the y-axis before it levels off and becomes horizontal. A blue line labeled, “N subscript 2 O subscript 4,” begins near the highest point on the y-axis and drops below the midpoint of the y-axis before leveling off. The right graph has a y-axis labeled, “Rate,” and an x-axis labeled, “Time.” A red line labeled, “k subscript f, [N subscript 2 O subscript 4],” begins in the bottom left corner of the graph at a point labeled, “0,” and rises near the middle of the y-axis before it levels off and becomes horizontal. A blue line labeled, “k subscript f, [N O subscript 2] superscript 2,” begins near the highest point on the y-axis and drops to the same point on the y-axis as the red line before leveling off. The point where both lines become horizontal is labeled, “Equilibrium achieved.”

The formation of NO_2 from N_2O_4 is a reversible reaction, which is identified by the equilibrium arrow (⇌). All reactions are reversible, but many reactions, for all practical purposes, proceed in one direction until the reactants are exhausted and will reverse only under certain conditions. Such reactions are often depicted with a one-way arrow from reactants to products. Many other reactions, such as the formation of NO_2 from N_2O_4, are reversible under more easily obtainable conditions and, therefore, are named as such. In a reversible reaction, the reactants can combine to form products and the products can react to form the reactants. Thus, not only can N_2O_4 decompose to form NO_2, but the NO_2 produced can react to form N_2O_4. As soon as the forward reaction produces any NO_2, the reverse reaction begins and NO_2 starts to react to form N_2O_4. At equilibrium, the concentrations of N_2O_4 and NO_2 no longer change because the rate of formation of NO_2 is exactly equal to the rate of consumption of NO_2, and the rate of formation of N_2O_4 is exactly equal to the rate of consumption of N_2O_4. *Chemical equilibrium is a dynamic process*: As with the swimmers and the sunbathers, the numbers of each remain constant, yet there is a flux back and forth between them (Figure 8.5.2).



Figure 8.5.2: These jugglers provide an illustration of dynamic equilibrium. Each throws clubs to the other at the same rate at which he receives clubs from that person. Because clubs are thrown continuously in both directions, the number of clubs moving in each direction is constant, and the number of clubs each juggler has at a given time remains (roughly) constant.

In a chemical equilibrium, the forward and reverse reactions do not stop, rather they continue to occur at the same rate, leading to constant concentrations of the reactants and the products. Plots showing how the reaction rates and concentrations change with respect to time are shown in Figure 8.5.1.

We can detect a state of equilibrium because the concentrations of reactants and products do not appear to change. However, it is important that we verify that the absence of change is due to equilibrium and not to a reaction rate that is so slow that changes in concentration are difficult to detect.

We use a double arrow when writing an equation for a reversible reaction. Such a reaction may or may not be at equilibrium. For example, Figure 8.5.1 shows the reaction:

$$\mathrm{N_2O_4\,(g)} \rightleftharpoons \mathrm{2\,NO_2\,(g)} \tag{8.5.2}$$

When we wish to speak about one particular component of a reversible reaction, we use a single arrow. For example, in the equilibrium shown in Figure 8.5.1, the rate of the forward reaction

$$\mathrm{2\,NO_2\,(g)} \rightarrow \mathrm{N_2O_4\,(g)} \tag{8.5.3}$$

is equal to the rate of the backward reaction

$$\mathrm{N_2O_4\,(g)} \rightarrow \mathrm{2\,NO_2\,(g)} \tag{8.5.4}$$

Equilibrium and Soft Drinks

The connection between chemistry and carbonated soft drinks goes back to 1767, when Joseph Priestley (1733–1804; mostly known today for his role in the discovery and identification of oxygen) discovered a method of infusing water with carbon dioxide to make carbonated water. In 1772, Priestly published a paper entitled “Impregnating Water with Fixed Air.” The paper describes dripping oil of vitriol (today we call this sulfuric acid, but what a great way to describe sulfuric acid: “oil of vitriol” literally means “liquid nastiness”) onto chalk (calcium carbonate). The resulting CO_2 falls into the container of water beneath the vessel in which the initial reaction takes place; agitation helps the gaseous CO_2 mix into the liquid water.

$$\mathrm{H_2SO_4\,(l) + CaCO_3\,(s)} \rightarrow \mathrm{CO_2\,(g) + H_2O\,(l) + CaSO_4\,(aq)}$$

Carbon dioxide is slightly soluble in water. There is an equilibrium reaction that occurs as the carbon dioxide reacts with the water to form carbonic acid (H_2CO_3). Since carbonic acid is a weak acid, it can dissociate into protons (H^+) and hydrogen carbonate ions (HCO_3^-).

$$\mathrm{CO_2\,(aq) + H_2O\,(l)} \rightleftharpoons \mathrm{H_2CO_3\,(aq)} \rightleftharpoons \mathrm{HCO_3^-\,(aq) + H^+\,(aq)}$$

Today, CO_2 can be pressurized into soft drinks, establishing the equilibrium shown above. Once you open the beverage container, however, a cascade of equilibrium shifts occurs. First, the CO_2 gas in the air space on top of the bottle escapes, causing the equilibrium between gas-phase CO_2 and dissolved or aqueous CO_2 to shift, lowering the concentration of CO_2 in the soft drink. Less CO_2 dissolved in the liquid leads to carbonic acid decomposing to dissolved CO_2 and H_2O. The lowered

carbonic acid concentration causes a shift of the final equilibrium. As long as the soft drink is in an open container, the CO_2 bubbles up out of the beverage, releasing the gas into the air (Figure 8.5.3). With the lid off the bottle, the CO_2 reactions are no longer at equilibrium and will continue until no more of the reactants remain. This results in a soft drink with a much lowered CO_2 concentration, often referred to as "flat."



Figure 8.5.3: When a soft drink is opened, several equilibrium shifts occur. (credit: modification of work by "D Coetzee"/Flickr)

A bottle of soda sitting on the ground is shown with a large amount of fizz-filled liquid spewing out of the top.

Sublimation of Bromine

Let us consider the evaporation of bromine as a second example of a system at equilibrium.

$$Br_2(l) \rightleftharpoons Br_2(g)$$

An equilibrium can be established for a physical change—like this liquid to gas transition—as well as for a chemical reaction. Figure 8.5.4 shows a sample of liquid bromine at equilibrium with bromine vapor in a closed container. When we pour liquid bromine into an empty bottle in which there is no bromine vapor, some liquid evaporates, the amount of liquid decreases, and the amount of vapor increases. If we cap the bottle so no vapor escapes, the amount of liquid and vapor will eventually stop changing and an equilibrium between the liquid and the vapor will be established. If the bottle were not capped, the bromine vapor would escape and no equilibrium would be reached.



Figure 8.5.4: An equilibrium is pictured between liquid bromine, $Br_2(l)$, the dark liquid, and bromine vapor, $Br_2(g)$, the orange gas. Because the container is sealed, bromine vapor cannot escape and equilibrium is maintained. (credit: Bromine [images-of-elements.com]).

A glass container is shown that is filled with an orange-brown gas and a small amount of dark orange liquid.

Summary

A reaction is at equilibrium when the amounts of reactants or products no longer change. Chemical equilibrium is a dynamic process, meaning the rate of formation of products by the forward reaction is equal to the rate at which the products re-form reactants by the reverse reaction.

Glossary

equilibrium

in chemical reactions, the state in which the conversion of reactants into products and the conversion of products back into reactants occur simultaneously at the same rate; state of balance

reversible reaction

chemical reaction that can proceed in both the forward and reverse directions under given conditions

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8.6: Equilibrium Constants

Learning Objectives

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

Now that we have a symbol (⇌) to designate reversible reactions, we will need a way to express mathematically how the amounts of reactants and products affect the equilibrium of the system. A general equation for a reversible reaction may be written as follows:

$$mA + nB + \rightleftharpoons xC + yD \tag{8.6.1}$$

We can write the reaction quotient (Q) for this equation. When evaluated using concentrations, it is called Q_c. We use brackets to indicate molar concentrations of reactants and products.

$$Q_c = \frac{[C]^x[D]^y}{[A]^m[B]^n} \tag{8.6.2}$$

The reaction quotient is equal to the molar concentrations of the products of the chemical equation (multiplied together) over the reactants (also multiplied together), with each concentration raised to the power of the coefficient of that substance in the balanced chemical equation. For example, the reaction quotient for the reversible reaction

$$2\,NO_{2(g)} \rightleftharpoons N_2O_{4(g)} \tag{8.6.3}$$

is given by this expression:

$$Q_c = \frac{[N_2O_4]}{[NO_2]^2} \tag{8.6.4}$$

Example 8.6.1: Writing Reaction Quotient Expressions

Write the expression for the reaction quotient for each of the following reactions:

a. $3\,O_{2(g)} \rightleftharpoons 2\,O_{3(g)}$
b. $N_{2(g)} + 3\,H_{2(g)} \rightleftharpoons 2\,NH_{3(g)}$
c. $4\,NH_{3(g)} + 7\,O_{2(g)} \rightleftharpoons 4\,NO_{2(g)} + 6\,H_2O_{(g)}$

Solution

a. $Q_c = \frac{[O_3]^2}{[O_2]^3}$
b. $Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$
c. $Q_c = \frac{[NO_2]^4[H_2O]^6}{[NH_3]^4[O_2]^7}$

Exercise 8.6.1

Write the expression for the reaction quotient for each of the following reactions:

a. $2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$
b. $C_4H_8(g) \rightleftharpoons 2\,C_2H_4(g)$
c. $2\,C_4H_{10}(g) + 13\,O_2(g) \rightleftharpoons 8\,CO_2(g) + 10\,H_2O(g)$

Answer a

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

Answer b

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

Answer c

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

The numeric value of Q_c for a given reaction varies; it depends on the concentrations of products and reactants present at the time when Q_c is determined. When pure reactants are mixed, Q_c is initially zero because there are no products present at that point. As the reaction proceeds, the value of Q_c increases as the concentrations of the products increase and the concentrations of the reactants simultaneously decrease (Figure 8.6.1). When the reaction reaches equilibrium, the value of the reaction quotient no longer changes because the concentrations no longer change.

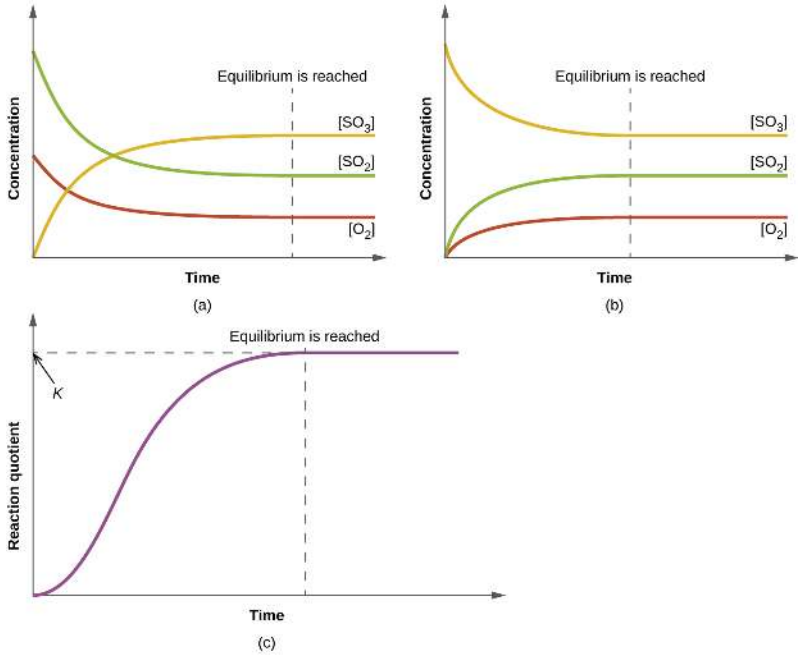


Figure 8.6.1: (a) The change in the concentrations of reactants and products is depicted as the $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ reaction approaches equilibrium. (b) The change in concentrations of reactants and products is depicted as the reaction $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ approaches equilibrium. (c) The graph shows the change in the value of the reaction quotient as the reaction approaches equilibrium.

Three graphs are shown and labeled, “a,” “b,” and “c.” All three graphs have a vertical dotted line running through the middle labeled, “Equilibrium is reached.” The y-axis on graph a is labeled, “Concentration,” and the x-axis is labeled, “Time.” Three curves are plotted on graph a. The first is labeled, “[S O subscript 2];” this line starts high on the y-axis, ends midway down the y-axis, has a steep initial slope and a more gradual slope as it approaches the far right on the x-axis. The second curve on this graph is labeled, “[O subscript 2];” this line mimics the first except that it starts and ends about fifty percent lower on the y-axis. The third curve is the inverse of the first in shape and is labeled, “[S O subscript 3].” The y-axis on graph b is labeled, “Concentration,” and the x-axis is labeled, “Time.” Three curves are plotted on graph b. The first is labeled, “[S O subscript 2];” this line starts low on the y-axis, ends midway up the y-axis, has a steep initial slope and a more gradual slope as it approaches the far right on the x-axis. The second curve on this graph is labeled, “[O subscript 2];” this line mimics the first except that it ends about fifty percent lower on the y-axis. The third curve is the inverse of the first in shape and is labeled, “[S O subscript 3].” The y-axis on graph c is labeled, “Reaction Quotient,” and the x-axis is labeled, “Time.” A single curve is plotted on graph c. This curve begins at the bottom of the y-axis and rises steeply up near the top of the y-axis, then levels off into a horizontal line. The top point of this line is labeled, “k.”

When a mixture of reactants and products of a reaction reaches equilibrium at a given temperature, its reaction quotient always has the same value. This value is called the equilibrium constant (K) of the reaction at that temperature. As for the reaction quotient, when evaluated in terms of concentrations, it is noted as K_c.

That a reaction quotient always assumes the same value at equilibrium can be expressed as:

$$Q_c \text{ at equilibrium} = K_c = \frac{[C]^x[D]^y\ldots}{[A]^m[B]^n\ldots} \tag{8.6.5}$$

This equation is a mathematical statement of the law of mass action: When a reaction has attained equilibrium at a given temperature, the reaction quotient for the reaction always has the same value.

Example 8.6.2: Evaluating a Reaction Quotient

Gaseous nitrogen dioxide forms dinitrogen tetroxide according to this equation:

$$2\,NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$$

When 0.10 mol NO_2 is added to a 1.0-L flask at 25 °C, the concentration changes so that at equilibrium, [NO_2] = 0.016 M and [N_2O_4] = 0.042 M.

a. What is the value of the reaction quotient before any reaction occurs?
b. What is the value of the equilibrium constant for the reaction?

Solution

a. Before any product is formed, $[NO_2] = \frac{0.10\text{ mol}}{1.0\text{ L}} = 0.10\ M$, and [$N_2O_4$] = 0 *M*. Thus,

$$Q_c = \frac{[N2O4]}{[NO2]^2} = \frac{0}{0.10^2} = 0$$

b. At equilibrium, the value of the equilibrium constant is equal to the value of the reaction quotient. At equilibrium,

$$K_c = Q_c = \frac{[N2O4]}{[NO2]^2} = \frac{0.042}{0.016^2} = 1.6 \times 10^2.$$

The equilibrium constant is 1.6×10^2.

Note that dimensional analysis would suggest the unit for this K_c value should be M^{-1}. However, it is common practice to omit units for K_c values computed as described here, since it is the magnitude of an equilibrium constant that relays useful information. As will be discussed later in this module, the rigorous approach to computing equilibrium constants uses dimensionless quantities derived from activities instead of molar concentrations, and so K_c values are truly unitless.

Exercise 8.6.2

For the reaction

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

the concentrations at equilibrium are [SO_2] = 0.90 *M*, [O_2] = 0.35 *M*, and [SO_3] = 1.1 *M*. What is the value of the equilibrium constant, K_c?

Answer

K_c = 4.3

The magnitude of an equilibrium constant is a measure of the yield of a reaction when it reaches equilibrium. A large value for K_c indicates that equilibrium is attained only after the reactants have been largely converted into products. A small value of K_c—much less than 1—indicates that equilibrium is attained when only a small proportion of the reactants have been converted into products.

Once a value of K_c is known for a reaction, it can be used to predict directional shifts when compared to the value of Q_c. A system that is not at equilibrium will proceed in the direction that establishes equilibrium. The data in Figure 8.6.2 illustrate this. When heated to a consistent temperature, 800 °C, different starting mixtures of CO, H_2O, CO_2, and H_2 react to reach compositions adhering to the same equilibrium (the value of Q_c changes until it equals the value of K_c). This value is 0.640, the equilibrium constant for the reaction under these conditions.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \quad K_c = 0.640 \quad T = 800°C \tag{8.6.6}$$

It is important to recognize that an equilibrium can be established starting either from reactants or from products, or from a mixture of both. For example, equilibrium was established from Mixture 2 in Figure 8.6.2 when the products of the reaction were heated in a closed container. In fact, one technique used to determine whether a reaction is truly at equilibrium is to approach equilibrium starting with reactants in one experiment and starting with products in another. If the same value of the reaction quotient is observed when the concentrations stop changing in both experiments, then we may be certain that the system has reached equilibrium.

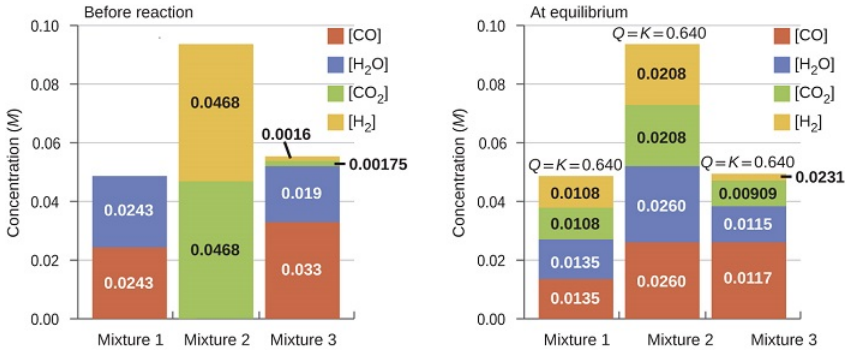


Figure 8.6.2: Concentrations of three mixtures are shown before and after reaching equilibrium at 800 °C for the so-called water gas shift reaction (Equation 8.6.6).

Two sets of bar graphs are shown. The left is labeled, “Before reaction,” and the right is labeled, “At equilibrium.” Both graphs have y-axes labeled, “Concentration (M),” and three bars on the x-axes labeled, “Mixture 1,” “Mixture 2,” and “Mixture 3.” The y-axis has a scale beginning at 0.00 and ending at 0.10, with measurement increments of 0.02. The bars on the graphs are color coded and a key is provided with a legend. Red is labeled, “C O;” blue is labeled, “H subscript 2 O;” green is labeled, “C O subscript 2,” and yellow is labeled, “H subscript 2.” The graph on the left shows the red bar for mixture one just above 0.02 and the blue bar near 0.05. For mixture two, the green bar is near 0.05, and the yellow bar is near 0.09. For mixture 3, the red bar is near 0.01, the blue bar is slightly above that with green and yellow topping it off at 0.02. On the right graph, the bar for mixture one shows the red bar slightly above 0.01, the blue bar stacked on it rising slightly above 0.02, the green rising near 0.04, and the yellow bar reaching near 0.05. A label above this bar reads, “Q equals 0.640.” The bar for mixture two shows the red bar slightly above 0.02, the blue bar stacked on it rising near 0.05, the green rising near 0.07, and the yellow bar reaching near 0.10. A label above this bar reads “Q equals 0.640.” The bar for mixture three shows the red bar near 0.01, the blue bar stacked on it rising slightly above 0.01, the green rising near 0.02, and the yellow bar reaching 0.02. A label above this bar reads “Q equals 0.640”.

Example 8.6.3: Predicting the Direction of Reaction

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

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

with $K_c = 0.64$. Determine in which direction the reaction proceeds as it goes to equilibrium in each of the three experiments shown.

Reactant/Products for Three Experiments

Reactants/Products	Experiment 1	Experiment 2	Experiment 3
$[CO]_i$	0.0203 M	0.011 M	0.0094 M
$[H_2O]_i$	0.0203 M	0.0011 M	0.0025 M
$[CO_2]_i$	0.0040 M	0.037 M	0.0015 M
$[H_2]_i$	0.0040 M	0.046 M	0.0076 M

Solution

Experiment 1:

$$Q_c = \frac{[CO2][H2]}{[CO][H2O]} = \frac{(0.0040)(0.0040)}{(0.0203)(0.0203)} = 0.039.$$

$Q_c < K_c$ (0.039 < 0.64)

The reaction will shift to the right.

Experiment 2:

$$Q_c = \frac{[CO2][H2]}{[CO][H2O]} = \frac{(0.037)(0.046)}{(0.011)(0.0011)} = 1.4 \times 10^2$$

$Q_c > K_c$ (140 > 0.64)

The reaction will shift to the left.

Experiment 3:

$$Q_c = \frac{[CO2][H2]}{[CO][H2O]} = \frac{(0.0015)(0.0076)}{(0.0094)(0.0025)} = 0.48$$

$Q_c < K_c$ (0.48 < 0.64)

The reaction will shift to the right.

Exercise 8.6.3

Calculate the reaction quotient and determine the direction in which each of the following reactions will proceed to reach equilibrium.

(a) A 1.00-L flask containing 0.0500 mol of NO(g), 0.0155 mol of Cl_2(g), and 0.500 mol of NOCl:

$$2\,NO(g) + Cl_2(g) \rightleftharpoons 2\,NOCl(g) \quad K_c = 4.6 \times 10^4$$

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

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

(c) A 2.00-L flask containing 230 g of SO_3(g):

$$2\,SO_3(g) \rightleftharpoons 2\,SO_2(g) + O_2(g) \quad K_c = 0.230$$

Answer a

Q_c = 6.45 × 10^3, shifts right.

Answer b

Q_c = 0.12, shifts left.

Answer c

Q_c = 0, shifts right

In Example **8.6.2**, it was mentioned that the common practice is to omit units when evaluating reaction quotients and equilibrium constants. It should be pointed out that using concentrations in these computations is a convenient but simplified approach that sometimes leads to results that seemingly conflict with the law of mass action. For example, equilibria involving aqueous ions often exhibit equilibrium constants that vary quite significantly (are *not* constant) at high solution concentrations. This may be avoided by computing K_c values using the *activities* of the reactants and products in the equilibrium system instead of their concentrations. The activity of a substance is a measure of its effective concentration under specified conditions. While a detailed discussion of this important quantity is beyond the scope of an introductory text, it is necessary to be aware of a few important aspects:

- Activities are dimensionless (**unitless**) quantities and are in essence “adjusted” concentrations.
- For relatively dilute solutions, a solute's activity and its molar concentration are roughly equal.
- Activities for pure condensed phases (solids and liquids) are equal to 1.
- Activities for solvents in dilute solutions are equal to 1.

As a consequence of this last two aspects, Q_c and K_c expressions do not contain terms for solids or liquids or solvents in dilute solutions (being numerically equal to 1, these terms have no effect on the expression's value). Several examples of equilibria yielding such expressions will be encountered in this section.

Homogeneous Equilibria

A homogeneous equilibrium is one in which all of the reactants and products are present in a single solution (by definition, a homogeneous mixture). In this chapter, we will concentrate on the two most common types of homogeneous equilibria: those occurring in liquid-phase solutions and those involving exclusively gaseous species. Reactions between solutes in liquid solutions belong to one type of homogeneous equilibria. The chemical species involved can be molecules, ions, or a mixture of both. Several examples are provided here:

Example 1

$$\mathrm{C_2H_2}(aq) + 2\,\mathrm{Br_2}(aq) \rightleftharpoons \mathrm{C_2H_2Br_4}(aq) \tag{8.6.7}$$

with associated equilibrium constant

$$K_c = \frac{[C2H2Br4]}{[C2H2][Br2]^2} \tag{8.6.8}$$

Example 2

$$\mathrm{I_2}(aq) + \mathrm{I^-}(aq) \rightleftharpoons \mathrm{I_3^-}(aq) \tag{8.6.9}$$

with associated equilibrium constant

$$K_c = \frac{[I3-]}{[I2][I-]} \tag{8.6.10}$$

Example 3

$$\mathrm{Hg_2^{2+}}(aq) + \mathrm{NO_3^-}(aq) + 3\,\mathrm{H_3O^+}(aq) \rightleftharpoons 2\,\mathrm{Hg^{2+}}(aq) + \mathrm{HNO_2}(aq) + 4\,\mathrm{H_2O}(l) \tag{8.6.11}$$

with associated equilibrium constant

$$K_c = \frac{[Hg^2+]^2[HNO2]}{[Hg2^2+][NO3-][H3O+]^3} \tag{8.6.12}$$

Example 4

$$\mathrm{HF}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{F^-}(aq) \tag{8.6.13}$$

with associated equilibrium constant

$$K_c = \frac{[H3O+][F-]}{[HF]} \tag{8.6.14}$$

Example 5

$$\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{NH_4^+}(aq) + \mathrm{OH^-}(aq) \tag{8.6.15}$$

with associated equilibrium constant

$$K_c = \frac{[NH4+][OH-]}{[NH3]} \tag{8.6.16}$$

In each of these examples, the equilibrium system is an aqueous solution, as denoted by the *aq* annotations on the solute formulas. Since $H_2O(l)$ is the solvent for these solutions, it is assigned an activity of 1, and thus **does not** appear explicitly as a term in the K_c expression, as discussed earlier, even though it may also appear as a reactant or product in the chemical equation.

Reactions in which all reactants and products are gases represent a second class of homogeneous equilibria. We use molar concentrations in the following examples, but we will see shortly that partial pressures of the gases may be used as well:

Example 1

$$\mathrm{C_2H_6}(g) \rightleftharpoons \mathrm{C_2H_4}(g) + \mathrm{H_2}(g) \tag{8.6.17}$$

with associated equilibrium constant

$$K_c = \frac{[C2H4][H2]}{[C2H6]} \tag{8.6.18}$$

Example 2

$$3\,\mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{O_3}(g) \tag{8.6.19}$$

with associated equilibrium constant

$$K_c = \frac{[O3]^2}{[O2]^3} \tag{8.6.20}$$

Example 3

$$\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \rightleftharpoons 2\,\mathrm{NH_3}(g) \tag{8.6.21}$$

with associated equilibrium constant

$$K_c = \frac{[NH3]^2}{[N2][H2]^3} \tag{8.6.22}$$

Example 4

$$\mathrm{C_3H_8}(g) + 5\,\mathrm{O_2}(g) \rightleftharpoons 3\,\mathrm{CO_2}(g) + 4\,\mathrm{H_2O}(g) \tag{8.6.23}$$

with associated equilibrium constant

$$K_c = \frac{[CO2]^3[H2O]^4}{[C3H8][O2]^5} \tag{8.6.24}$$

Note that the concentration of $\mathbf{H_2O_{(g)}}$ has been included in the last example because water is not the solvent in this gas-phase reaction and its concentration (and activity) changes.

Whenever gases are involved in a reaction, the partial pressure of each gas can be used instead of its concentration in the equation for the reaction quotient because the partial pressure of a gas is directly proportional to its concentration at constant temperature. This relationship can be derived from the ideal gas equation, where M is the molar concentration of gas, $\frac{n}{V}$.

$$PV = nRT \tag{8.6.25}$$

$$P = \left(\frac{n}{V}\right) RT \tag{8.6.26}$$

$$= MRT \tag{8.6.27}$$

Thus, at constant temperature, the pressure of a gas is **directly proportional** to its concentration. Using the partial pressures of the gases, we can write the reaction quotient for the system

$$\mathrm{C_2H_6}(g) \rightleftharpoons \mathrm{C_2H_4}(g) + \mathrm{H_2}(g) \tag{8.6.28}$$

by following the same guidelines for deriving concentration-based expressions:

$$Q_P = \frac{P_{\mathrm{C_2H_4}} P_{\mathrm{H_2}}}{P_{\mathrm{C_2H_6}}} \tag{8.6.29}$$

In this equation we use Q_P to indicate a reaction quotient written with partial pressures: $P_{\mathrm{C_2H_6}}$ is the partial pressure of C_2H_6; $P_{\mathrm{H_2}}$, the partial pressure of H_2; and $P_{\mathrm{C_2H_6}}$, the partial pressure of C_2H_4. At equilibrium:

$$K_P = Q_P = \frac{P_{\mathrm{C_2H_4}} P_{\mathrm{H_2}}}{P_{\mathrm{C_2H_6}}} \tag{8.6.30}$$

The subscript P in the symbol K_P designates an equilibrium constant derived using partial pressures instead of concentrations. The equilibrium constant, K_P, is still a constant, but its numeric value may differ from the equilibrium constant found for the same reaction by using concentrations.

Conversion between a value for K_c, an equilibrium constant expressed in terms of concentrations, and a value for K_P, an equilibrium constant expressed in terms of pressures, is straightforward (a K or Q without a subscript could be either concentration or pressure).

The equation relating K_c and K_P is derived as follows. For the gas-phase reaction:

$$m\mathrm{A} + n\mathrm{B} \rightleftharpoons x\mathrm{C} + y\mathrm{D} \tag{8.6.31}$$

with

$$K_P = \frac{(P_C)^x (P_D)^y}{(P_A)^m (P_B)^n} \tag{8.6.32}$$

$$= \frac{([\mathrm{C}] \times RT)^x ([\mathrm{D}] \times RT)^y}{([\mathrm{A}] \times RT)^m ([\mathrm{B}] \times RT)^n} \tag{8.6.33}$$

$$= \frac{[\mathrm{C}]^x [\mathrm{D}]^y}{[\mathrm{A}]^m [\mathrm{B}]^n} \times \frac{(RT)^{x+y}}{(RT)^{m+n}} \tag{8.6.34}$$

$$= K_c (RT)^{(x+y)-(m+n)} \tag{8.6.35}$$

$$= K_c (RT)^{\Delta n} \tag{8.6.36}$$

The relationship between K_c and K_P is

$$K_P = K_c (RT)^{\Delta n} \tag{8.6.37}$$

In this equation, Δn is the difference between the sum of the coefficients of the *gaseous* products and the sum of the coefficients of the *gaseous* reactants in the reaction (the change in moles of gas between the reactants and the products). For the gas-phase reaction $m\mathrm{A} + n\mathrm{B} \rightleftharpoons x\mathrm{C} + y\mathrm{D}$, we have

$$\Delta n = (x + y) - (m + n) \tag{8.6.38}$$

Example 8.6.4: Calculation of K_P

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

a. $\mathrm{C_2H_6}(g) \rightleftharpoons \mathrm{C_2H_4}(g) + \mathrm{H_2}(g)$
b. $\mathrm{CO}(g) + \mathrm{H_2O}(g) \rightleftharpoons \mathrm{CO_2}(g) + \mathrm{H_2}(g)$
c. $\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \rightleftharpoons 2\,\mathrm{NH_3}(g)$
d. K_c is equal to 0.28 for the following reaction at 900 °C:

$$\mathrm{CS_2}(g) + 4\,\mathrm{H_2}(g) \rightleftharpoons \mathrm{CH_4}(g) + 2\,\mathrm{H_2S}(g)$$

What is K_P at this temperature?

Solution

(a) $\Delta n = (2) - (1) = 1$

$$K_P = K_c (RT)^{\Delta n} = K_c (RT)^1 = K_c (RT)$$

(b) $\Delta n = (2) - (2) = 0$

$$K_P = K_c (RT)^{\Delta n} = K_c (RT)^0 = K_c$$

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

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

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

? Exercise 8.6.4

Write the equations for the conversion of K_c to K_P for each of the following reactions, which occur in the gas phase:

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

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

What would be the value of K_P at this temperature?

Answer a

$K_P = K_c\,(RT)^{-1}$

Answer b

$K_P = K_c\,(RT)$

Answer c

$K_P = K_c\,(RT)$;

Answer d

160 or 1.6×10^2

Heterogeneous Equilibria

A heterogeneous equilibrium is a system in which reactants and products are found in two or more phases. The phases may be any combination of solid, liquid, or gas phases, and solutions. When dealing with these equilibria, remember that solids and pure liquids do not appear in equilibrium constant expressions (the activities of pure solids, pure liquids, and solvents are 1).

Some heterogeneous equilibria involve chemical changes:

Example 1

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,Cl^-(aq) \tag{8.6.39}$$

with associated equilibrium constant

$$K_c = [Pb^{2+}][Cl^-]^2 \tag{8.6.40}$$

Example 1

$$CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s) \tag{8.6.41}$$

with associated equilibrium constant

$$K_c = \frac{1}{[CO_2]} \tag{8.6.42}$$

Example 1

$$C(s) + 2\,S(g) \rightleftharpoons CS_2(g) \tag{8.6.43}$$

with associated equilibrium constant

$$K_c = \frac{[CS2]}{[S]^2} \tag{8.6.44}$$

Other heterogeneous equilibria involve phase changes, for example, the evaporation of liquid bromine, as shown in the following equation:

$$Br_2(l) \rightleftharpoons Br_2(g) \tag{8.6.45}$$

with associated equilibrium constant

$$K_c = [\mathrm{Br_2}] \tag{8.6.46}$$

We can write equations for reaction quotients of heterogeneous equilibria that involve gases, using **partial pressures** instead of concentrations. Two examples are:

$$\mathrm{CaO}(s) + \mathrm{CO_2}(g) \rightleftharpoons \mathrm{CaCO_3}(s) \tag{8.6.47}$$

with associated equilibrium constant

$$K_P = \frac{1}{P_{\mathrm{CO_2}}} \tag{8.6.48}$$

$$\mathrm{C}(s) + 2\,\mathrm{S}(g) \rightleftharpoons \mathrm{CS_2}(g) \tag{8.6.49}$$

with associated equilibrium constant

$$K_P = \frac{P_{\mathrm{CS_2}}}{(P_{\mathrm{S}})^2} \tag{8.6.50}$$

Summary

For any reaction that is at equilibrium, the reaction quotient Q is equal to the equilibrium constant K for the reaction. If a reactant or product is a pure solid, a pure liquid, or the solvent in a dilute solution, the concentration of this component does not appear in the expression for the equilibrium constant. At equilibrium, the values of the concentrations of the reactants and products are constant. Their particular values may vary depending on conditions, but the value of the reaction quotient will always equal K (K_c when using concentrations or K_P when using partial pressures).

A homogeneous equilibrium is an equilibrium in which all components are in the same phase. A heterogeneous equilibrium is an equilibrium in which components are in two or more phases. We can decide whether a reaction is at equilibrium by comparing the reaction quotient with the equilibrium constant for the reaction.

Key Equations

- $Q = \dfrac{[\mathrm{C}]^x[\mathrm{D}]^y}{[\mathrm{A}]^m[\mathrm{B}]^n}$ where $m\mathrm{A} + n\mathrm{B} \rightleftharpoons x\mathrm{C} + y\mathrm{D}$
- $Q_P = \dfrac{(P_C)^x(P_D)^y}{(P_A)^m(P_B)^n}$ where $m\mathrm{A} + n\mathrm{B} \rightleftharpoons x\mathrm{C} + y\mathrm{D}$
- $P = MRT$
- $K_P = K_c\,(RT)^{\Delta n}$

Glossary

equilibrium constant (K)
value of the reaction quotient for a system at equilibrium

heterogeneous equilibria
equilibria between reactants and products in different phases

homogeneous equilibria
equilibria within a single phase

K_c
equilibrium constant for reactions based on concentrations of reactants and products

K_P
equilibrium constant for gas-phase reactions based on partial pressures of reactants and products

law of mass action

when a reversible reaction has attained equilibrium at a given temperature, the reaction quotient remains constant

reaction quotient (*Q*)

ratio of the product of molar concentrations (or pressures) of the products to that of the reactants, each concentration (or pressure) being raised to the power equal to the coefficient in the equation

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8.7: Shifting Equilibria - Le Chatelier's Principle

Learning Objectives

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

As we saw in the previous section, reactions proceed in both directions (reactants go to products and products go to reactants). We can tell a reaction is at equilibrium if the reaction quotient (Q) is equal to the equilibrium constant (K). We next address what happens when a system at equilibrium is disturbed so that Q is no longer equal to K. If a system at equilibrium is subjected to a perturbance or stress (such as a change in concentration) the position of equilibrium changes. Since this stress affects the concentrations of the reactants and the products, the value of Q will no longer equal the value of K. To re-establish equilibrium, the system will either shift toward the products (if $Q < K$) or the reactants (if $Q > K$) until Q returns to the same value as K.

This process is described by Le Chatelier's principle: When a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance. As described in the previous paragraph, the disturbance causes a change in Q; the reaction will shift to re-establish $Q = K$.

Predicting the Direction of a Reversible Reaction

Le Chatelier's principle can be used to predict changes in equilibrium concentrations when a system that is at equilibrium is subjected to a stress. However, if we have a mixture of reactants and products that have not yet reached equilibrium, the changes necessary to reach equilibrium may not be so obvious. In such a case, we can compare the values of Q and K for the system to predict the changes.

A chemical system at equilibrium can be **temporarily** shifted out of equilibrium by adding or removing one or more of the reactants or products. The concentrations of both reactants and products then undergo additional changes to return the system to equilibrium.

The stress on the system in Figure 8.7.1 is the reduction of the equilibrium concentration of SCN^- (lowering the concentration of one of the reactants would cause Q to be larger than K). As a consequence, Le Chatelier's principle leads us to predict that the concentration of $Fe(SCN)^{2+}$ should decrease, increasing the concentration of SCN^- part way back to its original concentration, and increasing the concentration of Fe^{3+} above its initial equilibrium concentration.



Figure 8.7.1: (a) The test tube contains 0.1 M Fe^{3+}. (b) Thiocyanate ion has been added to solution in (a), forming the red $Fe(SCN)^{2+}$ ion. $\mathbf{Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons Fe(SCN)^{2+}(aq)}$. *(c) Silver nitrate has been added to the solution in (b), precipitating some of the SCN− as the white solid AgSCN.* $\mathbf{Ag^+(aq) + SCN^-(aq) \rightleftharpoons AgSCN(s)}$. *The decrease in the SCN− concentration shifts the first equilibrium in the solution to the left, decreasing the concentration (and lightening color) of the* $Fe(SCN)^{2+}$. *(credit: modification of work by Mark Ott).*

Three capped test tubes held vertically in clamps are shown in pictures labeled, "a," "b," and "c." The test tube in picture a is half filled with a clear, orange liquid. The test tube in picture b is half filled with a dark, burgundy liquid. The test tube in picture c is half filled with a slightly cloudy, orange liquid.

The effect of a change in concentration on a system at equilibrium is illustrated further by the equilibrium of this chemical reaction:

$$\mathbf{H_{2(g)} + I_{2(g)} \rightleftharpoons 2\,HI_{(g)}} \tag{8.7.1}$$

$$K_c = 50.0 \text{ at } 400°C \tag{8.7.2}$$

The numeric values for this example have been determined experimentally. A mixture of gases at 400 °C with $[H_2] = [I_2] = 0.221\ M$ and $[HI] = 1.563\ M$ is at equilibrium; for this mixture, $Q_c = K_c = 50.0$. If H_2 is introduced into the system so quickly that its concentration doubles before it begins to react (new $[H_2] = 0.442\ M$), the reaction will shift so that a new equilibrium is reached, at which

- $[H_2] = 0.374\ M$,
- $[I_2] = 0.153\ M$, and
- $[HI] = 1.692\ M$.

This gives:

$$Q_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(1.692)^2}{(0.374)(0.153)} = 50.0 = K_c \tag{8.7.3}$$

We have stressed this system by introducing additional H_2. The stress is relieved when the reaction shifts to the right, using up some (but not all) of the excess H_2, reducing the amount of uncombined I_2, and forming additional HI.

Effect of Change in Pressure on Equilibrium

Sometimes we can change the position of equilibrium by changing the pressure of a system. However, changes in pressure have a measurable effect only in systems in which gases are involved, and then only when the chemical reaction produces a change in the total number of gas molecules in the system. An easy way to recognize such a system is to look for different numbers of moles of gas on the reactant and product sides of the equilibrium. While evaluating pressure (as well as related factors like volume), it is important to remember that equilibrium constants are defined with regard to concentration (for K_c) or partial pressure (for K_P). Some changes to total pressure, like adding an inert gas that is not part of the equilibrium, will change the total pressure but not the partial pressures of the gases in the equilibrium constant expression. Thus, addition of a gas not involved in the equilibrium will not perturb the equilibrium.

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:

$$2\,NO\,(g) + O_2\,(g) \rightleftharpoons 2\,NO_2\,(g) \tag{8.7.4}$$

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:

$$N_2\,(g) + O_2\,(g) \rightleftharpoons 2\,NO\,(g) \tag{8.7.5}$$

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.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \quad \Delta H = -9.4\ \text{kJ (exothermic)} \tag{8.7.6}$$

Because this reaction is exothermic, we can write it with heat as a product.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) + \text{heat} \tag{8.7.7}$$

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

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \quad \Delta H = 57.20\ \text{kJ} \tag{8.7.8}$$

The positive ΔH value tells us that the reaction is endothermic and could be written

$$\text{heat} + N_2O_4(g) \rightleftharpoons 2NO_2(g) \tag{8.7.9}$$

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.

Catalysts Do Not Affect Equilibrium

As we learned during our study of kinetics, a catalyst can speed up the rate of a reaction. Though this increase in reaction rate may cause a system to reach equilibrium more quickly (by speeding up the forward and reverse reactions), a catalyst has no effect on the value of an equilibrium constant nor on equilibrium concentrations.

The interplay of changes in concentration or pressure, temperature, and the lack of an influence of a catalyst on a chemical equilibrium is illustrated in the industrial synthesis of ammonia from nitrogen and hydrogen according to the equation

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \tag{8.7.10}$$

A large quantity of ammonia is manufactured by this reaction. Each year, ammonia is among the top 10 chemicals, by mass, manufactured in the world. About 2 billion pounds are manufactured in the United States each year. Ammonia plays a vital role in our global economy. It is used in the production of fertilizers and is, itself, an important fertilizer for the growth of corn, cotton, and other crops. Large quantities of ammonia are converted to nitric acid, which plays an important role in the production of fertilizers, explosives, plastics, dyes, and fibers, and is also used in the steel industry.

Fritz Haber

Haber was born in Breslau, Prussia (presently Wroclaw, Poland) in December 1868. He went on to study chemistry and, while at the University of Karlsruhe, he developed what would later be known as the Haber process: the catalytic formation of ammonia from hydrogen and atmospheric nitrogen under high temperatures and pressures.



The work of Nobel Prize recipient Fritz Haber revolutionized agricultural practices in the early 20th century. His work also affected wartime strategies, adding chemical weapons to the artillery.

For this work, Haber was awarded the 1918 Nobel Prize in Chemistry for synthesis of ammonia from its elements. The Haber process was a boon to agriculture, as it allowed the production of fertilizers to no longer be dependent on mined feed stocks such as sodium nitrate.

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

Currently, the annual production of synthetic nitrogen fertilizers exceeds 100 million tons and synthetic fertilizer production has increased the number of humans that arable land can support from 1.9 persons per hectare in 1908 to 4.3 in 2008. The availability of nitrogen is a strong limiting factor to the growth of plants. Despite accounting for 78% of air, diatomic nitrogen ($\mathrm{N_2}$) is nutritionally unavailable due the tremendous stability of the nitrogen-nitrogen triple bond. For plants to use atmospheric nitrogen, the nitrogen must be converted to a more bioavailable form (this conversion is called nitrogen fixation).

In addition to his work in ammonia production, Haber is also remembered by history as one of the fathers of chemical warfare. During World War I, he played a major role in the development of poisonous gases used for trench warfare. Regarding his role in these developments, Haber said, “During peace time a scientist belongs to the World, but during war time he belongs to his country.”[1] Haber defended the use of gas warfare against accusations that it was inhumane, saying that death was death, by whatever means it was inflicted. He stands as an example of the ethical dilemmas that face scientists in times of war and the double-edged nature of the sword of science.

Like Haber, the products made from ammonia can be multifaceted. In addition to their value for agriculture, nitrogen compounds can also be used to achieve destructive ends. Ammonium nitrate has also been used in explosives, including improvised explosive devices. Ammonium nitrate was one of the components of the bomb used in the attack on the Alfred P. Murrah Federal Building in downtown Oklahoma City on April 19, 1995.

It has long been known that nitrogen and hydrogen react to form ammonia. However, it became possible to manufacture ammonia in useful quantities by the reaction of nitrogen and hydrogen only in the early 20th century after the factors that influence its equilibrium were understood.

To be practical, an industrial process must give a large yield of product relatively quickly. One way to increase the yield of ammonia is to increase the pressure on the system in which N_2, H_2, and NH_3 are at equilibrium or are coming to equilibrium.

$$\mathrm{N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)} \tag{8.7.11}$$

The formation of additional amounts of ammonia reduces the total pressure exerted by the system and somewhat reduces the stress of the increased pressure.

Although increasing the pressure of a mixture of N_2, H_2, and NH_3 will increase the yield of ammonia, at low temperatures, the rate of formation of ammonia is slow. At room temperature, for example, the reaction is so slow that if we prepared a mixture of N_2 and H_2, no detectable amount of ammonia would form during our lifetime. The formation of ammonia from hydrogen and nitrogen is an exothermic process:

$$\mathrm{N_2(g) + 3\,H_2(g) \rightarrow 2\,NH_3(g)} \quad \Delta H = -92.2\ \mathrm{kJ} \tag{8.7.12}$$

Thus, increasing the temperature to increase the rate lowers the yield. If we lower the temperature to shift the equilibrium to favor the formation of more ammonia, equilibrium is reached more slowly because of the large decrease of reaction rate with decreasing temperature.

Part of the rate of formation lost by operating at lower temperatures can be recovered by using a catalyst. The net effect of the catalyst on the reaction is to cause equilibrium to be reached more rapidly. In the commercial production of ammonia, conditions of about 500 °C, 150–900 atm, and the presence of a catalyst are used to give the best compromise among rate, yield, and the cost of the equipment necessary to produce and contain high-pressure gases at high temperatures (Figure **8.7.2**).

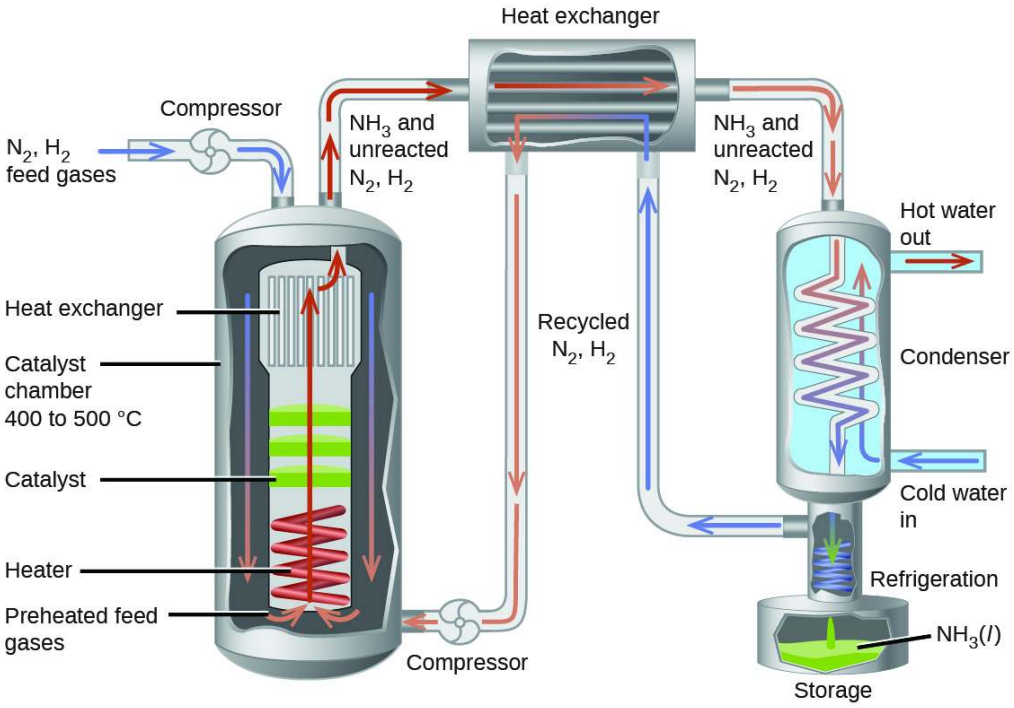


Figure **8.7.2**: Commercial production of ammonia requires heavy equipment to handle the high temperatures and pressures required. This schematic outlines the design of an ammonia plant.

Summary

Systems at equilibrium can be disturbed by changes to temperature, concentration, and, in some cases, volume and pressure; volume and pressure changes will disturb equilibrium if the number of moles of gas is different on the reactant and product sides of the reaction. The system's response to these disturbances is described by Le 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.

Table **8.7.1**: 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. 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

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8.8: Spontaneity (Thermodynamics)

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 **8.8.1**).

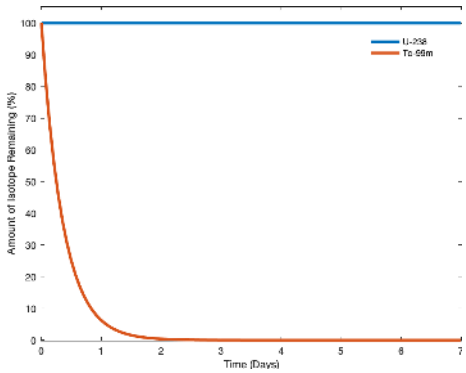


Figure **8.8.1**: Both U-238 and Tc-99m undergo spontaneous radioactive decay, but at drastically different rates. Over the course of one week, essentially all of a Tc-99m sample and none of a U-238 sample will have decayed. (CC by 4.0; Morgan Johnson via LibreTexts)

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 **8.8.2**).

$$\mathbf{C(s, diamond) \longrightarrow C(s, graphite)} \tag{8.8.1}$$

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.

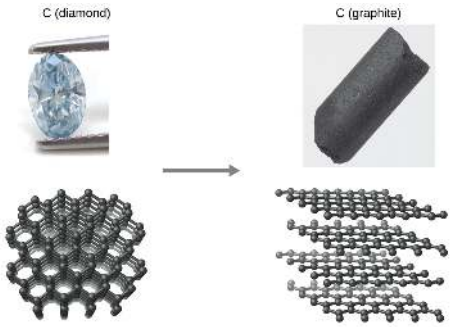


Figure **8.8.2**: The conversion of carbon from the diamond allotrope to the graphite allotrope is spontaneous at ambient pressure, but its rate is immeasurably slow at low to moderate temperatures. This process is known as graphitization, and its rate can be increased to easily measurable values at 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 **8.8.3**). 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.

$$w = -P\Delta V \tag{8.8.2}$$

$$= 0 \ \ (\mathbf{P = 0 \text{ in a vaccum}}) \tag{8.8.3}$$

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.

$$\Delta U = q + w \qquad \text{(First Law of Thermodynamics)}$$
$$= 0 + 0 = 0 \qquad (8.8.4)$$

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).

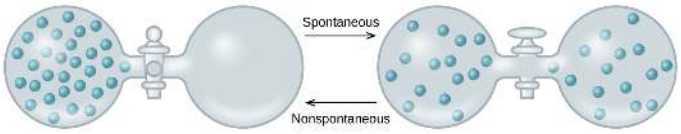


Figure **8.8.3**: An isolated system consists of an ideal gas in one flask that is connected by a closed valve to a second flask containing a vacuum. Once the valve is opened, the gas spontaneously becomes evenly distributed between the flasks.

When the valve is closed, all of the gas molecules accumulating 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 **8.8.4**). 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.

$$q_X < 0 \quad \text{and} \quad q_Y = -q_X > 0 \qquad (8.8.5)$$

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 **8.8.4**: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 8.8.1: 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 **8.8.5**:(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 8.8.1

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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8.9: Entropy (Thermodynamics)

Learning Objectives

- Define entropy
- Explain the relationship between entropy and the number of microstates
- Predict the sign of the entropy change for chemical and physical processes

In 1824, at the age of 28, Nicolas Léonard Sadi Carnot (Figure 8.9.2) published the results of an extensive study regarding the efficiency of steam heat engines. In a later review of Carnot's findings, Rudolf Clausius introduced a new thermodynamic property that relates the spontaneous heat flow accompanying a process to the temperature at which the process takes place. This new property was expressed as the ratio of the *reversible* heat (q_{rev}) and the kelvin temperature (T). The term reversible process refers to a process that takes place at such a slow rate that it is always at equilibrium and its direction can be changed (it can be "reversed") by an infinitesimally small change is some condition. Note that the idea of a reversible process is a formalism required to support the development of various thermodynamic concepts; no real processes are truly reversible, rather they are classified as *irreversible*.

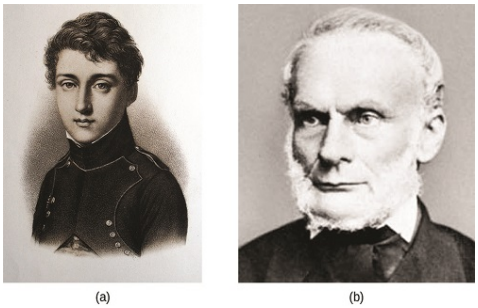


Figure 8.9.1: (a) Nicholas Léonard Sadi Carnot's research into steam-powered machinery and (b) Rudolf Clausius's later study of those findings led to groundbreaking discoveries about spontaneous heat flow processes.

Similar to other thermodynamic properties, this new quantity is a state function, and so its change depends only upon the initial and final states of a system. In 1865, Clausius named this property entropy (S) and defined its change for any process as the following:

$$\Delta S = \frac{q_{rev}}{T} \tag{8.9.1}$$

The entropy change for a real, irreversible process is then equal to that for the theoretical reversible process that involves the same initial and final states.

Entropy and Microstates

Following the work of Carnot and Clausius, Ludwig Boltzmann developed a molecular-scale statistical model that related the entropy of a system to the number of *microstates* 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:

$$S = k \ln \Omega \tag{8.9.2}$$

Here k is the Boltzmann constant and has a value of $1.38 \times 10^{-23}\ J/K$.

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:

$$\begin{aligned} \Delta S &= S_f - S_i \\ &= k \ln \Omega_f - k \ln \Omega_i \\ &= k \ln \frac{\Omega_f}{\Omega_i} \end{aligned} \tag{8.9.3}$$

For processes involving an increase in the number of microstates of the system, $\Omega_f > \Omega_i$, the entropy of the system increases, $\Delta S > 0$. Conversely, processes that reduce the number of microstates in the system, $\Omega_f < \Omega_i$, yield a decrease in system entropy, ΔS

< 0. This molecular-scale interpretation of entropy provides a link to the probability that a process will occur as illustrated in the next paragraphs.

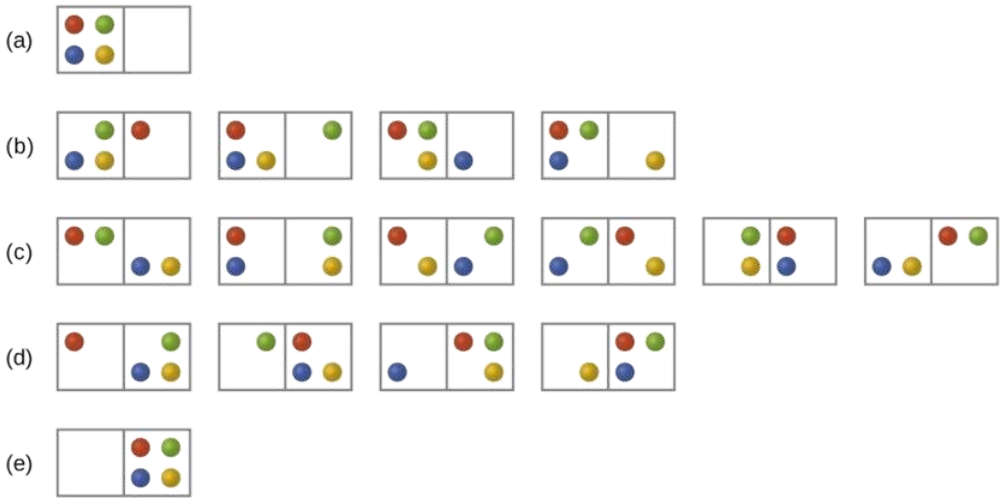


Figure 8.9.2: The sixteen microstates associated with placing four particles in two boxes are shown. The microstates are collected into five distributions—(a), (b), (c), (d), and (e)—based on the numbers of particles in each box.

Five rows of diagrams that look like dominoes are shown and labeled a, b, c, d, and e. Row a has one “domino” that has four dots on the left side, red, green, blue and yellow in a clockwise pattern from the top left, and no dots on the right. Row b has four “dominos,” each with three dots on the left and one dot on the right. The first shows a “domino” with green, yellow and blue on the left and red on the right. The second “domino” has yellow, blue and red on the left and green on the right. The third “domino” has red, green and yellow on the left and blue on the right while the fourth has red, green and blue on the left and yellow on the right. Row c has six “dominos”, each with two dots on either side. The first has a red and green on the left and a blue and yellow on the right. The second has a red and blue on the left and a green and yellow on the right while the third has a yellow and red on the left and a green and blue on the right. The fourth has a green and blue on the left and a red and yellow on the right. The fifth has a green and yellow on the left and a red and blue on the right. The sixth has a blue and yellow on the left and a green and red on the right. Row d has four “dominos,” each with one dot on the left and three on the right. The first “domino” has red on the left and a blue, green and yellow on the right. The second has a green on the left and a red, yellow and blue on the right. The third has a blue on the left and a red, green and yellow on the right. The fourth has a yellow on the left and a red, green and blue on the right. Row e has 1 “domino” with no dots on the left and four dots on the right that are red, green, blue and yellow.

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 8.9.2. Microstates with equivalent particle arrangements (not considering individual particle identities) are grouped together and are called *distributions* (sometimes called macrostates or configurations). The probability that a system will exist with its components in a given distribution is proportional to the number of microstates within the distribution. Since entropy increases logarithmically with the number of microstates, *the most probable distribution is therefore the one of greatest entropy*.

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 most probable distribution is therefore the one of greatest entropy.*

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.

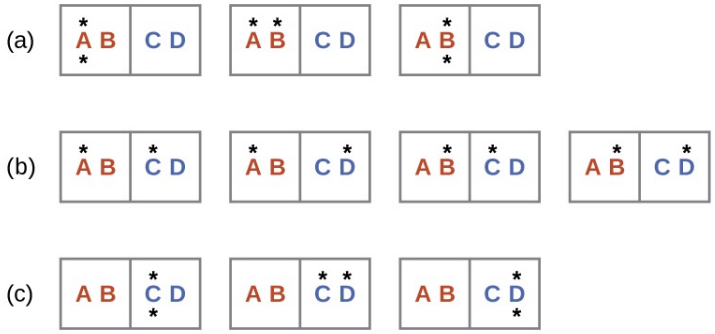


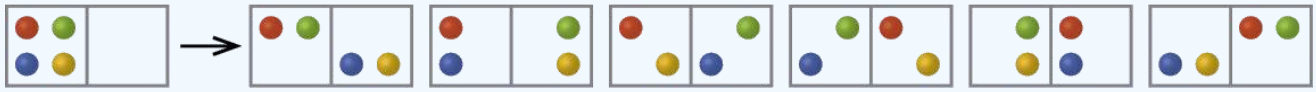
Figure **8.9.3**: This shows a microstate model describing the flow of heat from a hot object to a cold object. (a) Before the heat flow occurs, the object comprised of particles **A** and **B** contains both units of energy and as represented by a distribution of three microstates. (b) If the heat flow 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.

Three rows labeled a, b, and c are shown and each contains rectangles with two sides where the left side is labeled, “A,” and “B,” and the right is labeled, “C,” and “D.” Row a has three rectangles where the first has a dot above and below the letter A, the second has a dot above the A and B, and the third which has a dot above and below the letter B. Row b has four rectangles; the first has a dot above A and C, the second has a dot above A and D, the third has a dot above B and C and the fourth has a dot above B and D. Row c has three rectangles; the first has a dot above and below the letter C, the second has a dot above C and D and the third has a dot above and below the letter D.

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 **8.9.3**. 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 8.9.1: 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)?



A diagram shows one rectangle with two sides that has four dots, red, green, yellow and blue written on the left side. A right-facing arrow leads to six more two-sided rectangles, each with two dots on the left and right sides. The first rectangle has a red and green dot on the left and a blue and yellow on the right, while the second shows a red and blue on the left and a green and yellow on the right. The third rectangle has a red and yellow dot on the left and a blue and green on the right, while the fourth shows a green and blue on the left and a red and yellow on the right. The fifth rectangle has a yellow and green dot on the left and a blue and red on the right, while the sixth shows a yellow and blue on the left and a green and red on the right.

Solution

We are interested in the following change:

The initial number of microstates is one, the final six:

$$\begin{aligned}\Delta S &= k \ln \frac{\Omega_c}{\Omega_a} \\ &= 1.38 \times 10^{-23}\, J/K \times \ln \frac{6}{1} \\ &= 2.47 \times 10^{-23}\, J/K\end{aligned}$$

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 8.9.1

Consider the system shown in Figure **8.9.3**. What is the change in entropy for the process where *all* the energy is transferred from the hot object (**AB**) to the cold object (**CD**)?

Answer

0 J/K

Predicting the Sign of ΔS

The relationships between entropy, microstates, and matter/energy dispersal described previously allow us to make generalizations regarding the relative entropies of substances and to predict the sign of entropy changes for chemical and physical processes. Consider the phase changes illustrated in Figure **8.9.4**. 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, $\Delta S < 0$.

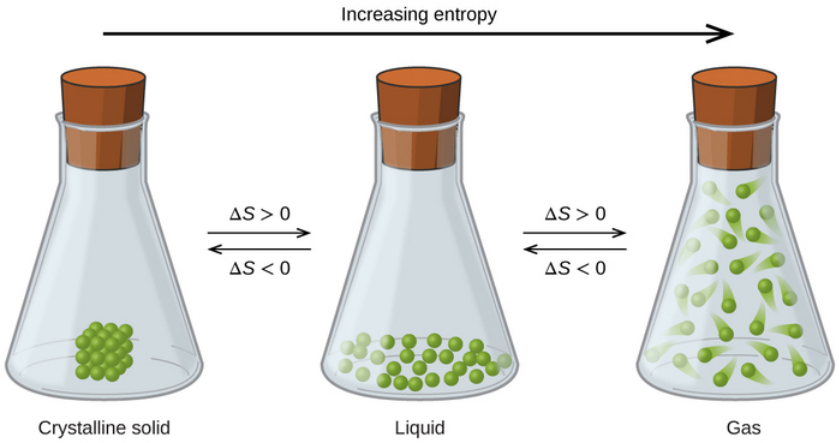


Figure **8.9.4**: The entropy of a substance increases (ΔS > 0) as it transforms from a relatively ordered solid, to a less-ordered liquid, and then to a still less-ordered gas. The entropy decreases (ΔS < 0) as the substance transforms from a gas to a liquid and then to a solid.

Three stoppered flasks are shown with right and left-facing arrows in between each; the first is labeled above as, “delta S greater than 0,” and below as, “delta S less than 0,” while the second is labeled above as, “delta S greater than 0,” and below as, “delta S less than 0.” A long, right-facing arrow is drawn above all the flasks and labeled, “Increasing entropy.” The left flask contains twenty-seven particles arranged in a cube in the bottom of the flask and is labeled, “Crystalline solid,” below. The middle flask contains twenty-seven particles dispersed randomly in the bottom of the flask and is labeled, “Liquid,” below. The right flask contains twenty-seven particles dispersed inside of the flask and moving rapidly and is labeled, “Gas,” below.

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, $S_{gas} > S_{liquid} > S_{solid}$, and the processes of vaporization and sublimation likewise involve increases in entropy, $\Delta S > 0$. Likewise, the reciprocal phase transitions, condensation and deposition, involve decreases in entropy, $\Delta S < 0$.

According to kinetic-molecular theory, the temperature of a substance is proportional to the average kinetic energy of its particles. Raising the temperature of a substance will result in more extensive vibrations of the particles in solids and more rapid translations of the particles in liquids and gases. At higher temperatures, the distribution of kinetic energies among the atoms or molecules of the substance is also broader (more dispersed) than at lower temperatures. Thus, the entropy for any substance increases with temperature (Figure **8.9.5**).

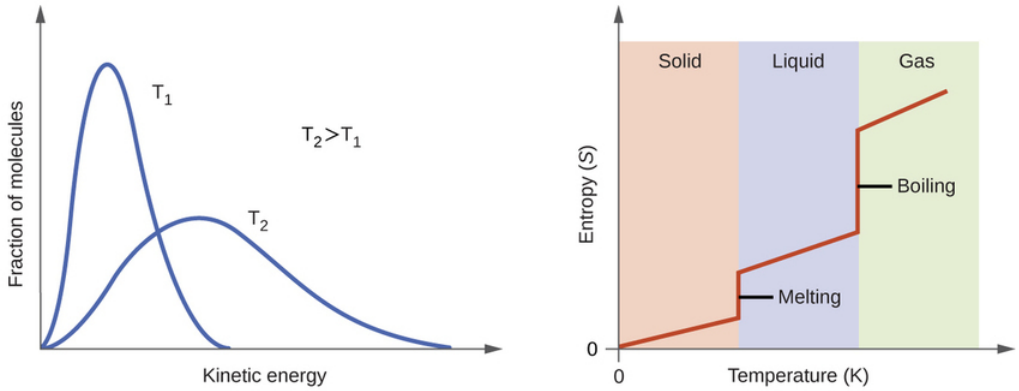


Figure 8.9.5: Entropy increases as the temperature of a substance is raised, which corresponds to the greater spread of kinetic energies. When a substance melts or vaporizes, it experiences a significant increase in entropy.

Two graphs are shown. The y-axis of the left graph is labeled, “Fraction of molecules,” while the x-axis is labeled, “Velocity, v (m / s),” and has values of 0 through 1,500 along the axis with increments of 500. Four lines are plotted on this graph. The first, labeled, “100 K,” peaks around 200 m / s while the second, labeled, “200 K,” peaks near 300 m / s and is slightly lower on the y-axis than the first. The third line, labeled, “500 K,” peaks around 550 m / s and is lower than the first two on the y-axis. The fourth line, labeled, “1000 K,” peaks around 750 m / s and is the lowest of the four on the y-axis. Each line get increasingly broad. The second graph has a y-axis labeled, “Entropy, S,” with an upward-facing arrow and an x-axis labeled, “Temperature (K),” and a right-facing arrow. The graph has three equally spaced columns in the background, labeled, “Solid,” “Liquid,” and, “Gas,” from left to right. A line extends slightly upward through the first column in a slight upward direction, then goes straight up in the transition between the first two columns. In then progresses in a slight upward direction through the second column, then goes up dramatically between the second and third columns, then continues in a slight upward direction once more. The first vertical region of this line is labeled, “Melting,” and the second is labeled, “Boiling.”

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 affects the entropy of a system. Compared to a pure substance, in which all particles are identical, the entropy of a mixture of two or more different particle types is greater. This is because of the additional orientations and interactions that are possible in a system comprised of nonidentical components. For example, when a solid dissolves in a liquid, the particles of the solid experience both a greater freedom of motion and additional interactions with the solvent particles. This corresponds to a more uniform dispersal of matter and energy and a greater number of microstates. The process of dissolution therefore involves an increase in entropy, $\Delta S > 0$.

Considering the various factors that affect entropy allows us to make informed predictions of the sign of ΔS for various chemical and physical processes as illustrated in Example .

Example 8.9.2: 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 8.9.2

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.

Key Equations

- $\Delta S = \frac{q_{\text{rev}}}{T}$
- $S = k \ln W$
- $\Delta S = k \ln \frac{W_{\text{f}}}{W_{\text{i}}}$

Glossary

entropy (*S*)
state function that is a measure of the matter and/or energy dispersal within a system, determined by the number of system microstates often described as a measure of the disorder of the system

microstate (*W*)
possible configuration or arrangement of matter and energy within a system

reversible process
process that takes place so slowly as to be capable of reversing direction in response to an infinitesimally small change in conditions; hypothetical construct that can only be approximated by real processes removed

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8.10: Gibbs Energy (Thermodynamics)

Learning Objectives

- Define Gibbs free energy, and describe its relation to spontaneity
- Calculate the standard free energy change for a process using standard free energies of formation for its reactants and products
- Calculate standard free energy change for a process using senthalpies of formation and the entropies for its reactants and products
- Explain how temperature affects the spontaneity of some processes
- Relate standard free energy changes to equilibrium constants

One of the challenges of using the second law of thermodynamics to determine if a chemical reaction is spontaneous is that we must determine the entropy change for the system *and* the entropy change for the surroundings. A second challenge when working with a chemical reaction is that we need to take into account the mixing of the substances, an issue that does not occur when observing the phase change if a pure substance. An alternative approach involving a new thermodynamic property defined in terms of system properties only was introduced in the late nineteenth century by American mathematician Josiah Willard Gibbs. This new property is called the Gibbs free energy (G) (or simply the *free energy*), and it is defined in terms of a system's enthalpy and entropy as the following:

$$G = H - TS$$

Free energy is a state function, and at constant temperature and pressure, the standard free energy change (ΔG°) may be expressed as the following:

$$\Delta G^{\circ}_{\text{sys}} = \Delta H^{\circ}_{\text{sys}} - T\Delta S^{\circ}_{\text{sys}}$$

(For simplicity's sake, the subscript "sys" will be omitted henceforth.) We can understand the relationship between this system property and the spontaneity of a process by recalling the previously derived second law expression:

$$\Delta S_{\text{univ}} = \Delta S + \frac{q_{\text{surr}}}{T}$$

The first law requires that $q_{surr} = -q_{sys}$, and at constant pressure $q_{sys} = \Delta H$, and so this expression may be rewritten as the following:

$$\Delta S_{\text{univ}} = \Delta S - \frac{\Delta H}{T}$$

ΔH is the enthalpy change of the system. Multiplying both sides of this equation by −T, and rearranging yields the following:

$$-T\Delta S_{\text{univ}} = \Delta H - T\Delta S$$

Comparing this equation to the previous one for free energy change shows the following relation:

$$\Delta G = -T\Delta S_{\text{univ}} \tag{8.10.1}$$

The free energy change is therefore a reliable indicator of the spontaneity of a process, being directly related to the previously identified spontaneity indicator, ΔS_{univ}. Table **8.10.1** summarizes the relation between the spontaneity of a process and the arithmetic signs of these indicators.

Table **8.10.1**: Relation between Process Spontaneity and Signs of Thermodynamic Properties

$\Delta S_{univ} > 0$	$\Delta G < 0$	moves spontaneously in the forward direction, as written, to reach equilibrium
$\Delta S_{univ} < 0$	$\Delta G > 0$	nonspontaneous in the forward direction, as written, but moves spontaneously in the reverse direction, as written, to reach equilibrium
$\Delta S_{univ} = 0$	$\Delta G = 0$	reversible (at equilibrium)

Calculating Free Energy Change

Free energy is a state function, so its value depends only on the conditions of the initial and final states of the system that have undergone some change. A convenient and common approach to the calculation of free energy changes for physical changes and chemical reactions is by use of widely available compilations of standard state thermodynamic data. One method involves the use of standard enthalpies and entropies to compute standard free energy changes according to the following relation as demonstrated in Example 8.10.1.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{8.10.2}$$

It is important to understand that for phase changes, ΔG° tells you if the phase change is spontaneous or not; will it happen, or not happen. For chemical reactions, ΔG° tells you the **extent** of a reaction. In other words, ΔG° for a reaction tells you how much product will be present at equilibrium. A reaction with $\Delta G^\circ < 0$ is considered **product-favored at equilibrium**; there will be more products than reactants when the reaction reaches equilibrium. A reaction with $\Delta G^\circ > 0$ is considered **reactant-favored at equilibrium**; there will be more reactants than products when the reaction reaches equilibrium.

Example 8.10.1: Evaluation of ΔG° for a Phase Change of a Pure Substance

Use standard enthalpy and entropy data from Tables T1 or T2 to calculate the standard free energy change for the vaporization of water at room temperature (298 K). What does the computed value for ΔG° say about the spontaneity of this physical change for a pure substance?

Solution

The process of interest is the following:

$$\mathrm{H_2O}(l) \longrightarrow \mathrm{H_2O}(g) \tag{8.10.3}$$

The standard change in free energy may be calculated using the following equation:

$$\Delta G^\circ_{298} = \Delta H^\circ - T\Delta S^\circ \tag{8.10.4}$$

From Tables T1 or T2, here are the data:

Data from Tables T1 or T2

Substance	ΔH°_f (kJ/mol)	S°_{298} (J/K·mol)
$H_2O(l)$	−286.83	70.0
$H_2O(g)$	−241.82	188.8

Combining at 298 K:

$$\begin{aligned}\Delta H^\circ = \Delta H^\circ_{298} &= \Delta H^\circ_f(\mathrm{H_2O}(g)) - \Delta H^\circ_f(\mathrm{H_2O}(l)) \\ &= [-241.82\ kJ - (-285.83)]\ kJ/mol \\ &= 44.01\ kJ/mol \\ \Delta S^\circ = \Delta S^\circ_{298} &= S^\circ_{298}(\mathrm{H_2O}(g)) - S^\circ_{298}(\mathrm{H_2O}(l)) \\ &= 188.8\ J/mol \cdot K - 70.0\ J/K \\ &= 118.8\ J/mol \cdot K\end{aligned}$$

then use Equation 8.10.2:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Converting everything into kJ and combining at 298 K:

$$\begin{aligned}\Delta G^\circ_{298} &= \Delta H^\circ - T\Delta S^\circ \\ &= 44.01\ kJ/mol - (298\ K \times 118.8\ J/mol \cdot K) \times \frac{1\ kJ}{1000\ J} \\ &\mathrm{44.01\ kJ/mol - 35.4\ kJ/mol = 8.6\ kJ/mol}\end{aligned}$$

At 298 K (25 °C) $\Delta G^\circ_{298} > 0$, and so boiling is nonspontaneous (not spontaneous) at 298 K.

? Exercise 8.10.1: Evaluation of ΔG° for a Chemical Reaction

Use standard enthalpy and entropy data from Tables T1 or T2 to calculate the standard free energy change for the reaction shown here (298 K). What does the computed value for ΔG° say about the extent of this reaction at 298 K?

$$\mathrm{C_2H_6}(g) \longrightarrow \mathrm{H_2}(g) + \mathrm{C_2H_4}(g)$$

Answer

$\Delta G^\circ_{298} = \mathrm{102.0\ kJ/mol}$; the reaction is reactant-favored at equilibrium at 25 °C. There will be more $\mathrm{C_2H_6}(g)$ than $\mathrm{H_2}(g)$ and $\mathrm{C_2H_4}(g)$ at equilibrium

Free energy changes may also use the standard free energy of formation (ΔG°_f), for each of the reactants and products involved in the reaction. The standard free energy of formation is the free energy change that accompanies the formation of one mole of a substance from its elements in their standard states. Similar to the standard enthalpies of formation, (ΔG°_f) is by definition zero for elemental substances under standard state conditions. The approach to computing the free energy change for a reaction using this approach is the same as that demonstrated previously for enthalpy and entropy changes. For the reaction

$$m\mathrm{A} + n\mathrm{B} \longrightarrow x\mathrm{C} + y\mathrm{D},$$

the standard free energy change at room temperature may be calculated as

$$\Delta G^\circ_{298} = \Delta G^\circ \tag{8.10.5}$$

$$= \sum \nu \Delta G^\circ_{298}(\mathrm{products}) - \sum \nu \Delta G^\circ_{298}(\mathrm{reactants}) \tag{8.10.6}$$

$$= [x\Delta G^\circ_f(\mathrm{C}) + y\Delta G^\circ_f(\mathrm{D})] - [m\Delta G^\circ_f(\mathrm{A}) + n\Delta G^\circ_f(\mathrm{B})]. \tag{8.10.7}$$

✓ Example 8.10.2: Calculation of ΔG°_{298}

Consider the decomposition of yellow mercury(II) oxide.

$$\mathrm{HgO}(s,\ \mathrm{yellow}) \longrightarrow \mathrm{Hg}(l) + \tfrac{1}{2}\,\mathrm{O_2}\,(\mathrm{g})$$

Calculate the standard free energy change at room temperature, ΔG°_{298}, using:

a. standard free energies of formation and
b. standard enthalpies of formation and standard entropies.

Do the results indicate the reaction to be product-favored or reactant-favored at equilibrium?

Solution

The required data are available in Tables T1 or T2 and are shown here.

Required data for Tables T1 or T2

Compound	ΔG_f° (kJ/mol)	ΔH_f° (kJ/mol)	S_{298}° (J/K·mol)
HgO (*s*, yellow)	−58.43	−90.46	71.13
Hg(*l*)	0	0	75.9
$O_2(g)$	0	0	205.2

(a) Using free energies of formation:

$$\begin{aligned}\Delta G_{298}^\circ &= \sum \nu G S_{298}^\circ(\text{products}) - \sum \nu \Delta G_{298}^\circ(\text{reactants}) \\ &= \left[1\Delta G_{298}^\circ \text{Hg}(l) + \frac{1}{2}\Delta G_{298}^\circ \text{O}_2(g)\right] - 1\Delta G_{298}^\circ \text{HgO}(s,\text{ yellow}) \\ &= \left[1\text{ mol}(0\text{ kJ/mol}) + \frac{1}{2}\text{mol}(0\text{ kJ/mol})\right] - 1\text{ mol}(-58.43\text{ kJ/mol}) = 58.43\text{ kJ/mol}\end{aligned}$$

(b) Using enthalpies and entropies of formation:

$$\begin{aligned}\Delta H_{298}^\circ &= \sum \nu \Delta H_{298}^\circ(\text{products}) - \sum \nu \Delta H_{298}^\circ(\text{reactants}) \\ &= \left[1\Delta H_{298}^\circ \text{Hg}(l) + \frac{1}{2}\Delta H_{298}^\circ \text{O}_2(g)\right] - 1\Delta H_{298}^\circ \text{HgO}(s,\text{ yellow}) \\ &= [1\text{ mol}(0\text{ kJ/mol}) + \frac{1}{2}\text{mol}(0\text{ kJ/mol})] - 1\text{ mol}(-90.46\text{ kJ/mol}) = 90.46\text{ kJ/mol} \\ \Delta S_{298}^\circ &= \sum \nu \Delta S_{298}^\circ(\text{products}) - \sum \nu \Delta S_{298}^\circ(\text{reactants}) \\ &= \left[1\Delta S_{298}^\circ \text{Hg}(l) + \frac{1}{2}\Delta S_{298}^\circ \text{O}_2(g)\right] - 1\Delta S_{298}^\circ \text{HgO}(s,\text{ yellow}) \\ &= \left[1\text{ mol}(75.9\text{ J/mol K}) + \frac{1}{2}\text{mol}(205.2\text{ J/mol K})\right] - 1\text{ mol}(71.13\text{ J/mol K}) \\ &= 107.4\text{ J/mol K}\end{aligned}$$

then we can use Equation \ref7} directly:

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= 90.46\text{ kJ} - 298.15\text{ K} \times 107.4\text{ J/K}\cdot\text{mol} \times \frac{1\text{ kJ}}{1000\text{ J}} \\ &= (90.46 - 32.01)\text{ kJ/mol} = 58.45\text{ kJ/mol}\end{aligned}$$

Both ways to calculate the standard free energy change at 25 °C give the same numerical value (to three significant figures), and both predict that the process is reactant-favored at equilibrium at room temperature.

? Exercise 8.10.2

Calculate ΔG° using (a) free energies of formation and (b) enthalpies of formation and entropies (Tables T1 or T2). Do the results indicate the reaction to be product-favored or reactant-favored at equilibrium at 25 °C?

$$C_2H_4(g) \longrightarrow H_2(g) + C_2H_2(g)$$

Answer

141.5 kJ/mol, reactant-favored at equilibrium

Temperature Dependence of Spontaneity and Extent of Reaction

As was previously demonstrated in this chapter's section on entropy, the spontaneity of a process may depend upon the temperature of the system. Phase transitions, for example, will proceed spontaneously in one direction or the other depending upon the temperature of the substance in question. In a similar, but not identical fashion, some chemical reactions can switch from being product-favored at equilibrium, to being reactant-favored at equilibrium, depending on the temperature.

> **Note**
>
> The numerical value of ΔG° is always dependent on the temperature. In this section we are determining whether or not the **sign** of ΔG° is dependent on the temperature.

To illustrate this concept, the equation relating free energy change to the enthalpy and entropy changes for the process is considered:

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

The extent of a process, as reflected in the arithmetic sign of its standard free energy change, is then determined by the signs of the enthalpy and entropy changes and, in some cases, the absolute temperature. Since T is the absolute (Kelvin) temperature, it can only have positive values. Four possibilities therefore exist with regard to the signs of the enthalpy and entropy changes:

1. **Both ΔH^{o} and ΔS^{o} are positive.** This condition describes an endothermic process that involves an increase in system entropy. In this case, ΔG^{o} will be negative if the magnitude of the $T\Delta S^{o}$ term is greater than ΔH^{o}. If the $T\Delta S^{o}$ term is less than ΔH^{o}, the free energy change will be positive. Such a process is *product-favored at equilibrium at high temperatures and reactant-favored at equilibrium at low temperatures.*
2. **Both ΔH^{o} and ΔS^{o} are negative.** This condition describes an exothermic process that involves a decrease in system entropy. In this case, ΔG^{o} will be negative if the magnitude of the $T\Delta S^{o}$ term is less than ΔH^{o}. If the $T\Delta S^{o}$ term's magnitude is greater than ΔH^{o}, the free energy change will be positive. Such a process is *product-favored at equilibrium at low temperatures* and *reactant-favored at equilibrium at high temperatures.*
3. **ΔH^{o} is positive and ΔS^{o} is negative.** This condition describes an endothermic process that involves a decrease in system entropy. In this case, ΔG^{o} will be positive regardless of the temperature. Such a process is *reactant-favored at equilibrium at all temperatures.*
4. **ΔH^{o} is negative and ΔS^{o} is positive.** This condition describes an exothermic process that involves an increase in system entropy. In this case, ΔG^{o} will be negative regardless of the temperature. Such a process is *product-favored at equilibrium at all temperatures.*

These four scenarios are summarized in Table **8.10.1**

Table **8.10.1**

Sign of ΔH^o	Sign of ΔS^o	Sign of ΔG^o	Temperature Dependence of ΔG^o
-	+	-	The sign of ΔG^o does not depend on the temperature.The reaction is product-favored at equilibrium at all temperatures.
+	-	+	The sign of ΔG^o does not depend on the temperature.The reaction is reactant-favored at equilibrium at all temperatures.
-	-	- or +	The sign of ΔG^o **does** depend on the temperature. The reaction will be product-favored at equilibrium at lower temperatures.
+	+	- or +	The sign of ΔG^o **does** depend on the temperature. The reaction will be product-favored at equilibrium at lower temperatures.

Example 8.10.3: Predicting the Temperature Dependence of Spontaneity

The incomplete combustion of carbon is described by the following equation:

$$2\,C(s) + O_2(g) \longrightarrow 2\,CO(g)$$

Does the sign of ΔG^o of this process depend upon temperature?

Solution

Combustion processes are exothermic ($\Delta H^o < 0$). This particular reaction involves an increase in entropy due to the accompanying increase in the amount of gaseous species (net gain of one mole of gas, $\Delta S^o > 0$). The reaction is therefore product-favored at equilibrium ($\Delta G^o < 0$) at all temperatures.

Exercise 8.10.3

Popular chemical hand warmers generate heat by the air-oxidation of iron:

$$4\,Fe(s) + 3\,O_2(g) \longrightarrow 2\,Fe_2O_3(s)$$

Does the sign of ΔG^o of this process depend upon temperature?

Answer

ΔH^o and ΔS^o are both negative; the reaction is product-favored at equilibrium at low temperatures.

When considering the conclusions drawn regarding the temperature dependence of the sign of ΔG^o, it is important to keep in mind what the terms “high” and “low” mean. Since these terms are adjectives, the temperatures in question are deemed high or low relative to some reference temperature. A process that is reactant-favored at equilibrium at one temperature but product-favored at equilibrium at another temperature will necessarily undergo a change in “extent” (as reflected by its ΔG^o) as temperature varies.

This is clearly illustrated by a graphical presentation of the free energy change equation, in which ΔG^o is plotted on the *y* axis versus *T* on the *x* axis:

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

$$y = b + mx$$

Such a plot is shown in Figure **8.10.2**. A process whose enthalpy and entropy changes are of the same arithmetic sign will exhibit a temperature-dependence for the sign of ΔG^o as depicted by the two yellow lines in the plot. Each line crosses from one spontaneity domain (positive or negative ΔG^o) to the other at a temperature that is characteristic of the process in question. This temperature is represented by the *x*-intercept of the line, that is, the value of *T* for which ΔG^o is zero:

$$\Delta G^o = 0 = \Delta H^o - T\Delta S^o$$

$$T = \frac{\Delta H^o}{\Delta S^o}$$

Thus, saying a process is product-favored at equilibrium at “high” or “low” temperatures means the temperature is above or below, respectively, that temperature at which ΔG^o for the process is zero.

Note

In this discussion, we have used two different descriptions for the meaning of the sign of ΔG^o. You should be aware of the meaning of each description.

a) **Extent of Reaction:** This description is used to predict the ratio of the product and reactant concentrations at equilibrium. In this description, we use the thermodynamic term ΔG^o to tell us the same information as the equilibrium constant, K. When $\Delta G^o < 0$, K > 1, and the reaction will be product-favored at equilibrium. When $\Delta G^o > 0$, K< 1, and the reaction is reactant-favored at equilibrium. When $\Delta G^o = 0$, K =1, and the reaction will have roughly equal amounts of products and reactants at equilibrium. In all cases, the reaction will form a mixture of products and reactants at equilibrium. We use the sign and magnitude of ΔG^o to tell us how much product will be made if the reaction is allowed to reach equilibrium.

b) **Spontaneity:** This description is much more complicated because it involves two different interpretations of how a reaction at standard state occurs. One interpretation involves the hypothetical process in which the reaction proceeds from a starting point of pure reactants to a finishing point of pure products, with all substances isolated in their own containers under standard state conditions. In the second, more realistic interpretation, the reaction starts with all reactants and all products in their standard state in one container. We then allow this specific mixture to react an infinitesimally small amount so that we can obtain a rate of change in free energy with respect to the extent of reaction when all reactants and products are mixed and (essentially) in their standard states. Although each interpretation describes a different reaction scenario, the value of the difference in free energy and the value of the rate of change in free energy are the same number. If $\Delta G^o < 0$, we say that the reaction is spontaneous, meaning that the reaction would proceed in the forward direction, as written, to form pure products in their standard state. If $\Delta G^o > 0$, we say that the reaction is nonspontaneous, meaning that the reaction would proceed in the reverse direction, as written, to form pure reactants in their standard state. If $\Delta G^o = 0$, we say that the neither the reactants nor the products are favored to be formed.

A detailed treatment of the meaning of ΔG^o can be found in the paper, "Free Energy versus Extent of Reaction" by Richard S. Treptow, Journal of Chemical Education, **1996**, Volume 73 (1), 51-54.

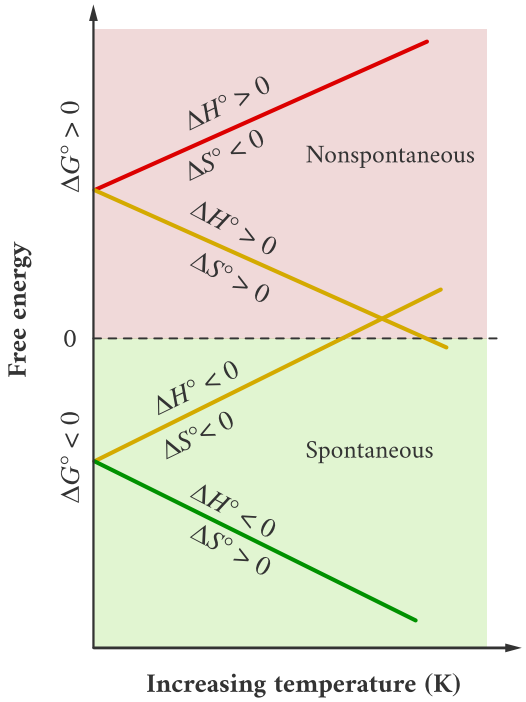


Figure **8.10.2**: These plots show the variation in ΔG° with temperature for the four possible combinations of arithmetic sign for ΔH° and ΔS°. Note that in this graph of ΔG°, "spontaneous" is synonymous with "product-favored at equilibrium", and "nonspontaneous" is synonymous with "reactant-favored at equilibrium".

Example 8.10.4: Equilibrium Temperature for a Phase Transition

As defined in the chapter on liquids and solids, the boiling point of a liquid is the temperature at which its solid and liquid phases are in equilibrium (that is, when vaporization and condensation occur at equal rates). Use the information in Tables T1 or T2 to estimate the boiling point of water.

Solution

The process of interest is the following phase change:

$$\mathrm{H_2O}(l) \longrightarrow \mathrm{H_2O}(g)$$

When this process is at equilibrium, $\Delta G = 0$, so the following is true:

$$0 = \Delta H^\circ - T\Delta S^\circ \qquad \text{or} \qquad T = \frac{\Delta H^\circ}{\Delta S^\circ}$$

Using the standard thermodynamic data from Tables T1 or T2,

$$\begin{aligned}\Delta H^\circ &= \Delta H_f^\circ(\mathrm{H_2O}(g)) - \Delta H_f^\circ(\mathrm{H_2O}(l)) \\ &= -241.82\ \mathrm{kJ/mol} - (-285.83\ \mathrm{kJ/mol}) = 44.01\ \mathrm{kJ/mol}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= \Delta S_{298}^\circ(\mathrm{H_2O}(g)) - \Delta S_{298}^\circ(\mathrm{H_2O}(l)) \\ &= 188.8\ \mathrm{J/K \cdot mol} - 70.0\ \mathrm{J/K \cdot mol} = 118.8\ \mathrm{J/K \cdot mol}\end{aligned}$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{44.01 \times 10^3\ \mathrm{J/mol}}{118.8\ \mathrm{J/K \cdot mol}} = 370.5\ \mathrm{K} = 97.3\ ^\circ\mathrm{C}$$

The accepted value for water's normal boiling point is 373.2 K (100.0 °C), and so this calculation is in reasonable agreement. Note that the values for enthalpy and entropy changes data used were derived from standard data at 298 K (Tables T1 or T2.). If desired, you could obtain more accurate results by using enthalpy and entropy changes determined at (or at least closer to) the actual boiling point.

Exercise 8.10.4

Use the information in Tables T1 or T2 to estimate the boiling point of CS_2.

Answer

313 K (accepted value 319 K).

Free Energy and Equilibrium

The free energy change for a process may be viewed as a measure of its driving force. A negative value for ΔG represents a finite driving force for the process in the forward direction, while a positive value represents a driving force for the process in the reverse direction. When ΔG is zero, the forward and reverse driving forces are equal, and so the process occurs in both directions at the same rate (the system is at equilibrium).

In the chapter on equilibrium the *reaction quotient*, Q, was introduced as a convenient measure of the status of an equilibrium system. Recall that Q is the numerical value of the mass action expression for the system, and that you may use its value to identify the direction in which a reaction will proceed in order to achieve equilibrium. When Q is lesser than the equilibrium constant, K, the reaction will proceed in the forward direction until equilibrium is reached and $Q = K$. Conversely, if $Q > K$, the process will proceed in the reverse direction until equilibrium is achieved.

The free energy change for a process taking place with reactants and products present under nonstandard conditions, ΔG, is related to the standard free energy change, $\Delta G°$, according to this equation:

$$\Delta G = \Delta G° + RT \ln Q \tag{8.10.8}$$

R is the gas constant (8.314 J/K mol), T is the kelvin or absolute temperature, and Q is the reaction quotient. We may use this equation to predict the spontaneity for a process under any given set of conditions as illustrated in Example 8.10.1.

Example 8.10.5: Calculating ΔG under Nonstandard Conditions

What is the free energy change for the process shown here under the specified conditions?

T = 25 °C, $P_{N_2} = 0.870\ \text{atm}$, $P_{H_2} = 0.250\ \text{atm}$, and $P_{NH_3} = 12.9\ \text{atm}$

$$2\,NH_3(g) \longrightarrow 3\,H_2(g) + N_2(g) \quad \Delta G° = 33.0\ \text{kJ/mol}$$

Solution

Equation 8.10.8 relates free energy change to standard free energy change and reaction quotient and may be used directly:

$$\begin{aligned}\Delta G &= \Delta G° + RT \ln Q \\ &= 33.0\ \frac{\text{kJ}}{\text{mol}} + \left(8.314\ \frac{\text{J}}{\text{mol K}} \times 298\ \text{K} \times \ln \frac{(0.250^3) \times 0.870}{12.9^2}\right) \\ &= 9680\ \frac{\text{J}}{\text{mol}}\ \text{or}\ 9.68\ \text{kJ/mol}\end{aligned}$$

Since the computed value for ΔG is positive, the reaction is nonspontaneous under these conditions. The reaction will proceed in the reverse direction to reach equilibrium.

Exercise 8.10.5

Calculate the free energy change for this same reaction at 875 °C in a 5.00 L mixture containing 0.100 mol of each gas. Is the reaction spontaneous under these conditions?

Answer

ΔG = −47 kJ; yes, the reaction proceeds in the forward direction, as written, to reach equilibrium.

For a system at equilibrium, $Q = K$ and $\Delta G = 0$, and the Equation 8.10.8 may be written as

$$\underbrace{0 = \Delta G^\circ + RT\ln K}_{\text{at equilibrium}}$$

$$\Delta G^\circ = -RT\ln K \tag{8.10.9}$$

or alternatively

$$K = e^{-\frac{\Delta G^\circ}{RT}} \tag{8.10.10}$$

This form of the equation provides a useful link between these two essential thermodynamic properties, and it can be used to derive equilibrium constants from standard free energy changes and vice versa. The relations between standard free energy changes and equilibrium constants are summarized in Table 8.10.1.

Table 8.10.1: Relations between Standard Free Energy Changes and Equilibrium Constants

K	ΔG°	Comments
< 1	> 0	Reactants are more abundant at equilibrium.
= 1	= 0	Reactants and products are equally abundant at equilibrium.
> 1	< 0	Products are more abundant at equilibrium.

Example 8.10.6: Equilibrium Constant using Standard Free Energy Change

Given that the standard free energies of formation of $Ag^+(aq)$, $Cl^-(aq)$, and $AgCl(s)$ are 77.1 kJ/mol, −131.2 kJ/mol, and −109.8 kJ/mol, respectively, calculate the solubility product, K_{sp}, for AgCl.

Solution

The reaction of interest is the following:

$$\mathrm{AgCl}(s) \rightleftharpoons \mathrm{Ag^+}(aq) + \mathrm{Cl^-}(aq) \quad K_{sp} = [\mathrm{Ag^+}][\mathrm{Cl^-}]$$

The standard free energy change for this reaction is first computed using standard free energies of formation for its reactants and products:

$$\begin{aligned}\Delta G^\circ = \Delta G^\circ_{298} &= [\Delta G^\circ_f(\mathrm{Ag^+}(aq)) + \Delta G^\circ_f(\mathrm{Cl^-}(aq))] - [\Delta G^\circ_f(\mathrm{AgCl}(s))] \\ &= [77.1\ kJ/mol - 131.2\ kJ/mol] - [-109.8\ kJ/mol] \\ &= 55.7\ kJ/mol\end{aligned}$$

The equilibrium constant for the reaction may then be derived from its standard free energy change via Equation 8.10.10:

$$\begin{aligned}K_{sp} = e^{-\frac{\Delta G^\circ}{RT}} &= \exp\left(-\frac{\Delta G^\circ}{RT}\right) \\ &= \exp\left(-\frac{55.7 \times 10^3\ \mathrm{J/mol}}{8.314\ \mathrm{J/mol \cdot K} \times 298.15\ \mathrm{K}}\right) \\ &= \exp(-22.470) = e^{-22.470} = 1.74 \times 10^{-10}\end{aligned}$$

Exercise 8.10.6: dissociation of dinitrogen tetroxide

Use the thermodynamic data provided in Tables T1 or T2 to calculate the equilibrium constant for the dissociation of dinitrogen tetroxide at 25 °C.

$$\mathrm{NO_{2(g)}} \rightleftharpoons \mathrm{N_2O_{4(g)}}$$

Answer

K = 6.9

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 **8.10.3**). 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.

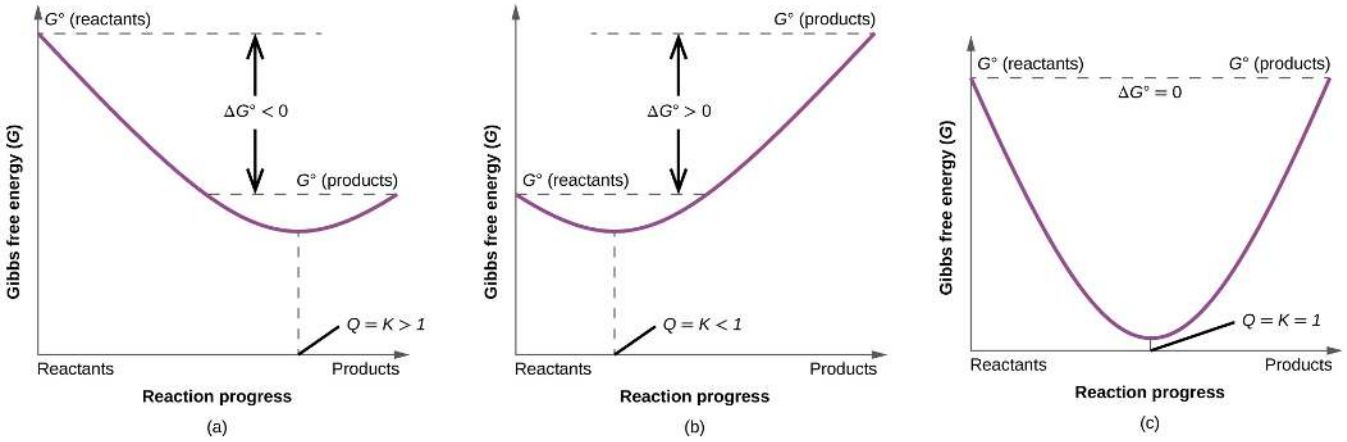


Figure **8.10.3**: These plots show the free energy versus reaction progress for systems whose standard free changes are (a) negative, (b) positive, and (c) zero. Nonequilibrium systems will proceed spontaneously in whatever direction is necessary to minimize free energy and establish equilibrium. Note that reactions with K equal to exactly 1.000 are rare.

Summary

Gibbs free energy (G) is a state function defined with regard to system quantities only and may be used to predict the spontaneity of a process. A negative value for ΔG indicates that the process will proceed in the forward direction to reach equilibrium; a positive ΔG indicates that the process will proceed in the reverse direction to reach equilibrium ; and a ΔG of zero indicates that the system is at equilibrium. A negative value for ΔG^o means that the reaction is product-favored at equilibrium. A positive value for ΔG^o means that the reaction is reactant-favored at equilibrium. If ΔG^o equals 0 (a rare occurrence), the reaction has roughly equal amounts of reactants and products at equilibrium.A number of approaches to the computation of free energy changes are possible.

Key Equations

- $\Delta G = \Delta H - T\Delta S$
- $\Delta G = \Delta G° + RT \ln Q$
- $\Delta G° = -RT \ln K$

Glossary

Gibbs free energy change (G)
thermodynamic property defined in terms of system enthalpy and entropy; all spontaneous processes involve a decrease in G

standard free energy change ($\Delta G°$)
change in free energy for a process occurring under standard conditions (1 bar pressure for gases, 1 M concentration for solutions)

standard free energy of formation (ΔG_f°)
change in free energy accompanying the formation of one mole of substance from its elements in their standard states

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CHAPTER OVERVIEW

9: Electrochemistry

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General Chemistry

Electrochemistry deals with chemical reactions that produce electricity and the changes associated with the passage of electrical current through matter. The reactions involve electron transfer, and so they are oxidation-reduction (or redox) reactions. Many metals may be purified or electroplated using electrochemical methods. Devices such as automobiles, smartphones, electronic tablets, watches, pacemakers, and many others use batteries for power. Batteries use chemical reactions that produce electricity spontaneously and that can be converted into useful work. All electrochemical systems involve the transfer of electrons in a reacting system. In many systems, the reactions occur in a region known as the cell, where the transfer of electrons occurs at electrodes.

9.1: Balancing Oxidation-Reduction Reactions
9.2: Galvanic Cells
9.3: Standard Reduction Potentials
9.4: The Nernst Equation
9.5: Batteries and Fuel Cells
9.6: Corrosion
9.7: Electrolysis
9.E: Electrochemistry (Exercises)

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9.1: Balancing Oxidation-Reduction Reactions

Learning Objectives

- Define electrochemistry and a number of important associated terms
- Split oxidation-reduction reactions into their oxidation half-reactions and reduction half-reactions
- Produce balanced oxidation-reduction equations for reactions in acidic or basic solution
- Identify oxidizing agents and reducing agents

Electricity refers to a number of phenomena associated with the presence and flow of electric charge. Electricity includes such diverse things as lightning, static electricity, the current generated by a battery as it discharges, and many other influences on our daily lives. The flow or movement of charge is an electric current (Figure **9.1.1**). Electrons or ions may carry the charge. The elementary unit of charge is the charge of a proton, which is equal in magnitude to the charge of an electron. The SI unit of charge is the coulomb (C) and the charge of a proton is 1.602×10^{-19} C. The presence of an electric charge generates an electric field. Electric current is the rate of flow of charge.



Figure **9.1.1**: Electricity-related phenomena include lightning, accumulation of static electricity, and current produced by a battery. (credit left: modification of work by Thomas Bresson; credit middle: modification of work by Chris Darling; credit right: modification of work by Windell Oskay).

The SI unit for electrical current is the SI base unit called the ampere (A), which is a flow rate of 1 coulomb of charge per second (1 A = 1 C/s). An electric current flows in a path, called an electric circuit. In most chemical systems, it is necessary to maintain a closed path for current to flow. The flow of charge is generated by an electrical potential difference, or potential, between two points in the circuit. Electrical potential is the ability of the electric field to do work on the charge. The SI unit of electrical potential is the volt (V). When 1 coulomb of charge moves through a potential difference of 1 volt, it gains or loses 1 joule (J) of energy. Table **9.1.1** summarizes some of this information about electricity.

Table **9.1.1**: Common Electrical Terms

Quantity	Definition	Measure or Unit
Electric charge	Charge on a proton	1.602×10^{-19} C
Electric current	The movement of charge	ampere = A = 1 C/s
Electric potential	The force trying to move the charge	volt = V = J/C
Electric field	The force acting upon other charges in the vicinity	

Electrochemistry studies oxidation-reduction reactions, which were first discussed in an earlier chapter, where we learned that oxidation was the loss of electrons and reduction was the gain of electrons. The reactions discussed tended to be rather simple, and conservation of mass (atom counting by type) and deriving a correctly balanced chemical equation were relatively simple. In this section, we will concentrate on the half-reaction method for balancing oxidation-reduction reactions. The use of half-reactions is important partly for balancing more complicated reactions and partly because many aspects of electrochemistry are easier to discuss in terms of half-reactions. There are alternate methods of balancing these reactions; however, there are no good alternatives to half-reactions for discussing what is occurring in many systems. The half-reaction method splits oxidation-reduction reactions into their oxidation “half” and reduction “half” to make finding the overall equation easier.

Electrochemical reactions frequently occur in solutions, which could be acidic, basic, or neutral. When balancing oxidation-reduction reactions, the nature of the solution may be important. It helps to see this in an actual problem. Consider the following unbalanced oxidation-reduction reaction in acidic solution:

$$\mathrm{MnO_4^-}(aq) + \mathrm{Fe^{2+}}(aq) \longrightarrow \mathrm{Mn^{2+}}(aq) + \mathrm{Fe^{3+}}(aq)$$

We can start by collecting the species we have so far into an unbalanced oxidation half-reaction and an unbalanced reduction half-reaction. Each of these half-reactions contain the same element in two different oxidation states. The Fe^{2+} has lost an electron to become Fe^{3+}; therefore, the iron underwent oxidation. The reduction is not as obvious; however, the manganese gained five electrons to change from Mn^{7+} to Mn^{2+}.

$$\text{oxidation (unbalanced): } \mathrm{Fe^{2+}}(aq) \longrightarrow \mathrm{Fe^{3+}}(aq)$$
$$\text{reduction (unbalanced): } \mathrm{MnO_4^-}(aq) \longrightarrow \mathrm{Mn^{2+}}(aq)$$

In acidic solution, there are hydrogen ions present, which are often useful in balancing half-reactions. It may be necessary to use the hydrogen ions directly or as a reactant that may react with oxygen to generate water. Hydrogen ions are very important in acidic solutions where the reactants or products contain hydrogen and/or oxygen. In this example, the oxidation half-reaction involves neither hydrogen nor oxygen, so hydrogen ions are not necessary to the balancing. However, the reduction half-reaction does involve oxygen. It is necessary to use hydrogen ions to convert this oxygen to water.

$$\text{charge not balanced: } \mathrm{MnO_4^-}(aq) + 8\,\mathrm{H^+}(aq) \longrightarrow \mathrm{Mn^{2+}}(aq) + 4\,\mathrm{H_2O}(l)$$

The situation is different in basic solution because the hydrogen ion concentration is lower and the hydroxide ion concentration is higher. After finishing this example, we will examine how basic solutions differ from acidic solutions. A neutral solution may be treated as acidic or basic, though treating it as acidic is usually easier.

The iron atoms in the oxidation half-reaction are balanced (mass balance); however, the charge is unbalanced, since the charges on the ions are not equal. It is necessary to use electrons to balance the charge. The way to balance the charge is by *adding* electrons to one side of the equation. Adding a single electron on the right side gives a balanced oxidation half-reaction:

$$\text{oxidation (balanced): } \mathrm{Fe^{2+}}(aq) \longrightarrow \mathrm{Fe^{3+}}(aq) + \mathrm{e^-}$$

You should check the half-reaction for the number of each atom type and the total charge on each side of the equation. The charges include the actual charges of the ions times the number of ions and the charge on an electron times the number of electrons.

$$\text{Fe: Does } (1 \times 1) = (1 \times 1)\text{? Yes.}$$
$$\text{Charge: Does } [1 \times (+2)] = [1 \times (+3) + 1 \times (-1)]\text{? Yes.}$$

If the atoms and charges balance, the half-reaction is balanced. In oxidation half-reactions, electrons appear as products (on the right). As discussed in the earlier chapter, since iron underwent oxidation, iron is the reducing agent.

Now return to the reduction half-reaction equation:

$$\text{reduction (unbalanced): } \mathrm{MnO_4^-}(aq) + 8\,\mathrm{H^+}(aq) \longrightarrow \mathrm{Mn^{2+}}(aq) + 4\,\mathrm{H_2O}(l)$$

The atoms are balanced (mass balance), so it is now necessary to check for charge balance. The total charge on the left of the reaction arrow is [(−1) × (1) + (8) × (+1)], or +7, while the total charge on the right side is [(1) × (+2) + (4) × (0)], or +2. The difference between +7 and +2 is five; therefore, it is necessary to add five electrons to the left side to achieve charge balance.

$$\text{Reduction (balanced): } \mathrm{MnO_4^-}(aq) + 8\,\mathrm{H^+}(aq) + 5\,\mathrm{e^-} \longrightarrow \mathrm{Mn^{2+}}(aq) + 4\,\mathrm{H_2O}(l)$$

You should check this half-reaction for each atom type and for the charge, as well:

$$\text{Mn: Does } (1 \times 1) = (1 \times 1)\text{? Yes.}$$
$$\text{H: Does } (8 \times 1) = (4 \times 2)\text{? Yes.}$$
$$\text{O: Does } (1 \times 4) = (4 \times 1)\text{? Yes.}$$
$$\text{Charge: Does } [1 \times (-1) + 8 \times (+1) + 5 \times (-1)] = [1 \times (+2)]\text{? Yes.}$$

Now that this half-reaction is balanced, it is easy to see it involves reduction because electrons were gained when MnO_4^- was reduced to Mn^{2+}. In all reduction half-reactions, electrons appear as reactants (on the left side). As discussed in the earlier chapter,

the species that was reduced, MnO_4^- in this case, is also called the oxidizing agent. We now have two balanced half-reactions.

$$\text{oxidation: } Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e^-$$
$$\text{reduction: } MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$$

It is now necessary to combine the two halves to produce a whole reaction. The key to combining the half-reactions is the electrons. The electrons lost during oxidation must go somewhere. These electrons go to cause reduction. The number of electrons transferred from the oxidation half-reaction to the reduction half-reaction must be equal. There can be no missing or excess electrons. In this example, the oxidation half-reaction generates one electron, while the reduction half-reaction requires five. The lowest common multiple of one and five is five; therefore, it is necessary to multiply every term in the oxidation half-reaction by five and every term in the reduction half-reaction by one. (In this case, the multiplication of the reduction half-reaction generates no change; however, this will not always be the case.) The multiplication of the two half-reactions by the appropriate factor followed by addition of the two halves gives

$$\text{oxidation: } 5 \times (Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e^-)$$
$$\underline{\text{reduction: } MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)}$$
$$\text{overall: } 5\,Fe^{2+}(aq) + MnO_4^-(aq) + 8\,H^+(aq) \longrightarrow 5\,Fe^{3+}(aq) + Mn^{2+}(aq) + 4\,H_2O(l)$$

The electrons do not appear in the final answer because the oxidation electrons are the same electrons as the reduction electrons and they "cancel." Carefully check each side of the overall equation to verify everything was combined correctly:

$$\text{Fe: Does } (5 \times 1) = (5 \times 1)\text{? Yes.}$$
$$\text{Mn: Does } (1 \times 1) = (1 \times 1)\text{? Yes.}$$
$$\text{H: Does } (8 \times 1) = (4 \times 2)\text{? Yes.}$$
$$\text{O: Does } (1 \times 4) = (4 \times 1)\text{? Yes.}$$
$$\text{Charge: Does } [5 \times (+2) + 1 \times (-1) + 8 \times (+1)] = [5 \times (+3) + 1 \times (+2)]\text{? Yes.}$$

Everything checks, so this is the overall equation in acidic solution. If something does not check, the most common error occurs during the multiplication of the individual half-reactions.

Now suppose we wanted the solution to be basic. Recall that basic solutions have excess hydroxide ions. Some of these hydroxide ions will react with hydrogen ions to produce water. The simplest way to generate the balanced overall equation in basic solution is to start with the balanced equation in acidic solution, then "convert" it to the equation for basic solution. However, it is necessary to exercise caution when doing this, as many reactants behave differently under basic conditions and many metal ions will precipitate as the metal hydroxide. We just produced the following reaction, which we want to change to a basic reaction:

$$5\,Fe^{2+}(aq) + MnO_4^-(aq) + 8\,H^+(aq) \longrightarrow 5\,Fe^{3+}(aq) + Mn^{2+}(aq) + 4\,H_2O(l)$$

However, under basic conditions, MnO_4^- normally reduces to MnO_2 and iron will be present as either $Fe(OH)_2$ or $Fe(OH)_3$. For these reasons, under basic conditions, this reaction will be

$$3\,Fe(OH)_2(s) + MnO_4^-(aq) + 2\,H_2O(l) \longrightarrow 3\,Fe(OH)_3(s) + MnO_2(s) + OH^-(aq)$$

(Under very basic conditions MnO_4^- will reduce to MnO_4^{2-}, instead of MnO_2.)

It is still possible to balance any oxidation-reduction reaction as an acidic reaction and then, when necessary, convert the equation to a basic reaction. This will work if the acidic and basic reactants and products are the same or if the basic reactants and products are used before the conversion from acidic or basic. There are very few examples in which the acidic and basic reactions will involve the same reactants and products. However, balancing a basic reaction as acidic and then converting to basic will work. To convert to a basic reaction, it is necessary to add the same number of hydroxide ions to each side of the equation so that all the hydrogen ions (H^+) are removed and mass balance is maintained. Hydrogen ion combines with hydroxide ion (OH^-) to produce water.

Let us now try a basic equation. We will start with the following basic reaction:

$$Cl^-(aq) + MnO_4^-(aq) \longrightarrow ClO_3^-(aq) + MnO_2(s)$$

Balancing this as acid gives

$$Cl^-(aq) + 2\,MnO_4^-(aq) + 2\,H^+(aq) \longrightarrow ClO_3^-(aq) + 2\,MnO_2(s) + H_2O(l)$$

In this case, it is necessary to add two hydroxide ions to each side of the equation to convert the two hydrogen ions on the left into water:

$$\begin{gathered}\mathrm{Cl^-}(aq) + 2\,\mathrm{MnO_4^-}(aq) + (2\,\mathrm{H^+} + 2\,\mathrm{OH^-})(aq) \\ \longrightarrow \mathrm{ClO_3^-}(aq) + 2\,\mathrm{MnO_2}(s) + \mathrm{H_2O}(l) + 2\,\mathrm{OH^-}(aq)\end{gathered}$$

$$\mathrm{Cl^-}(aq) + 2\,\mathrm{MnO_4^-}(aq) + (2\,\mathrm{H_2O})(l) \longrightarrow \mathrm{ClO_3^-}(aq) + 2\,\mathrm{MnO_2}(s) + \mathrm{H_2O}(l) + 2\,\mathrm{OH^-}(aq)$$

Note that both sides of the equation show water. Simplifying should be done when necessary, and gives the desired equation. In this case, it is necessary to remove one H_2O from each side of the reaction arrows.

$$\mathrm{Cl^-}(aq) + 2\,\mathrm{MnO_4^-}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{ClO_3^-}(aq) + 2\,\mathrm{MnO_2}(s) + 2\,\mathrm{OH^-}(aq)$$

Again, check each side of the overall equation to make sure there are no errors:

$$\begin{gathered}\text{Cl: Does } (1 \times 1) = (1 \times 1)\text{? Yes.} \\ \text{Mn: Does } (2 \times 1) = (2 \times 1)\text{? Yes.} \\ \text{H: Does } (1 \times 2) = (2 \times 1)\text{? Yes.} \\ \text{O: Does } (2 \times 4 + 1 \times 1) = (3 \times 1 + 2 \times 2 + 2 \times 1)\text{? Yes.} \\ \text{Charge: Does } [1 \times (-1) + 2 \times (-1)] = [1 \times (-1) + 2 \times (-1)]\text{? Yes.}\end{gathered}$$

Everything checks, so this is the overall equation in basic solution.

Example 9.1.1: Balancing Acidic Oxidation-Reduction Reactions

Balance the following reaction equation in acidic solution:

$$\mathrm{MnO_4^-}(aq) + \mathrm{Cr^{3+}}(aq) \longrightarrow \mathrm{Mn^{2+}}(aq) + \mathrm{Cr_2O_7^{2-}}(aq)$$

Solution

This is an oxidation-reduction reaction, so start by collecting the species given into an unbalanced oxidation half-reaction and an unbalanced reduction half-reaction.

$$\begin{gathered}\text{oxidation (unbalanced): } \mathrm{Cr^{3+}}(aq) \longrightarrow \mathrm{Cr_2O_7^{2-}}(aq) \\ \text{reduction (unbalanced): } \mathrm{MnO_4^-}(aq) \longrightarrow \mathrm{Mn^{2+}}(aq)\end{gathered}$$

Starting with the oxidation half-reaction, we can balance the chromium

$$\text{oxidation (unbalanced): } 2\,\mathrm{Cr^{3+}}(aq) \longrightarrow \mathrm{Cr_2O_7^{2-}}(aq)$$

In acidic solution, we can use or generate hydrogen ions (H^+). Adding seven water molecules to the left side provides the necessary oxygen; the “left over” hydrogen appears as 14 H^+ on the right:

$$\text{oxidation (unbalanced): } 2\,\mathrm{Cr^{3+}}(aq) + 7\,\mathrm{H_2O}(l) \longrightarrow \mathrm{Cr_2O_7^{2-}}(aq) + 14\,\mathrm{H^+}(aq)$$

The left side of the equation has a total charge of [2 × (+3) = +6], and the right side a total charge of [−2 + 14 × (+1) = +12]. The difference is six; adding six electrons to the right side produces a mass- and charge-balanced oxidation half-reaction (in acidic solution):

$$\text{oxidation (balanced): } 2\,\mathrm{Cr^{3+}}(aq) + 7\,\mathrm{H_2O}(l) \longrightarrow \mathrm{Cr_2O_7^{2-}}(aq) + 14\,\mathrm{H^+}(aq) + 6\,\mathrm{e^-}$$

Checking the half-reaction:

$$\begin{gathered}\text{Cr: Does } (2 \times 1) = (1 \times 2)\text{? Yes.} \\ \text{H: Does } (7 \times 2) = (14 \times 1)\text{? Yes.} \\ \text{O: Does } (7 \times 1) = (1 \times 7)\text{? Yes.} \\ \text{Charge: Does } [2 \times (+3)] = [1 \times (-2) + 14 \times (+1) + 6 \times (-1)]\text{? Yes.}\end{gathered}$$

Now work on the reduction. It is necessary to convert the four oxygen atoms in the permanganate into four water molecules. To do this, add eight H^+ to convert the oxygen into four water molecules:

$$\text{reduction (unbalanced): } \mathrm{MnO_4^-}(aq) + 8\,\mathrm{H^+}(aq) \longrightarrow \mathrm{Mn^{2+}}(aq) + 4\,\mathrm{H_2O}(l)$$

Then add five electrons to the left side to balance the charge:

$$\text{reduction (balanced): } \mathrm{MnO_4^-}(aq) + 8\,\mathrm{H^+}(aq) + 5\,\mathrm{e^-} \longrightarrow \mathrm{Mn^{2+}}(aq) + 4\,\mathrm{H_2O}(l)$$

Make sure to check the half-reaction:

$$\begin{aligned}&\text{Mn: Does } (1 \times 1) = (1 \times 1)\text{? Yes.}\\&\text{H: Does } (8 \times 1) = (4 \times 2)\text{? Yes.}\\&\text{O: Does } (1 \times 4) = (4 \times 1)\text{? Yes.}\\&\text{Charge: Does } [1 \times (-1) + 8 \times (+1) + 5 \times (-1)] = [1 \times (+2)]\text{? Yes.}\end{aligned}$$

Collecting what we have so far:

$$\begin{aligned}&\text{oxidation: } 2\,\mathrm{Cr^{3+}}(aq) + 7\,\mathrm{H_2O}(l) \longrightarrow \mathrm{Cr_2O_7^{2-}}(aq) + 14\,\mathrm{H^+}(aq) + 6\,\mathrm{e^-}\\&\text{reduction: } \mathrm{MnO_4^-}(aq) + 8\,\mathrm{H^+}(aq) + 5\,\mathrm{e^-} \longrightarrow \mathrm{Mn^{2+}}(aq) + 4\,\mathrm{H_2O}(l)\end{aligned}$$

The least common multiple for the electrons is 30, so multiply the oxidation half-reaction by five, the reduction half-reaction by six, combine, and simplify:

$$\begin{aligned}&10\,\mathrm{Cr^{3+}}(aq) + 35\,\mathrm{H_2O}(l) + 6\,\mathrm{MnO_4^-}(aq) + 48\,\mathrm{H^+}(aq)\\&\longrightarrow 5\,\mathrm{Cr_2O_7^{2-}}(aq) + 70\,\mathrm{H^+}(aq) + 6\,\mathrm{Mn^{2+}}(aq) + 24\,\mathrm{H_2O}(l)\end{aligned}$$

$$10\,\mathrm{Cr^{3+}}(aq) + 11\,\mathrm{H_2O}(l) + 6\,\mathrm{MnO_4^-}(aq) \longrightarrow 5\,\mathrm{Cr_2O_7^{2-}}(aq) + 22\,\mathrm{H^+}(aq) + 6\,\mathrm{Mn^{2+}}(aq)$$

Checking each side of the equation:

$$\begin{aligned}&\text{Mn: Does } (6 \times 1) = (6 \times 1)\text{? Yes.}\\&\text{Cr: Does } (10 \times 1) = (5 \times 2)\text{? Yes.}\\&\text{H: Does } (11 \times 2) = (22 \times 1)\text{? Yes.}\\&\text{O: Does } (11 \times 1 + 6 \times 4) = (5 \times 7)\text{? Yes.}\\&\text{Charge: Does } [10 \times (+3) + 6 \times (-1)] = [5 \times (-2) + 22 \times (+1) + 6 \times (+2)]\text{? Yes.}\end{aligned}$$

This is the balanced equation in acidic solution.

? Exercise 9.1.1

Balance the following equation in acidic solution:

$$\mathrm{Hg_2^{2+}} + \mathrm{Ag} \longrightarrow \mathrm{Hg} + \mathrm{Ag^+}$$

Answer

$$\mathrm{Hg_2^{2+}}(aq) + 2\,\mathrm{Ag}(s) \longrightarrow 2\,\mathrm{Hg}(l) + 2\,\mathrm{Ag^+}(aq)$$

✔ Example 9.1.2: Balancing Basic Oxidation-Reduction Reactions

Balance the following reaction equation in basic solution:

$$\mathrm{MnO_4^-}(aq) + \mathrm{Cr(OH)_3}(s) \longrightarrow \mathrm{MnO_2}(s) + \mathrm{CrO_4^{2-}}(aq)$$

Solution

This is an oxidation-reduction reaction, so start by collecting the species given into an unbalanced oxidation half-reaction and an unbalanced reduction half-reaction

$$\begin{aligned}&\text{oxidation (unbalanced): } \mathrm{Cr(OH)_3}(s) \longrightarrow \mathrm{CrO_4^{2-}}(aq)\\&\text{reduction (unbalanced): } \mathrm{MnO_4^-}(aq) \longrightarrow \mathrm{MnO_2}(s)\end{aligned}$$

Starting with the oxidation half-reaction, we can balance the chromium

$$\text{oxidation (unbalanced): } \mathrm{Cr(OH)_3}(s) \longrightarrow \mathrm{CrO_4^{2-}}(aq)$$

In acidic solution, we can use or generate hydrogen ions (H^+). Adding one water molecule to the left side provides the necessary oxygen; the "left over" hydrogen appears as five H^+ on the right side:

$$\text{oxidation (unbalanced): } Cr(OH)_3(s) + H_2O(l) \longrightarrow CrO_4^{2-}(aq) + 5\,H^+(aq)$$

The left side of the equation has a total charge of [0], and the right side a total charge of [−2 + 5 × (+1) = +3]. The difference is three, adding three electrons to the right side produces a mass- and charge-balanced oxidation half-reaction (in acidic solution):

$$\text{oxidation (balanced): } Cr(OH)_3(s) + H_2O(l) \longrightarrow CrO_4^{2-}(aq) + 5\,H^+(aq) + 3\,e^-$$

Checking the half-reaction:

$$\begin{aligned}&\text{Cr: Does } (1 \times 1) = (1 \times 1)\text{? Yes.}\\&\text{H: Does } (1 \times 3 + 1 \times 2) = (5 \times 1)\text{? Yes.}\\&\text{O: Does } (1 \times 3 + 1 \times 1) = (4 \times 1)\text{? Yes.}\\&\text{Charge: Does } [0 = [1 \times (-2) + 5 \times (+1) + 3 \times (-1)]\text{? Yes.}\end{aligned}$$

Now work on the reduction. It is necessary to convert the four O atoms in the MnO_4^- minus the two O atoms in MnO_2 into two water molecules. To do this, add four H^+ to convert the oxygen into two water molecules:

$$\text{reduction (unbalanced): } MnO_4^-(aq) + 4\,H^+(aq) \longrightarrow MnO_2(s) + 2\,H_2O(l)$$

Then add three electrons to the left side to balance the charge:

$$\text{reduction (balanced): } MnO_4^-(aq) + 4\,H^+(aq) + 3\,e^- \longrightarrow MnO_2(s) + 2\,H_2O(l)$$

Make sure to check the half-reaction:

$$\begin{aligned}&\text{Mn: Does } (1 \times 1) = (1 \times 1)\text{? Yes.}\\&\text{H: Does } (4 \times 1) = (2 \times 2)\text{? Yes.}\\&\text{O: Does } (1 \times 4) = (1 \times 2 + 2 \times 1)\text{? Yes.}\\&\text{Charge: Does } [1 \times (-1) + 4 \times (+1) + 3 \times (-1)] = [0]\text{? Yes.}\end{aligned}$$

Collecting what we have so far:

$$\begin{aligned}&\text{oxidation: } Cr(OH)_3(s) + H_2O(l) \longrightarrow CrO_4^{2-}(aq) + 5\,H^+(aq) + 3\,e^-\\&\text{reduction: } MnO_4^-(aq) + 4\,H^+(aq) + 3\,e^- \longrightarrow MnO_2(s) + 2\,H_2O(l)\end{aligned}$$

In this case, both half reactions involve the same number of electrons; therefore, simply add the two half-reactions together.

$$\begin{aligned}&MnO_4^-(aq) + 4\,H^+(aq) + Cr(OH)_3(s) + H_2O(l)\\&\longrightarrow CrO_4^{2-}(aq) + MnO_2(s) + 2\,H_2O(l) + 5\,H^+(aq)\end{aligned}$$

$$MnO_4^-(aq) + Cr(OH)_3(s) \longrightarrow CrO_4^{2-}(aq) + MnO_2(s) + H_2O(l) + H^+(aq)$$

Checking each side of the equation:

$$\begin{aligned}&\text{Mn: Does } (1 \times 1) = (1 \times 1)\text{? Yes.}\\&\text{Cr: Does } (1 \times 1) = (1 \times 1)\text{? Yes.}\\&\text{H: Does } (1 \times 3) = (2 \times 1 + 1 \times 1)\text{? Yes.}\\&\text{O: Does } (1 \times 4 + 1 \times 3) = (1 \times 4 + 1 \times 2 + 1 \times 1)\text{? Yes.}\\&\text{Charge: Does } [1 \times (-1)] = [1 \times (-2) + 1 \times (+1)]\text{? Yes.}\end{aligned}$$

This is the balanced equation in acidic solution. For a basic solution, add one hydroxide ion to each side and simplify:

$$\begin{aligned}&OH^-(aq) + MnO_4^-(aq) + Cr(OH)_3(s)\\&\longrightarrow CrO_4^{2-}(aq) + MnO_2(s) + H_2O(l) + (H^+ + OH^-)(aq)\end{aligned}$$

$$OH^-(aq) + MnO_4^-(aq) + Cr(OH)_3(s) \longrightarrow CrO_4^{2-}(aq) + MnO_2(s) + 2\,H_2O(l)$$

Checking each side of the equation:

Mn: Does $(1 \times 1) = (1 \times 1)$? Yes.
Cr: Does $(1 \times 1) = (1 \times 1)$? Yes.
H: Does $(1 \times 1 + 1 \times 3) = (2 \times 2)$? Yes.
O: Does $(1 \times 1 + 1 \times 4 + 1 \times 3) = (1 \times 4 + 1 \times 2 + 2 \times 1)$? Yes.
Charge: Does $[1 \times (-1) + 1 \times (-1)] = [1 \times (-2)]$? Yes.

This is the balanced equation in basic solution.

? Exercise 9.1.2

Balance the following in the type of solution indicated.

a. $H_2 + Cu^{2+} \longrightarrow Cu$ (acidic solution)
b. $H_2 + Cu(OH)_2 \longrightarrow Cu$ (basic solution)
c. $Fe + Ag^+ \longrightarrow Fe^{2+} + Ag$
d. Identify the oxidizing agents in reactions (a), (b), and (c).
e. Identify the reducing agents in reactions (a), (b), and (c).

Answer a

$$H_2(g) + Cu^{2+}(aq) \longrightarrow 2\,H^+(aq) + Cu(s)$$

Answer b

$$H_2(g) + Cu(OH)_2(s) \longrightarrow 2\,H_2O(l) + Cu(s)$$

Answer c

$$Fe(s) + 2\,Ag^+(aq) \longrightarrow Fe^{2+}(aq) + 2\,Ag(s)$$

Answer d

oxidizing agent = species reduced: Cu^{2+}, $Cu(OH)_2$, Ag^+

Answer e

reducing agent = species oxidized: H_2, H_2, Fe.

Summary

An electric current consists of moving charge. The charge may be in the form of electrons or ions. Current flows through an unbroken or closed circular path called a circuit. The current flows through a conducting medium as a result of a difference in electrical potential between two points in a circuit. Electrical potential has the units of energy per charge. In SI units, charge is measured in coulombs (C), current in amperes $\left(A = \frac{C}{s}\right)$, and electrical potential in volts $\left(V = \frac{J}{C}\right)$.

Oxidation is the loss of electrons, and the species that is oxidized is also called the reducing agent. Reduction is the gain of electrons, and the species that is reduced is also called the oxidizing agent. Oxidation-reduction reactions can be balanced using the half-reaction method. In this method, the oxidation-reduction reaction is split into an oxidation half-reaction and a reduction half-reaction. The oxidation half-reaction and reduction half-reaction are then balanced separately. Each of the half-reactions must have the same number of each type of atom on both sides of the equation *and* show the same total charge on each side of the equation. Charge is balanced in oxidation half-reactions by adding electrons as products; in reduction half-reactions, charge is balanced by adding electrons as reactants. The total number of electrons gained by reduction must exactly equal the number of electrons lost by oxidation when combining the two half-reactions to give the overall balanced equation. Balancing oxidation-reduction reaction equations in aqueous solutions frequently requires that oxygen or hydrogen be added or removed from a reactant. In acidic solution, hydrogen is added by adding hydrogen ion (H^+) and removed by producing hydrogen ion; oxygen is removed by adding hydrogen ion and producing water, and added by adding water and producing hydrogen ion. A balanced equation in basic solution can be obtained by first balancing the equation in acidic solution, and then adding hydroxide ion to each side of the balanced equation in such numbers that all the hydrogen ions are converted to water.

Glossary

circuit
path taken by a current as it flows because of an electrical potential difference

current
flow of electrical charge; the SI unit of charge is the coulomb (C) and current is measured in amperes $\left(1\ \mathrm{A} = 1\ \frac{\mathrm{C}}{\mathrm{s}}\right)$

electrical potential
energy per charge; in electrochemical systems, it depends on the way the charges are distributed within the system; the SI unit of electrical potential is the volt $\left(1\ \mathrm{V} = 1\ \frac{\mathrm{J}}{\mathrm{C}}\right)$

half-reaction method
method that produces a balanced overall oxidation-reduction reaction by splitting the reaction into an oxidation “half” and reduction “half,” balancing the two half-reactions, and then combining the oxidation half-reaction and reduction half-reaction in such a way that the number of electrons generated by the oxidation is exactly canceled by the number of electrons required by the reduction

oxidation half-reaction
the “half” of an oxidation-reduction reaction involving oxidation; the half-reaction in which electrons appear as products; balanced when each atom type, as well as the charge, is balanced

reduction half-reaction
the “half” of an oxidation-reduction reaction involving reduction; the half-reaction in which electrons appear as reactants; balanced when each atom type, as well as the charge, is balanced

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9.2: Galvanic Cells

Learning Objectives

- Use cell notation to describe galvanic cells
- Describe the basic components of galvanic cells

Galvanic cells, also known as voltaic cells, are electrochemical cells in which spontaneous oxidation-reduction reactions produce electrical energy. In writing the equations, it is often convenient to separate the oxidation-reduction reactions into half-reactions to facilitate balancing the overall equation and to emphasize the actual chemical transformations.

Consider what happens when a clean piece of copper metal is placed in a solution of silver nitrate (Figure **9.2.1**). As soon as the copper metal is added, silver metal begins to form and copper ions pass into the solution. The blue color of the solution on the far right indicates the presence of copper ions. The reaction may be split into its two half-reactions. Half-reactions separate the oxidation from the reduction, so each can be considered individually.

$$\text{oxidation: } \mathrm{Cu}(s) \longrightarrow \mathrm{Cu}^{2+}(aq) + 2\,\mathrm{e}^- \tag{9.2.1}$$

$$\text{reduction: } 2 \times (\mathrm{Ag}^+(aq) + \mathrm{e}^- \longrightarrow \mathrm{Ag}(s)) \quad \text{or} \quad 2\,\mathrm{Ag}^+(aq) + 2\,\mathrm{e}^- \longrightarrow 2\,\mathrm{Ag}(s) \tag{9.2.2}$$

$$\text{overall: } 2\,\mathrm{Ag}^+(aq) + \mathrm{Cu}(s) \longrightarrow 2\,\mathrm{Ag}(s) + \mathrm{Cu}^{2+}(aq) \tag{9.2.3}$$

The equation for the reduction half-reaction had to be doubled so the number electrons “gained” in the reduction half-reaction equaled the number of electrons “lost” in the oxidation half-reaction.

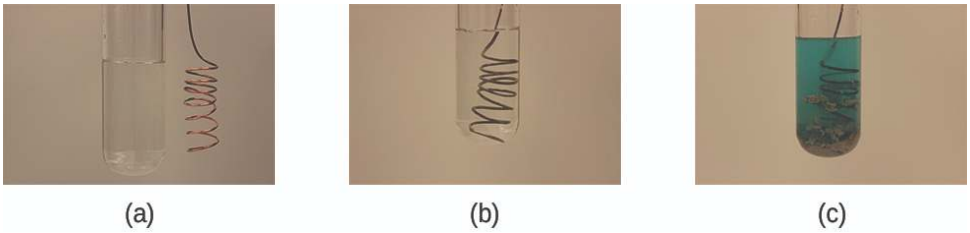


Figure **9.2.1**: When a clean piece of copper metal is placed into a clear solution of silver nitrate (a), an oxidation-reduction reaction occurs that results in the exchange of Cu^{2+} for Ag^+ ions in solution. As the reaction proceeds (b), the solution turns blue (c) because of the copper ions present, and silver metal is deposited on the copper strip as the silver ions are removed from solution. (credit: modification of work by Mark Ott)

Galvanic or voltaic cells involve spontaneous electrochemical reactions in which the half-reactions are separated (Figure **9.2.2**) so that current can flow through an external wire. The beaker on the left side of the figure is called a half-cell, and contains a 1 *M* solution of copper(II) nitrate [$Cu(NO_3)_2$] with a piece of copper metal partially submerged in the solution. The copper metal is an electrode. The copper is undergoing oxidation; therefore, the copper electrode is the anode. The anode is connected to a voltmeter with a wire and the other terminal of the voltmeter is connected to a silver electrode by a wire. The silver is undergoing reduction; therefore, the silver electrode is the cathode. The half-cell on the right side of the figure consists of the silver electrode in a 1 *M* solution of silver nitrate ($AgNO_3$). At this point, no current flows—that is, no significant movement of electrons through the wire occurs because the circuit is open. The circuit is closed using a salt bridge, which transmits the current with moving ions. The salt bridge consists of a concentrated, nonreactive, electrolyte solution such as the sodium nitrate ($NaNO_3$) solution used in this example. As electrons flow from left to right through the electrode and wire, nitrate ions (anions) pass through the porous plug on the left into the copper(II) nitrate solution. This keeps the beaker on the left electrically neutral by neutralizing the charge on the copper(II) ions that are produced in the solution as the copper metal is oxidized. At the same time, the nitrate ions are moving to the left, sodium ions (cations) move to the right, through the porous plug, and into the silver nitrate solution on the right. These added cations “replace” the silver ions that are removed from the solution as they were reduced to silver metal, keeping the beaker on the right electrically neutral. Without the salt bridge, the compartments would not remain electrically neutral and no significant current would flow. However, if the two compartments are in direct contact, a salt bridge is not necessary. The instant the circuit is completed, the voltmeter reads +0.46 V, this is called the cell potential. The cell potential is created when the two dissimilar metals are connected, and is a measure of the energy per unit charge available from the oxidation-reduction reaction. The volt is the derived SI unit for electrical potential

$$\text{volt} = V = \frac{\text{J}}{\text{C}}$$

In this equation, A is the current in amperes and C the charge in coulombs. Note that volts must be multiplied by the charge in coulombs (C) to obtain the energy in joules (J).

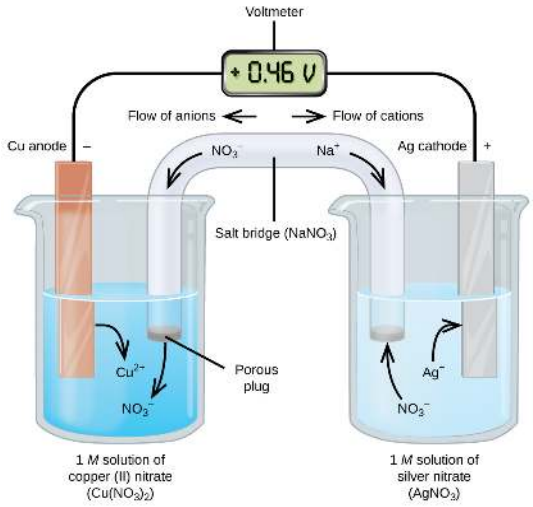


Figure **9.2.2**: In this standard galvanic cell, the half-cells are separated; electrons can flow through an external wire and become available to do electrical work.

When the electrochemical cell is constructed in this fashion, a positive cell potential indicates a spontaneous reaction *and* that the electrons are flowing from the left to the right. There is a lot going on in Figure **9.2.2**, so it is useful to summarize things for this system:

- Electrons flow from the anode to the cathode: left to right in the standard galvanic cell in the figure.
- The electrode in the left half-cell is the anode because oxidation occurs here. The name refers to the flow of anions in the salt bridge toward it.
- The electrode in the right half-cell is the cathode because reduction occurs here. The name refers to the flow of cations in the salt bridge toward it.
- Oxidation occurs at the anode (the left half-cell in the figure).
- Reduction occurs at the cathode (the right half-cell in the figure).
- The cell potential, +0.46 V, in this case, results from the inherent differences in the nature of the materials used to make the two half-cells.
- The salt bridge must be present to close (complete) the circuit and both an oxidation and reduction must occur for current to flow.

There are many possible galvanic cells, so a shorthand notation is usually used to describe them. The cell notation (sometimes called a cell diagram) provides information about the various species involved in the reaction. This notation also works for other types of cells. A vertical line, $|$, denotes a phase boundary and a double line, $\|$, the salt bridge. Information about the anode is written to the left, followed by the anode solution, then the salt bridge (when present), then the cathode solution, and, finally, information about the cathode to the right. The cell notation for the galvanic cell in Figure **9.2.2** is then

$$\text{Cu}(s)\,|\,\text{Cu}^{2+}(aq,\,1\,M)\,\|\,\text{Ag}^{+}(aq,\,1\,M)\,|\,\text{Ag}(s)$$

Note that spectator ions are not included and that the simplest form of each half-reaction was used. When known, the initial concentrations of the various ions are usually included.

One of the simplest cells is the Daniell cell. It is possible to construct this battery by placing a copper electrode at the bottom of a jar and covering the metal with a copper sulfate solution. A zinc sulfate solution is floated on top of the copper sulfate solution; then a zinc electrode is placed in the zinc sulfate solution. Connecting the copper electrode to the zinc electrode allows an electric current to flow. This is an example of a cell without a salt bridge, and ions may flow across the interface between the two solutions.

Some oxidation-reduction reactions involve species that are poor conductors of electricity, and so an electrode is used that does not participate in the reactions. Frequently, the electrode is platinum, gold, or graphite, all of which are inert to many chemical reactions. One such system is shown in Figure **9.2.3**. Magnesium undergoes oxidation at the anode on the left in the figure and hydrogen ions undergo reduction at the cathode on the right. The reaction may be summarized as

$$\text{oxidation: } \mathrm{Mg}(s) \longrightarrow \mathrm{Mg^{2+}}(aq) + 2\,\mathrm{e^-} \tag{9.2.4}$$

$$\text{reduction: } 2\,\mathrm{H^+}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{H_2}(g) \tag{9.2.5}$$

$$\text{overall: } \mathrm{Mg}(s) + 2\,\mathrm{H^+}(aq) \longrightarrow \mathrm{Mg^{2+}}(aq) + \mathrm{H_2}(g) \tag{9.2.6}$$

The cell used an inert platinum wire for the cathode, so the cell notation is

$$\mathrm{Mg}(s)\,|\,\mathrm{Mg^{2+}}(aq)\,\|\,\mathrm{H^+}(aq)\,|\,\mathrm{H_2}(g)\,|\,\mathrm{Pt}(s)$$

The magnesium electrode is an active electrode because it participates in the oxidation-reduction reaction. Inert electrodes, like the platinum electrode in Figure **9.2.3**, do not participate in the oxidation-reduction reaction and are present so that current can flow through the cell. Platinum or gold generally make good inert electrodes because they are chemically unreactive.

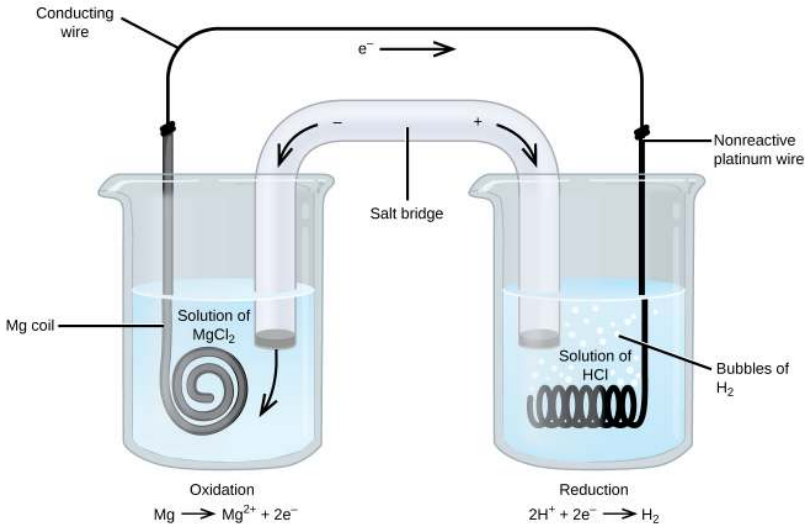


Figure **9.2.2**: The oxidation of magnesium to magnesium ion occurs in the beaker on the left side in this apparatus; the reduction of hydrogen ions to hydrogen occurs in the beaker on the right. A nonreactive, or inert, platinum wire allows electrons from the left beaker to move into the right beaker. The overall reaction is: $\mathrm{Mg} + 2\,\mathrm{H^+} \longrightarrow \mathrm{Mg^{2+}} + \mathrm{H_2}$, *which is represented in cell notation as:* $\mathrm{Mg}(s)\,|\,\mathrm{Mg^{2+}}(aq)\,\|\,\mathrm{H^+}(aq)\,|\,\mathrm{H_2}(g)\,|\,\mathrm{Pt}(s)$.

✔ Example 9.2.1: Using Cell Notation

Consider a galvanic cell consisting of

$$2\,\mathrm{Cr}(s) + 3\,\mathrm{Cu^{2+}}(aq) \longrightarrow 2\,\mathrm{Cr^{3+}}(aq) + 3\,\mathrm{Cu}(s)$$

Write the oxidation and reduction half-reactions and write the reaction using cell notation. Which reaction occurs at the anode? The cathode?

Solution

By inspection, Cr is oxidized when three electrons are lost to form $\mathrm{Cr^{3+}}$, and $\mathrm{Cu^{2+}}$ is reduced as it gains two electrons to form Cu. Balancing the charge gives

$$\text{oxidation: } 2\,\mathrm{Cr}(s) \longrightarrow 2\,\mathrm{Cr^{3+}}(aq) + 6\,\mathrm{e^-} \tag{9.2.7}$$

$$\text{reduction: } 3\,\mathrm{Cu^{2+}}(aq) + 6\,\mathrm{e^-} \longrightarrow 3\,\mathrm{Cu}(s) \tag{9.2.8}$$

$$\text{overall: } 2\,\mathrm{Cr}(s) + 3\,\mathrm{Cu^{2+}}(aq) \longrightarrow 2\,\mathrm{Cr^{3+}}(aq) + 3\,\mathrm{Cu}(s) \tag{9.2.9}$$

Cell notation uses the simplest form of each of the equations, and starts with the reaction at the anode. No concentrations were specified so:

$$\mathrm{Cr}(s)\,|\,\mathrm{Cr}^{3+}(aq)\,\|\,\mathrm{Cu}^{2+}(aq)\,|\,\mathrm{Cu}(s).$$

Oxidation occurs at the anode and reduction at the cathode.

Example 9.2.2: Using Cell Notation

Consider a galvanic cell consisting of

$$5\,\mathrm{Fe}^{2+}(aq) + \mathrm{MnO_4}^{-}(aq) + 8\,\mathrm{H}^{+}(aq) \longrightarrow 5\,\mathrm{Fe}^{3+}(aq) + \mathrm{Mn}^{2+}(aq) + 4\,\mathrm{H_2O}(l)$$

Write the oxidation and reduction half-reactions and write the reaction using cell notation. Which reaction occurs at the anode? The cathode?

Solution

By inspection, Fe^{2+} undergoes oxidation when one electron is lost to form Fe^{3+}, and $\mathrm{MnO_4}^{-}$ is reduced as it gains five electrons to form Mn^{2+}. Balancing the charge gives

$$\text{oxidation: } 5(\mathrm{Fe}^{2+}(aq) \longrightarrow \mathrm{Fe}^{3+}(aq) + \mathrm{e}^{-}) \tag{9.2.10}$$

$$\text{reduction: } \mathrm{MnO_4}^{-}(aq) + 8\,\mathrm{H}^{+}(aq) + 5\,\mathrm{e}^{-} \longrightarrow \mathrm{Mn}^{2+}(aq) + 4\,\mathrm{H_2O}(l) \tag{9.2.11}$$

$$\text{overall: } 5\,\mathrm{Fe}^{2+}(aq) + \mathrm{MnO_4}^{-}(aq) + 8\,\mathrm{H}^{+}(aq) \longrightarrow 5\,\mathrm{Fe}^{3+}(aq) + \mathrm{Mn}^{2+}(aq) + 4\,\mathrm{H_2O}(l) \tag{9.2.12}$$

Cell notation uses the simplest form of each of the equations, and starts with the reaction at the anode. It is necessary to use an inert electrode, such as platinum, because there is no metal present to conduct the electrons from the anode to the cathode. No concentrations were specified so:

$$\mathrm{Pt}(s)\,|\,\mathrm{Fe}^{2+}(aq),\ \mathrm{Fe}^{3+}(aq)\,\|\,\mathrm{MnO_4}^{-}(aq),\ \mathrm{H}^{+}(aq),\ \mathrm{Mn}^{2+}(aq)\,|\,\mathrm{Pt}(s).$$

Oxidation occurs at the anode and reduction at the cathode.

Exercise 9.2.1

Use cell notation to describe the galvanic cell where copper(II) ions are reduced to copper metal and zinc metal is oxidized to zinc ions.

Answer

From the information given in the problem:

$$\text{anode (oxidation): } \mathrm{Zn}(s) \longrightarrow \mathrm{Zn}^{2+}(aq) + 2\,\mathrm{e}^{-} \tag{9.2.13}$$

$$\text{cathode (reduction): } \mathrm{Cu}^{2+}(aq) + 2\,\mathrm{e}^{-} \longrightarrow \mathrm{Cu}(s) \tag{9.2.14}$$

$$\text{overall: } \mathrm{Zn}(s) + \mathrm{Cu}^{2+}(aq) \longrightarrow \mathrm{Zn}^{2+}(aq) + \mathrm{Cu}(s) \tag{9.2.15}$$

Using cell notation:

$$\mathrm{Zn}(s)\,|\,\mathrm{Zn}^{2+}(aq)\,\|\,\mathrm{Cu}^{2+}(aq)\,|\,\mathrm{Cu}(s).$$

Summary

Electrochemical cells typically consist of two half-cells. The half-cells separate the oxidation half-reaction from the reduction half-reaction and make it possible for current to flow through an external wire. One half-cell, normally depicted on the left side in a figure, contains the anode. Oxidation occurs at the anode. The anode is connected to the cathode in the other half-cell, often shown on the right side in a figure. Reduction occurs at the cathode. Adding a salt bridge completes the circuit allowing current to flow. Anions in the salt bridge flow toward the anode and cations in the salt bridge flow toward the cathode. The movement of these ions completes the circuit and keeps each half-cell electrically neutral. Electrochemical cells can be described using cell notation. In this notation, information about the reaction at the anode appears on the left and information about the reaction at the cathode on the right. The salt bridge is represented by a double line, ‖. The solid, liquid, or aqueous phases within a half-cell are separated by a single line, |. The phase and concentration of the various species is included after the species name. Electrodes that participate in

the oxidation-reduction reaction are called active electrodes. Electrodes that do not participate in the oxidation-reduction reaction but are there to allow current to flow are inert electrodes. Inert electrodes are often made from platinum or gold, which are unchanged by many chemical reactions.

Glossary

active electrode
: electrode that participates in the oxidation-reduction reaction of an electrochemical cell; the mass of an active electrode changes during the oxidation-reduction reaction

anode
: electrode in an electrochemical cell at which oxidation occurs; information about the anode is recorded on the left side of the salt bridge in cell notation

cathode
: electrode in an electrochemical cell at which reduction occurs; information about the cathode is recorded on the right side of the salt bridge in cell notation

cell notation
: shorthand way to represent the reactions in an electrochemical cell

cell potential
: difference in electrical potential that arises when dissimilar metals are connected; the driving force for the flow of charge (current) in oxidation-reduction reactions

galvanic cell
: electrochemical cell that involves a spontaneous oxidation-reduction reaction; electrochemical cells with positive cell potentials; also called a voltaic cell

inert electrode
: electrode that allows current to flow, but that does not otherwise participate in the oxidation-reduction reaction in an electrochemical cell; the mass of an inert electrode does not change during the oxidation-reduction reaction; inert electrodes are often made of platinum or gold because these metals are chemically unreactive.

voltaic cell
: another name for a galvanic cell

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9.3: Standard Reduction Potentials

Learning Objectives

- Determine standard cell potentials for oxidation-reduction reactions
- Use standard reduction potentials to determine the better oxidizing or reducing agent from among several possible choices

The cell potential results from the difference in the electrical potentials for each electrode. While it is impossible to determine the electrical potential of a single electrode, we can assign an electrode the value of zero and then use it as a reference. The electrode chosen as the zero is shown in Figure 17.4.1 and is called the standard hydrogen electrode (SHE). The SHE consists of 1 atm of hydrogen gas bubbled through a 1 M HCl solution, usually at room temperature. Platinum, which is chemically inert, is used as the electrode. The reduction half-reaction chosen as the reference is

$$2\,H^+(aq,\,1\,M) + 2\,e^- \rightleftharpoons H_2(g,\,1\text{ atm}) \quad E^\circ = 0\text{ V}$$

$E°$ is the standard reduction potential. The superscript "°" on the E denotes standard conditions (1 bar or 1 atm for gases, 1 M for solutes). The voltage is defined as zero for all temperatures.

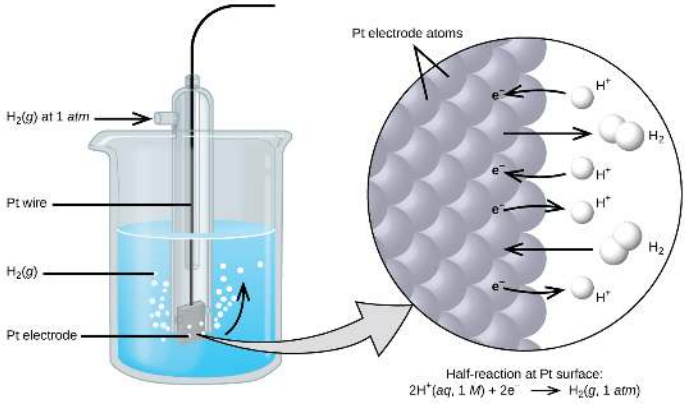


Figure **9.3.1**: Hydrogen gas at 1 atm is bubbled through 1 M HCl solution. Platinum, which is inert to the action of the 1 M HCl, is used as the electrode. Electrons on the surface of the electrode combine with H^+ in solution to produce hydrogen gas.

A galvanic cell consisting of a SHE and Cu^{2+}/Cu half-cell can be used to determine the standard reduction potential for Cu^{2+} (Figure **9.3.2**). In cell notation, the reaction is

$$Pt(s)\,|\,H_2(g,\,1\text{ atm})\,|\,H^+(aq,\,1\,M)\,\|\,Cu^{2+}(aq,\,1\,M)\,|\,Cu(s)$$

Electrons flow from the anode to the cathode. The reactions, which are reversible, are

$$\begin{aligned}&\text{Anode (oxidation): } H_2(g) \longrightarrow 2\,H^+(aq) + 2\,e^-\\ &\text{Cathode (reduction): } Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)\\ &\overline{\text{Overall: } Cu^{2+}(aq) + H_2(g) \longrightarrow 2\,H^+(aq) + Cu(s)}\end{aligned}$$

The standard reduction potential can be determined by subtracting the standard reduction potential for the reaction occurring at the anode from the standard reduction potential for the reaction occurring at the cathode. The minus sign is necessary because oxidation is the reverse of reduction.

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

$$+0.34\text{ V} = E^\circ_{Cu^{2+}/Cu} - E^\circ_{H^+/H_2} = E^\circ_{Cu^{2+}/Cu} - 0 = E^\circ_{Cu^{2+}/Cu}$$

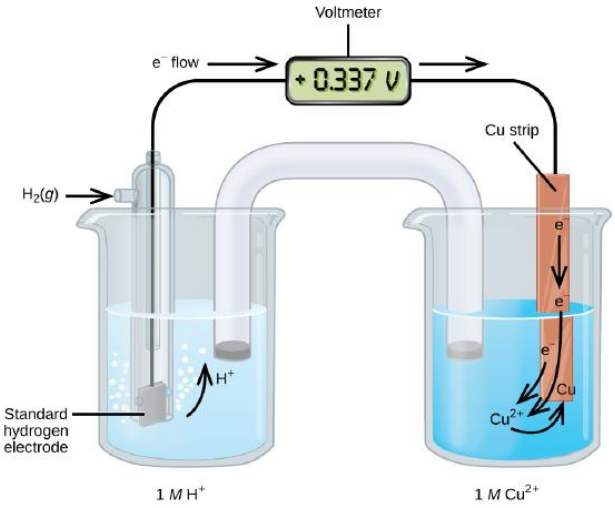


Figure **9.3.2**: A galvanic cell can be used to determine the standard reduction potential of Cu^{2+}.

Using the SHE as a reference, other standard reduction potentials can be determined. Consider the cell shown in Figure **9.3.2**, where

$$\mathrm{Pt}(s)\,|\,\mathrm{H_2}(g,\ 1\ \mathrm{atm})\,|\,\mathrm{H^+}(aq,\ 1\ M)\,\|\,\mathrm{Ag^+}(aq,\ 1\ M)\,|\,\mathrm{Ag}(s)$$

Electrons flow from left to right, and the reactions are

$$\begin{aligned}&\text{anode (oxidation): } \mathrm{H_2}(g) \longrightarrow 2\,\mathrm{H^+}(aq) + 2\,\mathrm{e^-}\\ &\text{cathode (reduction): } 2\,\mathrm{Ag^+}(aq) + 2\,\mathrm{e^-} \longrightarrow 2\,\mathrm{Ag}(s)\\ &\text{overall: } 2\,\mathrm{Ag^+}(aq) + \mathrm{H_2}(g) \longrightarrow 2\,\mathrm{H^+}(aq) + 2\,\mathrm{Ag}(s)\end{aligned}$$

The standard reduction potential can be determined by subtracting the standard reduction potential for the reaction occurring at the anode from the standard reduction potential for the reaction occurring at the cathode. The minus sign is needed because oxidation is the reverse of reduction.

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$+0.80\ \mathrm{V} = E^\circ_{\mathrm{Ag^+/Ag}} - E^\circ_{\mathrm{H^+/H_2}} = E^\circ_{\mathrm{Ag^+/Ag}} - 0 = E^\circ_{\mathrm{Ag^+/Ag}}$$

It is important to note that the potential is *not* doubled for the cathode reaction.

The SHE is rather dangerous and rarely used in the laboratory. Its main significance is that it established the zero for standard reduction potentials. Once determined, standard reduction potentials can be used to determine the standard cell potential, E°_{cell}, for any cell. For example, for the following cell:

$$\mathrm{Cu}(s)\,|\,\mathrm{Cu^{2+}}(aq,\ 1\ M)\,\|\,\mathrm{Ag^+}(aq,\ 1\ M)\,|\,\mathrm{Ag}(s)$$

$$\begin{aligned}&\text{anode (oxidation): } \mathrm{Cu}(s) \longrightarrow \mathrm{Cu^{2+}}(aq) + 2\,\mathrm{e^-}\\ &\text{cathode (reduction): } 2\,\mathrm{Ag^+}(aq) + 2\,\mathrm{e^-} \longrightarrow 2\,\mathrm{Ag}(s)\\ &\text{overall: } \mathrm{Cu}(s) + 2\,\mathrm{Ag^+}(aq) \longrightarrow \mathrm{Cu^{2+}}(aq) + 2\,\mathrm{Ag}(s)\end{aligned}$$

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = E^\circ_{\mathrm{Ag^+/Ag}} - E^\circ_{\mathrm{Cu^{2+}/Cu}} = 0.80\ \mathrm{V} - 0.34\ \mathrm{V} = 0.46\ \mathrm{V}$$

Again, note that when calculating E°_{cell}, standard reduction potentials always remain the same even when a half-reaction is multiplied by a factor. Standard reduction potentials for selected reduction reactions are shown in Table **9.3.1**. A more complete list is provided in Tables P1 or P2.

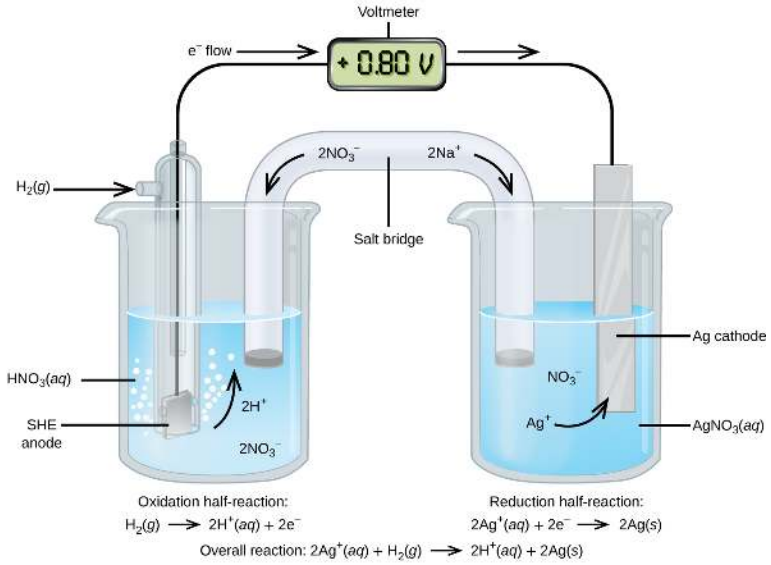


Figure **9.3.3**: A galvanic cell can be used to determine the standard reduction potential of Ag^+. The SHE on the left is the anode and assigned a standard reduction potential of zero.

Table **9.3.1**: Selected Standard Reduction Potentials at 25 °C

Half-Reaction	E° (V)
$F_2(g) + 2\,e^- \longrightarrow 2\,F^-(aq)$	+2.866
$PbO_2(s) + SO_4^{2-}(aq) + 4\,H^+(aq) + 2\,e^- \longrightarrow PbSO_4(s) + 2\,H_2O(l)$	+1.69
$MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$	+1.507
$Au^{3+}(aq) + 3\,e^- \longrightarrow Au(s)$	+1.498
$Cl_2(g) + 2\,e^- \longrightarrow 2\,Cl^-(aq)$	+1.35827
$O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(l)$	+1.229
$Pt^{2+}(aq) + 2\,e^- \longrightarrow Pt(s)$	+1.20
$Br_2(aq) + 2\,e^- \longrightarrow 2\,Br^-(aq)$	+1.0873
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.7996
$Hg_2^{2+}(aq) + 2\,e^- \longrightarrow 2\,Hg(l)$	+0.7973
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.771
$MnO_4^-(aq) + 2\,H_2O(l) + 3\,e^- \longrightarrow MnO_2(s) + 4\,OH^-(aq)$	+0.558
$I_2(s) + 2\,e^- \longrightarrow 2\,I^-(aq)$	+0.5355
$NiO_2(s) + 2\,H_2O(l) + 2\,e^- \longrightarrow Ni(OH)_2(s) + 2\,OH^-(aq)$	+0.49
$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$	+0.34
$Hg_2Cl_2(s) + 2\,e^- \longrightarrow 2\,Hg(l) + 2\,Cl^-(aq)$	+0.26808
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	+0.22233
$Sn^{4+}(aq) + 2\,e^- \longrightarrow Sn^{2+}(aq)$	+0.151
$2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2\,e^- \longrightarrow Pb(s)$	−0.1262
$Sn^{2+}(aq) + 2\,e^- \longrightarrow Sn(s)$	−0.1375
$Ni^{2+}(aq) + 2\,e^- \longrightarrow Ni(s)$	−0.257
$Co^{2+}(aq) + 2\,e^- \longrightarrow Co(s)$	−0.28
$PbSO_4(s) + 2\,e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$	−0.3505
$Cd^{2+}(aq) + 2\,e^- \longrightarrow Cd(s)$	−0.4030
$Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s)$	−0.447
$Cr^{3+}(aq) + 3\,e^- \longrightarrow Cr(s)$	−0.744
$Mn^{2+}(aq) + 2\,e^- \longrightarrow Mn(s)$	−1.185
$Zn(OH)_2(s) + 2\,e^- \longrightarrow Zn(s) + 2\,OH^-(aq)$	−1.245
$Zn^{2+}(aq) + 2\,e^- \longrightarrow Zn(s)$	−0.7618
$Al^{3+}(aq) + 3\,e^- \longrightarrow Al(s)$	−1.662
$Mg^{2+}(aq) + 2\,e^- \longrightarrow Mg(s)$	−2.372
$Na^+(aq) + e^- \longrightarrow Na(s)$	−2.71

Half-Reaction	E° (V)
$Ca^{2+}(aq) + 2\,e^- \longrightarrow Ca(s)$	−2.868
$Ba^{2+}(aq) + 2\,e^- \longrightarrow Ba(s)$	−2.912
$K^+(aq) + e^- \longrightarrow K(s)$	−2.931
$Li^+(aq) + e^- \longrightarrow Li(s)$	−3.04

Tables like this make it possible to determine the standard cell potential for many oxidation-reduction reactions.

Example 9.3.1: Cell Potentials from Standard Reduction Potentials

What is the standard cell potential for a galvanic cell that consists of Au^{3+}/Au and Ni^{2+}/Ni half-cells? Identify the oxidizing and reducing agents.

Solution

Using Table 9.3.1, the reactions involved in the galvanic cell, both written as reductions, are

$$Au^{3+}(aq) + 3\,e^- \longrightarrow Au(s) \quad E^\circ_{Au^{3+}/Au} = +1.498\ V$$

$$Ni^{2+}(aq) + 2\,e^- \longrightarrow Ni(s) \quad E^\circ_{Ni^{2+}/Ni} = -0.257\ V$$

Galvanic cells have positive cell potentials, and all the reduction reactions are reversible. The reaction at the anode will be the half-reaction with the smaller or more negative standard reduction potential. Reversing the reaction at the anode (to show the oxidation) but *not* its standard reduction potential gives:

$$\text{Anode (oxidation): } Ni(s) \longrightarrow Ni^{2+}(aq) + 2\,e^- \quad E^\circ_{anode} = E^\circ_{Ni^{2+}/Ni} = -0.257\ V$$
$$\text{Cathode (reduction): } Au^{3+}(aq) + 3\,e^- \longrightarrow Au(s) \quad E^\circ_{cathode} = E^\circ_{Au^{3+}/Au} = +1.498\ V$$

The least common factor is six, so the overall reaction is

$$3\,Ni(s) + 2\,Au^{3+}(aq) \longrightarrow 3\,Ni^{2+}(aq) + 2\,Au(s)$$

The reduction potentials are *not* scaled by the stoichiometric coefficients when calculating the cell potential, and the unmodified standard reduction potentials must be used.

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 1.498\ V - (-0.257\ V) = 1.755\ V$$

From the half-reactions, Ni is oxidized, so it is the reducing agent, and Au^{3+} is reduced, so it is the oxidizing agent.

Exercise 9.3.1

A galvanic cell consists of a Mg electrode in 1 *M* $Mg(NO_3)_2$ solution and a Ag electrode in 1 *M* $AgNO_3$ solution. Calculate the standard cell potential at 25 °C.

Answer

$$Mg(s) + 2\,Ag^+(aq) \longrightarrow Mg^{2+}(aq) + 2\,Ag(s) \quad E^\circ_{cell} = 0.7996\ V - (-2.372\ V) = 3.172\ V$$

Summary

Assigning the potential of the standard hydrogen electrode (SHE) as zero volts allows the determination of standard reduction potentials, E°, for half-reactions in electrochemical cells. As the name implies, standard reduction potentials use standard states (1 bar or 1 atm for gases; 1 *M* for solutes, often at 298.15 K) and are written as reductions (where electrons appear on the left side of the equation). The reduction reactions are reversible, so standard cell potentials can be calculated by subtracting the standard reduction potential for the reaction at the anode from the standard reduction for the reaction at the cathode. When calculating the

standard cell potential, the standard reduction potentials are *not* scaled by the stoichiometric coefficients in the balanced overall equation.

Key Equations

- $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$

Glossary

standard cell potential (E°_{cell})

the cell potential when all reactants and products are in their standard states (1 bar or 1 atm or gases; 1 *M* for solutes), usually at 298.15 K; can be calculated by subtracting the standard reduction potential for the half-reaction at the anode from the standard reduction potential for the half-reaction occurring at the cathode

standard hydrogen electrode (SHE)

the electrode consists of hydrogen gas bubbling through hydrochloric acid over an inert platinum electrode whose reduction at standard conditions is assigned a value of 0 V; the reference point for standard reduction potentials

standard reduction potential (E°)

the value of the reduction under standard conditions (1 bar or 1 atm for gases; 1 *M* for solutes) usually at 298.15 K; tabulated values used to calculate standard cell potentials

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9.4: The Nernst Equation

Learning Objectives

- Relate cell potentials to free 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

We will now extend electrochemistry by determining the relationship between E°_{cell} and the thermodynamics quantities such as ΔG° (Gibbs free energy) and K (the equilibrium constant). In galvanic cells, chemical energy is converted into electrical energy, which can do work. The electrical work is the product of the charge transferred multiplied by the potential difference (voltage):

$$\text{electrical work} = \text{volts} \times (\text{charge in coulombs}) = \text{J}$$

The charge on 1 mole of electrons is given by Faraday's constant (F)

$$\begin{aligned} F &= \frac{6.022 \times 10^{23}\ e^-}{mol} \times \frac{1.602 \times 10^{-19}\ C}{e^-} \\ &= 9.648 \times 10^4\ \frac{C}{mol} \\ &= 9.648 \times 10^4\ \frac{J}{V \cdot mol} \end{aligned}$$

Therefore

$$\text{total charge} = (\text{number of moles of e}^-) \times F = nF$$

In this equation, n is the number of moles of electrons for the *balanced* oxidation-reduction reaction. The measured cell potential is the maximum potential the cell can produce and is related to the electrical work (w_{ele}) by

$$E_{\text{cell}} = \frac{-w_{\text{ele}}}{nF} \qquad \text{or} \qquad w_{\text{ele}} = -nFE_{\text{cell}}$$

The negative sign for the work indicates that the electrical work is done by the system (the galvanic cell) on the surroundings. In an earlier chapter, the free energy was defined as the energy that was available to do work. In particular, the change in free energy was defined in terms of the maximum work (w_{max}), which, for electrochemical systems, is w_{ele}.

$$\begin{aligned} \Delta G &= w_{\text{max}} = w_{\text{ele}} \\ &= -nFE_{\text{cell}} \end{aligned}$$

We can verify the signs are correct when we realize that n and F are positive constants and that galvanic cells, which have positive cell potentials, involve spontaneous reactions. Thus, spontaneous reactions, which have $\Delta G < 0$, must have $E_{cell} > 0$. If all the reactants and products are in their standard states, this becomes

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

This provides a way to relate standard cell potentials to equilibrium constants, since

$$\Delta G^\circ = -RT \ln K$$

$$-nFE^\circ_{\text{cell}} = -RT \ln K$$

or

$$E^\circ_{\text{cell}} = \frac{RT}{nF} \ln K$$

Most of the time, the electrochemical reactions are run at standard temperature (298.15 K). Collecting terms at this temperature yields

$$E^\circ_{\text{cell}} = \frac{RT}{nF} \ln K$$
$$= \frac{\left(8.314 \, \frac{\text{J}}{\text{K·mol}}\right)(298.15 \, K)}{n \times 96,485 \, \text{C/V·mol}} \ln K$$
$$= \frac{0.0257 \, \text{V}}{n} \ln K$$

where n is the number of moles of electrons. The logarithm in equations involving cell potentials is often expressed using base 10 logarithms (i.e., $\log_{10}$ or just log), which changes the constant by a factor of 2.303:

$$E^\circ_{\text{cell}} = \frac{0.0592 \, \text{V}}{n} \log K$$

Thus, if $\Delta G°$, K, or E°_{cell} is known or can be calculated, the other two quantities can be readily determined. The relationships are shown graphically in Figure 9.4.1.

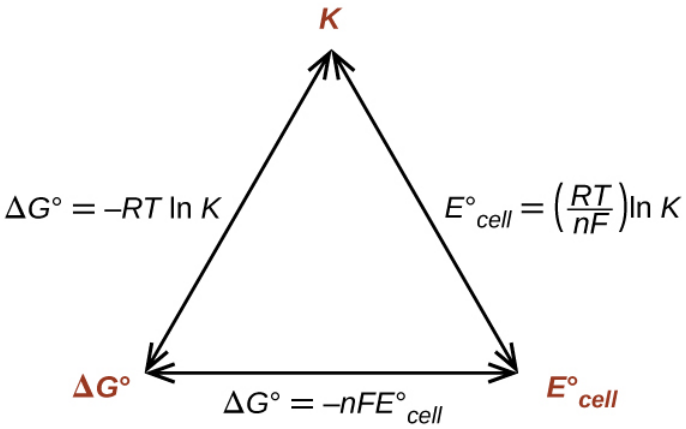


Figure 9.4.1: The relationships between ΔG°, K, and E°_{cell}. *Given any one of the three quantities, the other two can be calculated, so any of the quantities could be used to determine whether a process was spontaneous.*

A diagram is shown that involves three double headed arrows positioned in the shape of an equilateral triangle. The vertices are labeled in red. The top vertex is labeled “K.“ The vertex at the lower left is labeled “delta G superscript degree symbol.” The vertex at the lower right is labeled “E superscript degree symbol subscript cell.” The right side of the triangle is labeled “E superscript degree symbol subscript cell equals (R T divided by n F) l n K.” The lower side of the triangle is labeled “delta G superscript degree symbol equals negative n F E superscript degree symbol subscript cell.” The left side of the triangle is labeled “delta G superscript degree symbol equals negative R T l n K.”

Given any one of the quantities, the other two can be calculated.

✔ Example 9.4.1: Equilibrium Constants, Potentials, & Free Energy Changes

What is the standard Gibbs free energy change and equilibrium constant for the following reaction at 25 °C?

$$2\,\text{Ag}^+(aq) + \text{Fe}(s) \rightleftharpoons 2\,\text{Ag}(s) + \text{Fe}^{2+}(aq)$$

Solution

The reaction involves an oxidation-reduction reaction, so the standard cell potential can be calculated using the data in Table P1.

$$\text{anode (oxidation): } \text{Fe}(s) \longrightarrow \text{Fe}^{2+}(aq) + 2\,\text{e}^- \qquad E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.447 \, \text{V}$$
$$\text{cathode (reduction): } 2 \times (\text{Ag}^+(aq) + \text{e}^- \longrightarrow \text{Ag}(s)) \qquad E^\circ_{\text{Ag}^+/\text{Ag}} = 0.7996 \, \text{V}$$
$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = E^\circ_{\text{Ag}^+/\text{Ag}} - E^\circ_{\text{Fe}^{2+}/\text{Fe}} = +1.247 \, \text{V}$$

Remember that the cell potential for the cathode is not multiplied by two when determining the standard cell potential. With n = 2, the equilibrium constant is then

$$E^\circ_{\text{cell}} = \frac{0.0592\ \text{V}}{n} \log K$$

$$\begin{aligned} K &= 10^{n \times E^\circ_{\text{cell}}/0.0592\ \text{V}} \\ &= 10^{2 \times 1.247\ \text{V}/0.0592\ \text{V}} \\ &= 10^{42.128} \\ &= 1.3 \times 10^{42} \end{aligned}$$

The standard free energy is then

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

$$\Delta G^\circ = -2 \times 96,485\ \frac{\text{J}}{\text{V} \cdot \text{mol}} \times 1.247\ \text{V} = -240.6\ \frac{\text{kJ}}{\text{mol}}$$

Check your answer: A positive standard cell potential means a spontaneous reaction, so the standard free energy change should be negative, and an equilibrium constant should be >1.

? Exercise 9.4.1

What is the standard Gibbs free energy change and the equilibrium constant for the following reaction at room temperature? Is the reaction spontaneous?

$$\text{Sn}(s) + 2\,\text{Cu}^{2+}(aq) \rightleftharpoons \text{Sn}^{2+}(aq) + 2\,\text{Cu}^{+}(aq)$$

Answer

Spontaneous; n = 2; $E^\circ_{\text{cell}} = +0.291\ \text{V}$; $\Delta G^\circ = -56.2\ \frac{\text{kJ}}{\text{mol}}$; $K = 6.8 \times 10^9$.

Now that the connection has been made between the free energy and cell potentials, nonstandard concentrations follow. Recall that

$$\Delta G = \Delta G^\circ + RT \ln Q$$

where Q is the reaction quotient (see the chapter on equilibrium fundamentals). Converting to cell potentials:

$$-nFE_{\text{cell}} = -nFE^\circ_{\text{cell}} + RT \ln Q \tag{9.4.1}$$

or

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln Q \tag{9.4.2}$$

Equation 9.4.2 is the generalized Nernst equation that is applicable at any temperature. However, is can be simplified for reactions occuring at 25 °C (298.15 K) by rewriting it as

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0257\ \text{V}}{n} \ln Q \tag{9.4.3}$$

or

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592\ \text{V}}{n} \log_{10} Q \tag{9.4.4}$$

If the temperature is not 298.15 K, it is necessary to recalculate the potential with Equation9.4.2. With the Nernst equation, it is possible to calculate the cell potential at nonstandard conditions. This adjustment is necessary because potentials determined under different conditions will have different values.

✓ Example 9.4.2: Cell Potentials at Nonstandard Conditions

Consider the following reaction at room temperature:

$$\text{Co}(s) + \text{Fe}^{2+}(aq,\ 1.94\ M) \longrightarrow \text{Co}^{2+}(aq,\ 0.15\ M) + \text{Fe}(s)$$

Is the process spontaneous?

Solution

There are two ways to solve the problem. If the thermodynamic information in Table T1 were available, you could calculate the free energy change. If the free energy change is negative, the process is spontaneous. The other approach, which we will use, requires information like that given in Table P1. Using those data, the cell potential can be determined. If the cell potential is positive, the process is spontaneous. Collecting information from Table P1 and the problem,

$$\begin{aligned}&\text{Anode (oxidation): } \mathrm{Co}(s) \longrightarrow \mathrm{Co}^{2+}(aq) + 2\,\mathrm{e}^- \qquad E^\circ_{\mathrm{Co}^{2+}/\mathrm{Co}} = -0.28\ \mathrm{V}\\ &\text{Cathode (reduction): } \mathrm{Fe}^{2+}(aq) + 2\,\mathrm{e}^- \longrightarrow \mathrm{Fe}(s) \qquad E^\circ_{\mathrm{Fe}^{2+}/\mathrm{Fe}} = -0.447\ \mathrm{V}\\ &E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = -0.447\ \mathrm{V} - (-0.28\ \mathrm{V}) = -0.17\ \mathrm{V}\end{aligned}$$

The process is not spontaneous under standard conditions. Using the Nernst equation and the concentrations stated in the problem and $n = 2$,

$$Q = \frac{[Co^2+]}{[Fe^2+]} = \frac{0.15\ M}{1.94\ M} = 0.077$$

Now we can insert these into the Nernst Equation at room temperature (Equation 9.4.4)

$$\begin{aligned}E_{\text{cell}} &= E^\circ_{\text{cell}} - \frac{0.0592\ \mathrm{V}}{n}\log Q\\ &= -0.17\ \mathrm{V} - \frac{0.0592\ \mathrm{V}}{2}\log 0.077\\ &= -0.17\ \mathrm{V} + 0.033\ \mathrm{V} = -0.14\ \mathrm{V}\end{aligned}$$

The process is (still) nonspontaneous.

? Exercise 9.4.2

What is the cell potential for the following reaction at room temperature?

$$\mathrm{Al}(s)\,|\,\mathrm{Al}^{3+}(aq,\ 0.15\ M)\,\|\,\mathrm{Cu}^{2+}(aq,\ 0.025\ M)\,|\,\mathrm{Cu}(s)$$

What are the values of *n* and Q for the overall reaction? Is the reaction spontaneous under these conditions?

Answer

n = 6; *Q* = 1440; E_{cell} = +1.97 V, spontaneous.

Finally, we will take a brief look at a special type of cell called a concentration cell. In a concentration cell, the electrodes are the same material and the half-cells differ only in concentration. Since one or both compartments is not standard, the cell potentials will be unequal; therefore, there will be a potential difference, which can be determined with the aid of the Nernst equation.

✓ Example 9.4.3: Concentration Cells

What is the cell potential of the concentration cell described by

$$\mathrm{Zn}(s)\,|\,\mathrm{Zn}^{2+}(aq,\ 0.10\ M)\,\|\,\mathrm{Zn}^{2+}(aq,\ 0.50\ M)\,|\,\mathrm{Zn}(s)$$

Solution

From the information given:

$$\begin{aligned}&\text{Anode: } \mathrm{Zn}(s) \longrightarrow \mathrm{Zn}^{2+}(aq,\ 0.10\ M) + 2\,\mathrm{e}^- \qquad E^\circ_{\text{anode}} = -0.7618\ \mathrm{V}\\ &\text{Cathode: } \mathrm{Zn}^{2+}(aq,\ 0.50\ M) + 2\,\mathrm{e}^- \longrightarrow \mathrm{Zn}(s) \qquad E^\circ_{\text{cathode}} = -0.7618\ \mathrm{V}\\ &\hline\\ &\text{Overall: } \mathrm{Zn}^{2+}(aq,\ 0.50\ M) \longrightarrow \mathrm{Zn}^{2+}(aq,\ 0.10\ M) \qquad E^\circ_{\text{cell}} = 0.000\ \mathrm{V}\end{aligned}$$

The standard cell potential is zero because the anode and cathode involve the same reaction; only the concentration of Zn^{2+} changes. Substituting into the Nernst equation,

$$E_{cell} = 0.000\ V - \frac{0.0592\ V}{2} \log \frac{0.10}{0.50} = +0.021\ V$$

and the process is spontaneous at these conditions.

Check your answer: In a concentration cell, the standard cell potential will always be zero. To get a positive cell potential (spontaneous process) the reaction quotient Q must be <1. $Q < 1$ in this case, so the process is spontaneous.

? Exercise 9.4.3

What value of Q for the previous concentration cell would result in a voltage of 0.10 V? If the concentration of zinc ion at the cathode was 0.50 M, what was the concentration at the anode?

Answer

Q = 0.00042; $[Zn^{2+}]_{cat}$ = 2.1 \times 10^{-4} M.

Summary

Electrical work (w_{ele}) is the negative of the product of the total charge (Q) and the cell potential (E_{cell}). The total charge can be calculated as the number of moles of electrons (n) times the Faraday constant (F = 96,485 C/mol e^-). Electrical work is the maximum work that the system can produce and so is equal to the change in free energy. Thus, anything that can be done with or to a free energy change can also be done to or with a cell potential. The Nernst equation relates the cell potential at nonstandard conditions to the logarithm of the reaction quotient. Concentration cells exploit this relationship and produce a positive cell potential using half-cells that differ only in the concentration of their solutes.

Key Equations

- $E^\circ_{cell} = \frac{RT}{nF} \ln K$
- $E^\circ_{cell} = \frac{0.0257\ V}{n} \ln K = \frac{0.0592\ V}{n} \log K \quad (\text{at } 298.15\ K)$
- $E_{cell} = E^\circ_{cell} - \frac{RT}{nF} \ln Q \quad (\text{Nernst equation})$
- $E_{cell} = E^\circ_{cell} - \frac{0.0257\ V}{n} \ln Q = E^\circ_{cell} - \frac{0.0592\ V}{n} \log Q \quad (\text{at } 298.15\ K)$
- $\Delta G = -nFE_{cell}$
- $\Delta G^\circ = -nFE^\circ_{cell}$
- $w_{ele} = w_{max} = -nFE_{cell}$

Glossary

concentration cell

galvanic cell in which the two half-cells are the same except for the concentration of the solutes; spontaneous when the overall reaction is the dilution of the solute

electrical work (w_{ele})

negative of total charge times the cell potential; equal to w_{max} for the system, and so equals the free energy change (ΔG)

Faraday's constant (F)

charge on 1 mol of electrons; F = 96,485 C/mol e^-

Nernst equation

equation that relates the logarithm of the reaction quotient (Q) to nonstandard cell potentials; can be used to relate equilibrium constants to standard cell potentials

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9.5: Batteries and Fuel Cells

Learning Objectives

- Classify batteries as primary or secondary
- List some of the characteristics and limitations of batteries
- Provide a general description of a fuel cell

A battery is an electrochemical cell or series of cells that produces an electric current. In principle, any galvanic cell could be used as a battery. An ideal battery would never run down, produce an unchanging voltage, and be capable of withstanding environmental extremes of heat and humidity. Real batteries strike a balance between ideal characteristics and practical limitations. For example, the mass of a car battery is about 18 kg or about 1% of the mass of an average car or light-duty truck. This type of battery would supply nearly unlimited energy if used in a smartphone, but would be rejected for this application because of its mass. Thus, no single battery is "best" and batteries are selected for a particular application, keeping things like the mass of the battery, its cost, reliability, and current capacity in mind. There are two basic types of batteries: primary and secondary. A few batteries of each type are described next.

> *Visit this site to learn more about batteries.*

Primary Batteries

Primary batteries are single-use batteries because they cannot be recharged. A common primary battery is the dry cell (Figure **9.5.1**). The dry cell is a zinc-carbon battery. The zinc can serves as both a container and the negative electrode. The positive electrode is a rod made of carbon that is surrounded by a paste of manganese(IV) oxide, zinc chloride, ammonium chloride, carbon powder, and a small amount of water. The reaction at the anode can be represented as the ordinary oxidation of zinc:

$$\mathrm{Zn}(s) \longrightarrow \mathrm{Zn^{2+}}(aq) + 2\,\mathrm{e^-} \quad E^\circ_{\mathrm{Zn^{2+}/Zn}} = -0.7618\ \mathrm{V}$$

The reaction at the cathode is more complicated, in part because more than one reaction occurs. The series of reactions that occurs at the cathode is approximately

$$2\,\mathrm{MnO_2}(s) + 2\,\mathrm{NH_4Cl}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Mn_2O_3}(s) + 2\,\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) + 2\,\mathrm{Cl^-}$$

The overall reaction for the zinc–carbon battery can be represented as

$$2\,\mathrm{MnO_2}(s) + 2\,\mathrm{NH_4Cl}(aq) + \mathrm{Zn}(s) \longrightarrow \mathrm{Zn^{2+}}(aq) + \mathrm{Mn_2O_3}(s) + 2\,\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) + 2\,\mathrm{Cl^-}$$

with an overall cell potential which is initially about 1.5 V, but decreases as the battery is used. It is important to remember that the voltage delivered by a battery is the same regardless of the size of a battery. For this reason, D, C, A, AA, and AAA batteries all have the same voltage rating. However, larger batteries can deliver more moles of electrons. As the zinc container oxidizes, its contents eventually leak out, so this type of battery should not be left in any electrical device for extended periods.



Figure **9.5.1**: The diagram shows a cross section of a flashlight battery, a zinc-carbon dry cell.

A diagram of a cross section of a dry cell battery is shown. The overall shape of the cell is cylindrical. The lateral surface of the cylinder, indicated as a thin red line, is labeled "zinc can (electrode)." Just beneath this is a slightly thicker dark grey surface that covers the lateral surface, top, and bottom of the battery, which is labeled "Porous separator." Inside is a purple region with many evenly spaced small darker purple dots, labeled "Paste of M n O subscript 2, N H subscript 4 C l, Z n C l subscript 2, water (cathode)." A dark grey rod, labeled "Carbon rod (electrode)," extends from the top of the battery, leaving a gap of less than one-fifth the height of the battery below the rod to the bottom of the cylinder. A thin grey line segment at the very bottom of the cylinder is labeled "Metal bottom cover (negative)." The very top of the cylinder has a thin grey surface that curves upward at the center over the top of the carbon electrode at the center of the cylinder. This upper surface is labeled "Metal top cover (positive)." A thin dark grey line just below this surface is labeled "Insulator." Below this, above the purple region, and outside of the carbon electrode at the center is an orange region that is labeled "Seal."

Alkaline batteries (Figure **9.5.2**) were developed in the 1950s partly to address some of the performance issues with zinc–carbon dry cells. They are manufactured to be exact replacements for zinc-carbon dry cells. As their name suggests, these types of batteries use alkaline electrolytes, often potassium hydroxide. The reactions are

$$\begin{aligned}&\text{anode: } \mathrm{Zn}(s) + 2\,\mathrm{OH^-}(aq) \longrightarrow \mathrm{ZnO}(s) + \mathrm{H_2O}(l) + 2\,\mathrm{e^-} \qquad E^\circ_{\text{anode}} = -1.28\ \mathrm{V}\\ &\underline{\text{cathode: } 2\,\mathrm{MnO_2}(s) + \mathrm{H_2O}(l) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Mn_2O_3}(s) + 2\,\mathrm{OH^-}(aq) \qquad E^\circ_{\text{cathode}} = +0.15\ \mathrm{V}}\\ &\text{overall: } \mathrm{Zn}(s) + 2\,\mathrm{MnO_2}(s) \longrightarrow \mathrm{ZnO}(s) + \mathrm{Mn_2O_3}(s) \qquad E^\circ_{\text{cell}} = +1.43\ \mathrm{V}\end{aligned}$$

An alkaline battery can deliver about three to five times the energy of a zinc-carbon dry cell of similar size. Alkaline batteries are prone to leaking potassium hydroxide, so these should also be removed from devices for long-term storage. While some alkaline batteries are rechargeable, most are not. Attempts to recharge an alkaline battery that is not rechargeable often leads to rupture of the battery and leakage of the potassium hydroxide electrolyte.

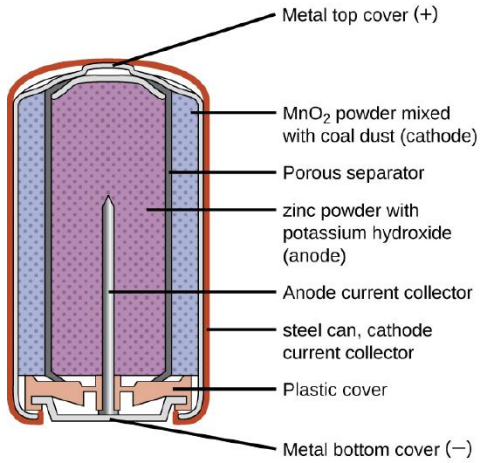


Figure **9.5.2**: Alkaline batteries were designed as direct replacements for zinc-carbon (dry cell) batteries.

Secondary Batteries

Secondary batteries are rechargeable. These are the types of batteries found in devices such as smartphones, electronic tablets, and automobiles.

Nickel-cadmium, or NiCd, batteries (Figure **9.5.3**) consist of a nickel-plated cathode, cadmium-plated anode, and a potassium hydroxide electrode. The positive and negative plates, which are prevented from shorting by the separator, are rolled together and put into the case. This is a “jelly-roll” design and allows the NiCd cell to deliver much more current than a similar-sized alkaline battery. The reactions are

$$\begin{aligned}&\text{anode: } \mathrm{Cd}(s) + 2\,\mathrm{OH^-}(aq) \longrightarrow \mathrm{Cd(OH)_2}(s) + 2\,\mathrm{e^-}\\ &\underline{\text{cathode: } \mathrm{NiO_2}(s) + 2\,\mathrm{H_2O}(l) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Ni(OH)_2}(s) + 2\,\mathrm{OH^-}(aq)}\\ &\text{overall: } \mathrm{Cd}(s) + \mathrm{NiO_2}(s) + 2\,\mathrm{H_2O}(l) \longrightarrow \mathrm{Cd(OH)_2}(s) + \mathrm{Ni(OH)_2}(s)\end{aligned}$$

The voltage is about 1.2 V to 1.25 V as the battery discharges. When properly treated, a NiCd battery can be recharged about 1000 times. Cadmium is a toxic heavy metal so NiCd batteries should never be opened or put into the regular trash.

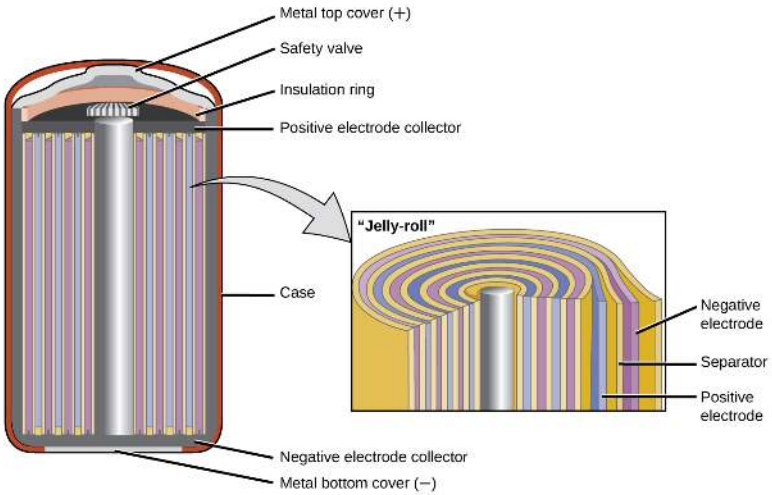


Figure 9.5.3: NiCd batteries use a "jelly-roll" design that significantly increases the amount of current the battery can deliver as compared to a similar-sized alkaline battery.

Lithium ion batteries (Figure 9.5.4) are among the most popular rechargeable batteries and are used in many portable electronic devices. The reactions are

$$\begin{aligned}&\text{anode: } \mathrm{LiCoO_2} \rightleftharpoons \mathrm{Li_{1-x}CoO_2} + x\mathrm{Li^+} + x\mathrm{e^-}\\ &\text{cathode: } x\mathrm{Li^+} + x\mathrm{e^-} + x\mathrm{C_6} \rightleftharpoons x\mathrm{LiC_6}\\ \hline &\text{overall: } \mathrm{LiCoO_2} + x\mathrm{C_6} \rightleftharpoons \mathrm{Li_{1-x}CoO_2} + x\mathrm{LiC_6}\end{aligned}$$

With the coefficients representing moles, x is no more than about 0.5 moles. The battery voltage is about 3.7 V. Lithium batteries are popular because they can provide a large amount current, are lighter than comparable batteries of other types, produce a nearly constant voltage as they discharge, and only slowly lose their charge when stored.

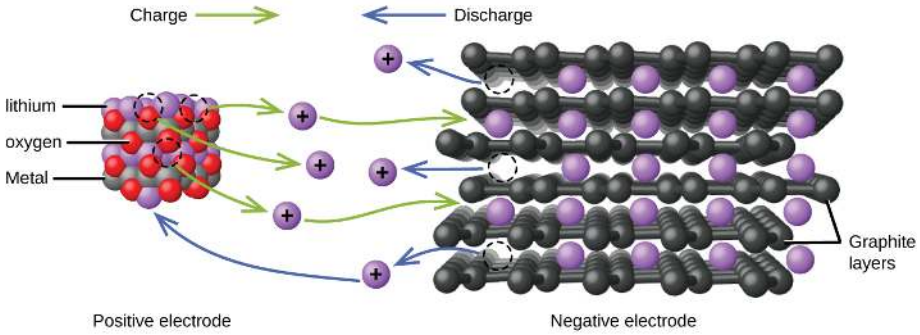


Figure 9.5.4: In a lithium ion battery, charge flows between the electrodes as the lithium ions move between the anode and cathode.

The lead acid battery (Figure 9.5.5) is the type of secondary battery used in your automobile. It is inexpensive and capable of producing the high current required by automobile starter motors. The reactions for a lead acid battery are

$$\begin{aligned}&\text{anode: } \mathrm{Pb}(s) + \mathrm{HSO_4^-}(aq) \longrightarrow \mathrm{PbSO_4}(s) + \mathrm{H^+}(aq) + 2\,\mathrm{e^-}\\ &\text{cathode: } \mathrm{PbO_2}(s) + \mathrm{HSO_4^-}(aq) + 3\,\mathrm{H^+}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{PbSO_4}(s) + 2\,\mathrm{H_2O}(l)\\ \hline &\text{overall: } \mathrm{Pb}(s) + \mathrm{PbO_2}(s) + 2\,\mathrm{H_2SO_4}(aq) \longrightarrow 2\,\mathrm{PbSO_4}(s) + 2\,\mathrm{H_2O}(l)\end{aligned}$$

Each cell produces 2 V, so six cells are connected in series to produce a 12-V car battery. Lead acid batteries are heavy and contain a caustic liquid electrolyte, but are often still the battery of choice because of their high current density. Since these batteries contain a significant amount of lead, they must always be disposed of properly.

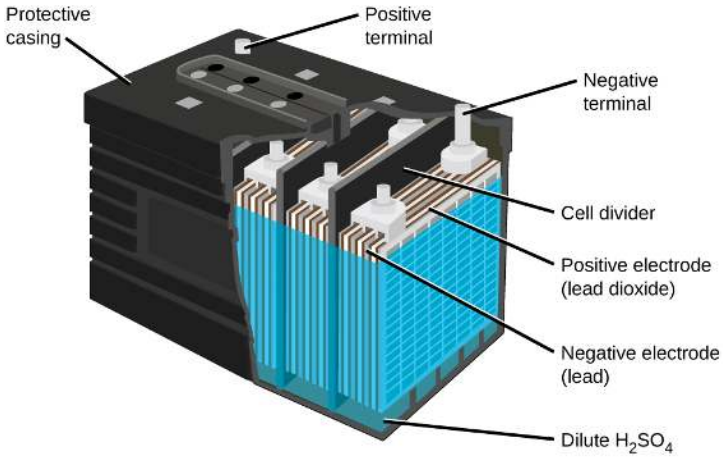


Figure **9.5.5**: The lead acid battery in your automobile consists of six cells connected in series to give 12 V. Their low cost and high current output makes these excellent candidates for providing power for automobile starter motors.

Fuel Cells

A fuel cell is a device that converts chemical energy into electrical energy. Fuel cells are similar to batteries but require a continuous source of fuel, often hydrogen. They will continue to produce electricity as long as fuel is available. Hydrogen fuel cells have been used to supply power for satellites, space capsules, automobiles, boats, and submarines (Figure **9.5.6**).

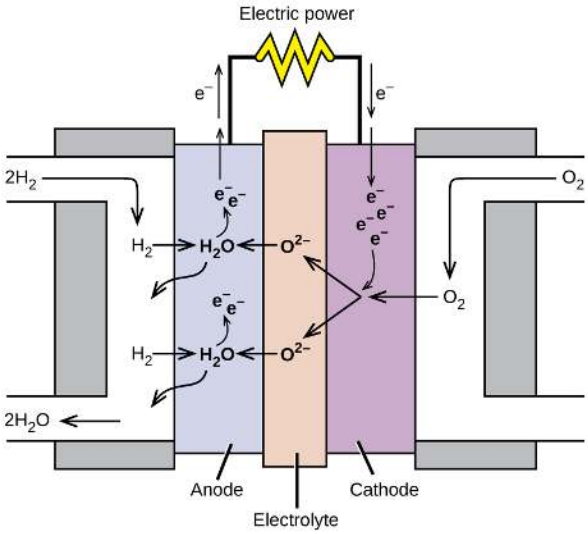


Figure **9.5.6**: In this hydrogen fuel-cell schematic, oxygen from the air reacts with hydrogen, producing water and electricity.

In a hydrogen fuel cell, the reactions are

$$\begin{aligned}&\text{anode: } 2\,H_2 + 2\,O^{2-} \longrightarrow 2\,H_2O + 4\,e^-\\ &\text{cathode: } O_2 + 4\,e^- \longrightarrow 2\,O^{2-}\\ &\text{overall: } 2\,H_2 + O_2 \longrightarrow 2\,H_2O\end{aligned}$$

The voltage is about 0.9 V. The efficiency of fuel cells is typically about 40% to 60%, which is higher than the typical internal combustion engine (25% to 35%) and, in the case of the hydrogen fuel cell, produces only water as exhaust. Currently, fuel cells are rather expensive and contain features that cause them to fail after a relatively short time.

Summary

Batteries are galvanic cells, or a series of cells, that produce an electric current. When cells are combined into batteries, the potential of the battery is an integer multiple of the potential of a single cell. There are two basic types of batteries: primary and secondary. Primary batteries are “single use” and cannot be recharged. Dry cells and (most) alkaline batteries are examples of

primary batteries. The second type is rechargeable and is called a secondary battery. Examples of secondary batteries include nickel-cadmium (NiCd), lead acid, and lithium ion batteries. Fuel cells are similar to batteries in that they generate an electrical current, but require continuous addition of fuel and oxidizer. The hydrogen fuel cell uses hydrogen and oxygen from the air to produce water, and is generally more efficient than internal combustion engines.

Summary

alkaline battery

primary battery that uses an alkaline (often potassium hydroxide) electrolyte; designed to be an exact replacement for the dry cell, but with more energy storage and less electrolyte leakage than typical dry cell

battery

galvanic cell or series of cells that produces a current; in theory, any galvanic cell

dry cell

primary battery, also called a zinc-carbon battery; can be used in any orientation because it uses a paste as the electrolyte; tends to leak electrolyte when stored

fuel cell

devices that produce an electrical current as long as fuel and oxidizer are continuously added; more efficient than internal combustion engines

lead acid battery

secondary battery that consists of multiple cells; the lead acid battery found in automobiles has six cells and a voltage of 12 V

lithium ion battery

very popular secondary battery; uses lithium ions to conduct current and is light, rechargeable, and produces a nearly constant potential as it discharges

nickel-cadmium battery

(NiCd battery) secondary battery that uses cadmium, which is a toxic heavy metal; heavier than lithium ion batteries, but with similar performance characteristics

primary battery

single-use nonrechargeable battery

secondary battery

battery that can be recharged

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9.6: Corrosion

Learning Objectives

- Define corrosion
- List some of the methods used to prevent or slow corrosion

Corrosion is usually defined as the degradation of metals due to an electrochemical process. The formation of rust on iron, tarnish on silver, and the blue-green patina that develops on copper are all examples of corrosion. The total cost of corrosion in the United States is significant, with estimates in excess of half a trillion dollars a year.

Changing Colors

The Statue of Liberty is a landmark every American recognizes. The Statue of Liberty is easily identified by its height, stance, and unique blue-green color. When this statue was first delivered from France, its appearance was not green. It was brown, the color of its copper "skin." So how did the Statue of Liberty change colors? The change in appearance was a direct result of corrosion. The copper that is the primary component of the statue slowly underwent oxidation from the air. The oxidation-reduction reactions of copper metal in the environment occur in several steps. Copper metal is oxidized to copper(I) oxide ($\mathbf{Cu_2O}$), which is red, and then to copper(II) oxide, which is black.

$$2\,\mathrm{Cu\,(s)} + \tfrac{1}{2}\,\mathrm{O_2\,(g)} \rightarrow \underset{\text{red}}{\mathrm{Cu_2O\,(s)}}$$

$$\mathrm{Cu_2O\,(s)} + \tfrac{1}{2}\,\mathrm{O_2\,(g)} \rightarrow 2\,\underset{\text{black}}{\mathrm{CuO\,(s)}}$$

Coal, which was often high in sulfur, was burned extensively in the early part of the last century. As a result, sulfur trioxide, carbon dioxide, and water all reacted with the $\mathbf{CuO}$.

$$2\,\mathrm{CuO\,(s)} + \mathrm{CO_2\,(g)} + \mathrm{H_2O\,(l)} \rightarrow \underset{\text{green}}{\mathrm{Cu_2CO_3(OH)_2\,(s)}}$$

$$3\,\mathrm{CuO\,(s)} + 2\,\mathrm{CO_2\,(g)} + \mathrm{H_2O\,(l)} \rightarrow \underset{\text{blue}}{\mathrm{Cu_2(CO_3)_2(OH)_2\,(s)}}$$

$$4\,\mathrm{CuO\,(s)} + \mathrm{SO_3\,(g)} + 3\,\mathrm{H_2O\,(l)} \rightarrow \underset{\text{green}}{\mathrm{Cu_4SO_4(OH)_6\,(s)}}$$

These three compounds are responsible for the characteristic blue-green patina seen today. Fortunately, formation of the patina created a protective layer on the surface, preventing further corrosion of the copper skin. The formation of the protective layer is a form of passivation, which is discussed further in a later chapter.

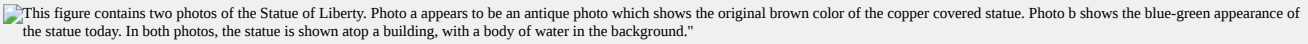


Figure **9.6.1**: (a) The Statue of Liberty is covered with a copper skin, and was originally brown, as shown in this painting. (b) Exposure to the elements has resulted in the formation of the blue-green patina seen today.

Perhaps the most familiar example of corrosion is the formation of rust on iron. Iron will rust when it is exposed to oxygen and water. The main steps in the rusting of iron appear to involve the following. Once exposed to the atmosphere, iron rapidly oxidizes.

$$\text{anode: } \mathrm{Fe_{(s)}} \rightarrow \mathrm{Fe^{2+}{}_{(aq)}} + 2\,\mathrm{e^-} \quad E^\circ_{\mathrm{Fe^{2+}/Fe}} = -0.44\ \mathrm{V}$$

The electrons reduce oxygen in the air in acidic solutions.

$$\text{cathode: } \mathrm{O_{2(g)}} + 4\,\mathrm{H^+{}_{(aq)}} + 4\,\mathrm{e^-} \rightarrow 2\,\mathrm{H_2O_{(l)}} \quad E^\circ_{\mathrm{O_2/O_2}} = +1.23\ \mathrm{V}$$

$$\text{overall: } 2\,\mathrm{Fe_{(s)}} + \mathrm{O_{2(g)}} + 4\,\mathrm{H^+{}_{(aq)}} \rightarrow 2\,\mathrm{Fe^{2+}{}_{(aq)}} + 2\,\mathrm{H_2O_{(l)}} \quad E^\circ_{\text{cell}} = +1.67\ \mathrm{V}$$

What we call rust is hydrated iron(III) oxide, which forms when iron(II) ions react further with oxygen.

$$4\,\mathrm{Fe^{2+}{}_{(aq)}} + \mathrm{O_{2(g)}} + (4+2x)\mathrm{H_2O_{(l)}} \rightarrow 2\,\mathrm{Fe_2O_3 \cdot}\,x\mathrm{H_2O_{(s)}} + 8\,\mathrm{H^+{}_{(aq)}}$$

The number of water molecules is variable, so it is represented by *x*. Unlike the patina on copper, the formation of rust does not create a protective layer and so corrosion of the iron continues as the rust flakes off and exposes fresh iron to the atmosphere.

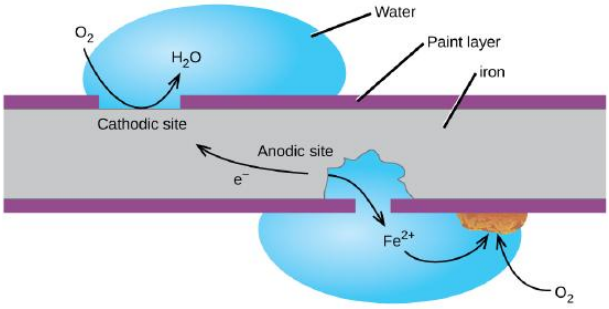


Figure **9.6.2**: Once the paint is scratched on a painted iron surface, corrosion occurs and rust begins to form. The speed of the spontaneous reaction is increased in the presence of electrolytes, such as the sodium chloride used on roads to melt ice and snow or in salt water.

A grey rectangle, labeled “iron,” is shown with thin purple layers, labeled “Paint layer,” at its upper and lower surfaces. A gap in the upper purple layer at the upper left of the diagram is labeled “Cathodic site.” A blue droplet labeled “water” is positioned on top of the gap. A curved arrow extends from a space above the droplet to the surface of the grey region and into the water droplet. The base of the arrow is labeled “O subscript 2” and the tip of the arrow is labeled “H subscript 2 O.” A gap to the right and on the bottom side of the grey region shows that some of the grey region is gone from the region beneath the purple layer. A water droplet covers this gap and extends into the open space in the grey rectangle. The label “F e superscript 2 positive” is at the center of the droplet. A curved arrow points from the edge of the grey area below to the label. A second curved arrow extends from the F e superscript 2 positive arrow to a rust brown chunk on the lower surface of the purple layer at the edge of the water droplet. A curved arrow extends from O subscript 2 outside the droplet into the droplet to the rust brown chunk. The grey region at the lower right portion of the diagram is labeled “Anodic site.” An arrow extends from the anodic site toward the cathodic site, which is labeled “e superscript negative.”

One way to keep iron from corroding is to keep it painted. The layer of paint prevents the water and oxygen necessary for rust formation from coming into contact with the iron. As long as the paint remains intact, the iron is protected from corrosion.

Other strategies include alloying the iron with other metals. For example, stainless steel is mostly iron with a bit of chromium. The chromium tends to collect near the surface, where it forms an oxide layer that protects the iron.

Zinc-plated or galvanized iron uses a different strategy. Zinc is more easily oxidized than iron because zinc has a lower reduction potential. Since zinc has a lower reduction potential, it is a more active metal. Thus, even if the zinc coating is scratched, the zinc will still oxidize before the iron. This suggests that this approach should work with other active metals.



Figure **9.6.3**: One way to protect an underground iron storage tank is through cathodic protection. Using an active metal like zinc or magnesium for the anode effectively makes the storage tank the cathode, preventing it from corroding (oxidizing).

A diagram is shown of an underground storage tank system. Underground, to the left end of the diagram is a horizontal grey tank which is labeled “Object to be protected.” A black line extends upward from the center of the tank above ground. An arrow points upward at the left side of the line segment. A horizontal black line segment continues right above ground, which is labeled “No power source is needed.” A line segment extends up and to the right, which is labeled “ Lead wire.” A line segment with a downward pointing arrow to its right extends downward below the ground to a second metal tank-like structure, labeled “Sacrificial anode” which is vertically oriented. Five black arrows point left underground toward the first tank. These arrows are collectively labeled “Protective current.”

Another important way to protect metal is to make it the cathode in a galvanic cell. This is cathodic protection and can be used for metals other than just iron. For example, the rusting of underground iron storage tanks and pipes can be prevented or greatly reduced by connecting them to a more active metal such as zinc or magnesium. This is also used to protect the metal parts in water heaters. The more active metals (lower reduction potential) are called sacrificial anodes because as they get used up as they corrode (oxidize) at the anode. The metal being protected serves as the cathode, and so does not oxidize (corrode). When the anodes are properly monitored and periodically replaced, the useful lifetime of the iron storage tank can be greatly extended.

Summary

Corrosion is the degradation of a metal caused by an electrochemical process. Large sums of money are spent each year repairing the effects of, or preventing, corrosion. Some metals, such as aluminum and copper, produce a protective layer when they corrode

in air. The thin layer that forms on the surface of the metal prevents oxygen from coming into contact with more of the metal atoms and thus “protects” the remaining metal from further corrosion. Iron corrodes (forms rust) when exposed to water and oxygen. The rust that forms on iron metal flakes off, exposing fresh metal, which also corrodes. One way to prevent, or slow, corrosion is by coating the metal. Coating prevents water and oxygen from contacting the metal. Paint or other coatings will slow corrosion, but they are not effective once scratched. Zinc-plated or galvanized iron exploits the fact that zinc is more likely to oxidize than iron. As long as the coating remains, even if scratched, the zinc will oxidize before the iron. Another method for protecting metals is cathodic protection. In this method, an easily oxidized and inexpensive metal, often zinc or magnesium (the sacrificial anode), is electrically connected to the metal that must be protected. The more active metal is the sacrificial anode, and is the anode in a galvanic cell. The “protected” metal is the cathode, and remains unoxidized. One advantage of cathodic protection is that the sacrificial anode can be monitored and replaced if needed.

Glossary

cathodic protection
: method of protecting metal by using a sacrificial anode and effectively making the metal that needs protecting the cathode, thus preventing its oxidation

corrosion
: degradation of metal through an electrochemical process

galvanized iron
: method for protecting iron by covering it with zinc, which will oxidize before the iron; zinc-plated iron

sacrificial anode
: more active, inexpensive metal used as the anode in cathodic protection; frequently made from magnesium or zinc

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9.7: Electrolysis

Learning Objectives

- Describe electrolytic cells and their relationship to galvanic cells
- Perform various calculations related to electrolysis

In galvanic cells, chemical energy is converted into electrical energy. The opposite is true for electrolytic cells. In electrolytic cells, electrical energy causes nonspontaneous reactions to occur in a process known as electrolysis. The charging electric barttery shows one such process. Electrical energy is converted into the chemical energy in the battery as it is charged. Once charged, the battery can be used to power the automobile. The same principles are involved in electrolytic cells as in galvanic cells. We will look at three electrolytic cells and the quantitative aspects of electrolysis.

The Electrolysis of Molten Sodium Chloride

In molten sodium chloride, the ions are free to migrate to the electrodes of an electrolytic cell. A simplified diagram of the cell commercially used to produce sodium metal and chlorine gas is shown in Figure **9.7.1**. Sodium is a strong reducing agent and chlorine is used to purify water, and is used in antiseptics and in paper production. The reactions are

$$\text{anode: } 2\,Cl^-(l) \longrightarrow Cl_2(g) + 2\,e^- \quad E^\circ_{Cl_2/Cl^-} = +1.3\,V \tag{9.7.1}$$

$$\text{cathode: } Na^+(l) + e^- \longrightarrow Na(l) \quad E^\circ_{Na^+/Na} = -2.7\,V \tag{9.7.2}$$

$$\text{overall: } 2\,Na^+(l) + 2\,Cl^-(l) \longrightarrow 2\,Na(l) + Cl_2(g) \quad E^\circ_{cell} = -4.0\,V \tag{9.7.3}$$

The power supply (battery) must supply a minimum of 4 V, but, in practice, the applied voltages are typically higher because of inefficiencies in the process itself.

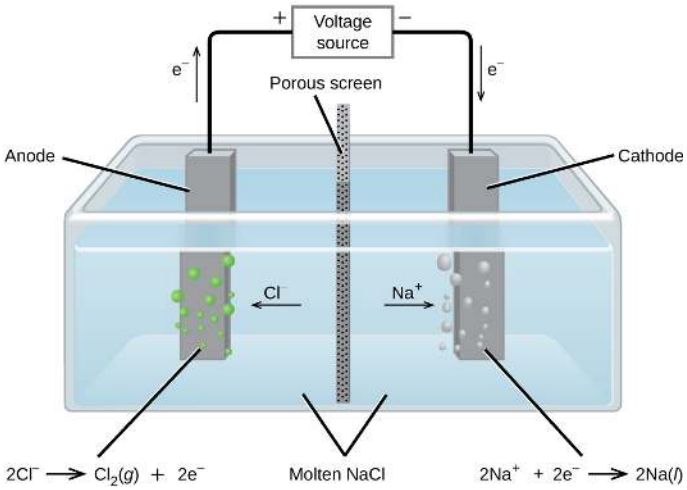


Figure **9.7.1**: Passing an electric current through molten sodium chloride decomposes the material into sodium metal and chlorine gas. Care must be taken to keep the products separated to prevent the spontaneous formation of sodium chloride.

The Electrolysis of Water

It is possible to split water into hydrogen and oxygen gas by electrolysis. Acids are typically added to increase the concentration of hydrogen ion in solution (Figure **9.7.2**). The reactions are

$$\text{anode: } 2\,H_2O(l) \longrightarrow O_2(g) + 4\,H^+(aq) + 4\,e^- \quad E^\circ_{anode} = +1.229\,V \tag{9.7.4}$$

$$\text{cathode: } 2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g) \quad E^\circ_{cathode} = 0\,V \tag{9.7.5}$$

$$\text{overall: } 2\,H_2O(l) \longrightarrow 2\,H_2(g) + O_2(g) \quad E^\circ_{cell} = -1.229\,V \tag{9.7.6}$$

Note that the sulfuric acid is not consumed and that the volume of hydrogen gas produced is twice the volume of oxygen gas produced. The minimum applied voltage is 1.229 V.

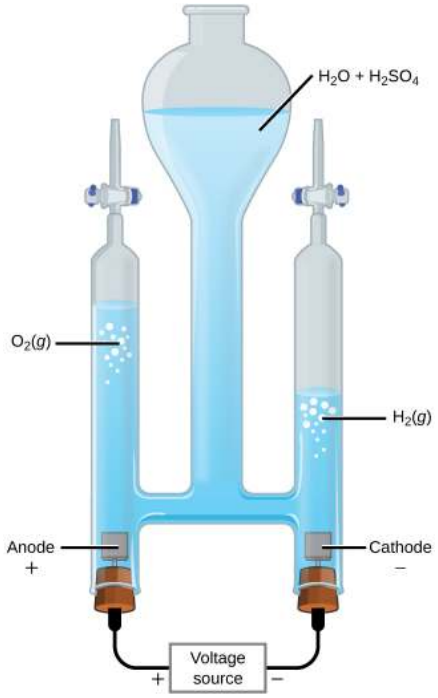


Figure **9.7.2**: Water decomposes into oxygen and hydrogen gas during electrolysis. Sulfuric acid was added to increase the concentration of hydrogen ions and the total number of ions in solution, but does not take part in the reaction. The volume of hydrogen gas collected is twice the volume of oxygen gas collected, due to the stoichiometry of the reaction.

The Electrolysis of Aqueous Sodium Chloride

The electrolysis of aqueous sodium chloride is the more common example of electrolysis because more than one species can be oxidized and reduced. Considering the anode first, the possible reactions are

$$\text{(i) } 2\,Cl^-(aq) \longrightarrow Cl_2(g) + 2\,e^- \quad E^\circ_{anode} = +1.35827\ V \tag{9.7.7}$$
$$\text{(ii) } 2\,H_2O(l) \longrightarrow O_2(g) + 4\,H^+(aq) + 4\,e^- \quad E^\circ_{anode} = +1.229\ V \tag{9.7.8}$$

These values suggest that water should be oxidized at the anode because a smaller potential would be needed—using reaction (ii) for the oxidation would give a less-negative cell potential. When the experiment is run, it turns out chlorine, not oxygen, is produced at the anode. The unexpected process is so common in electrochemistry that it has been given the name overpotential. The overpotential is the difference between the theoretical cell voltage and the actual voltage that is necessary to cause electrolysis. It turns out that the overpotential for oxygen is rather high and effectively makes the reduction potential more positive. As a result, under normal conditions, chlorine gas is what actually forms at the anode.

Now consider the cathode. Three reductions could occur:

$$\text{(iii) } 2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g) \quad E^\circ_{cathode} = 0\ V \tag{9.7.9}$$
$$\text{(iv) } 2\,H_2O(l) + 2\,e^- \longrightarrow H_2(g) + 2\,OH^-(aq) \quad E^\circ_{cathode} = -0.8277\ V \tag{9.7.10}$$
$$\text{(v) } Na^+(aq) + e^- \longrightarrow Na(s) \quad E^\circ_{cathode} = -2.71\ V \tag{9.7.11}$$

Reaction (v) is ruled out because it has such a negative reduction potential. Under standard state conditions, reaction (iii) would be preferred to reaction (iv). However, the pH of a sodium chloride solution is 7, so the concentration of hydrogen ions is only 1×10^{-7} *M*. At such low concentrations, reaction (iii) is unlikely and reaction (iv) occurs. The overall reaction is then

$$\text{overall: } 2\,H_2O(l) + 2\,Cl^-(aq) \longrightarrow H_2(g) + Cl_2(g) + 2\,OH^-(aq) \quad E^\circ_{cell} = -2.186\ V$$

As the reaction proceeds, hydroxide ions replace chloride ions in solution. Thus, sodium hydroxide can be obtained by evaporating the water after the electrolysis is complete. Sodium hydroxide is valuable in its own right and is used for things like oven cleaner, drain opener, and in the production of paper, fabrics, and soap.

Electroplating

An important use for electrolytic cells is in electroplating. Electroplating results in a thin coating of one metal on top of a conducting surface. Reasons for electroplating include making the object more corrosion resistant, strengthening the surface, producing a more attractive finish, or for purifying metal. The metals commonly used in electroplating include cadmium, chromium, copper, gold, nickel, silver, and tin. Common consumer products include silver-plated or gold-plated tableware, chrome-plated automobile parts, and jewelry. We can get an idea of how this works by investigating how silver-plated tableware is produced (Figure **9.7.3**).

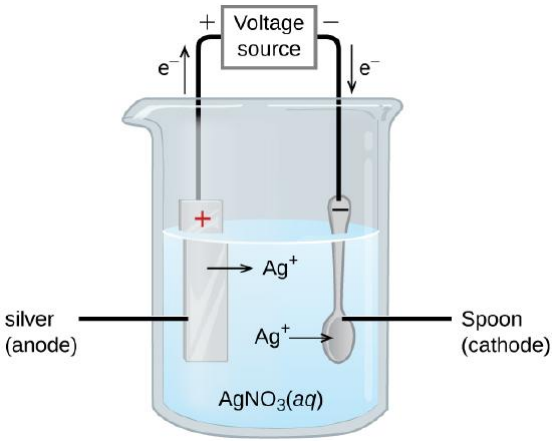


Figure **9.7.3**: The spoon, which is made of an inexpensive metal, is connected to the negative terminal of the voltage source and acts as the cathode. The anode is a silver electrode. Both electrodes are immersed in a silver nitrate solution. When a steady current is passed through the solution, the net result is that silver metal is removed from the anode and deposited on the cathode.

In the figure, the anode consists of a silver electrode, shown on the left. The cathode is located on the right and is the spoon, which is made from inexpensive metal. Both electrodes are immersed in a solution of silver nitrate. As the potential is increased, current flows. Silver metal is lost at the anode as it goes into solution.

$$\textbf{anode: } \mathrm{Ag}(s) \longrightarrow \mathrm{Ag^+}(aq) + \mathrm{e^-}$$

The mass of the cathode increases as silver ions from the solution are deposited onto the spoon

$$\textbf{cathode: } \mathrm{Ag^+}(aq) + \mathrm{e^-} \longrightarrow \mathrm{Ag}(s)$$

The net result is the transfer of silver metal from the anode to the cathode. The quality of the object is usually determined by the thickness of the deposited silver and the rate of deposition.

Quantitative Aspects of Electrolysis

The amount of current that is allowed to flow in an electrolytic cell is related to the number of moles of electrons. The number of moles of electrons can be related to the reactants and products using stoichiometry. Recall that the SI unit for current (I) is the ampere (A), which is the equivalent of 1 coulomb per second (1 A = $1\ \frac{\mathrm{C}}{\mathrm{s}}$). The total charge ($Q$, in coulombs) is given by

$$Q = I \times t = n \times F$$

where

- t is the time in seconds,
- n the number of moles of electrons, and
- F is the Faraday constant.

Moles of electrons can be used in stoichiometry problems. The time required to deposit a specified amount of metal might also be requested, as in the second of the following examples.

Example 9.7.1: Converting Current to Moles of Electrons

In one process used for electroplating silver, a current of 10.23 A was passed through an electrolytic cell for exactly 1 hour. How many moles of electrons passed through the cell? What mass of silver was deposited at the cathode from the silver nitrate solution?

Solution

Faraday's constant can be used to convert the charge (Q) into moles of electrons (n). The charge is the current (I) multiplied by the time

$$n = \frac{Q}{F} = \frac{\frac{10.23\ \text{C}}{\text{s}} \times 1\ \text{hr} \times \frac{60\ \text{min}}{\text{hr}} \times \frac{60\ \text{s}}{\text{min}}}{96,485\ \text{C/mol e}^-} = \frac{36,830\ \text{C}}{96,485\ \text{C/mol e}^-} = 0.3817\ \text{mol e}^-$$

From the problem, the solution contains $AgNO_3$, so the reaction at the cathode involves 1 mole of electrons for each mole of silver

$$\text{cathode: } Ag^+(aq) + e^- \longrightarrow Ag(s)$$

The atomic mass of silver is 107.9 g/mol, so

$$\text{mass Ag} = 0.3817\ \text{mol e}^- \times \frac{1\ \text{mol Ag}}{1\ \text{mol e}^-} \times \frac{107.9\ \text{g Ag}}{1\ \text{mol Ag}} = 41.19\ \text{g Ag}$$

Check your answer: From the stoichiometry, 1 mole of electrons would produce 1 mole of silver. Less than one-half a mole of electrons was involved and less than one-half a mole of silver was produced.

Exercise 9.7.1

Aluminum metal can be made from aluminum ions by electrolysis. What is the half-reaction at the cathode? What mass of aluminum metal would be recovered if a current of 2.50×10^3 A passed through the solution for 15.0 minutes? Assume the yield is 100%.

Answer

$Al^{3+}(aq) + 3\,e^- \longrightarrow Al(s)$; 7.77 mol Al = 210.0 g Al.

Example 9.7.2: Time Required for Deposition

In one application, a 0.010-mm layer of chromium must be deposited on a part with a total surface area of 3.3 m^2 from a solution of containing chromium(III) ions. How long would it take to deposit the layer of chromium if the current was 33.46 A? The density of chromium (metal) is 7.19 g/cm^3.

Solution This problem brings in a number of topics covered earlier. An outline of what needs to be done is:

- If the total charge can be determined, the time required is just the charge divided by the current
- The total charge can be obtained from the amount of Cr needed and the stoichiometry
- The amount of Cr can be obtained using the density and the volume Cr required
- The volume Cr required is the thickness times the area

Solving in steps, and taking care with the units, the volume of Cr required is

$$\text{volume} = \left(0.010\ \text{mm} \times \frac{1\ \text{cm}}{10\ \text{mm}}\right) \times \left(3.3\ \text{m}^2 \times \left(\frac{10,000\ \text{cm}^2}{1\ \text{m}^2}\right)\right) = 33\ \text{cm}^3$$

Cubic centimeters were used because they match the volume unit used for the density. The amount of Cr is then

$$\text{mass} = \text{volume} \times \text{density} = 33\ \cancel{\text{cm}^3} \times \frac{7.19\ \text{g}}{\cancel{\text{cm}^3}} = 237\ \text{g Cr}$$

$$\text{mol Cr} = 237\ \text{g Cr} \times \frac{1\ \text{mol Cr}}{52.00\ \text{g Cr}} = 4.56\ \text{mol Cr}$$

Since the solution contains chromium(III) ions, 3 moles of electrons are required per mole of Cr. The total charge is then

$$Q = 4.56\ \text{mol Cr} \times \frac{3\ \text{mol e}^-}{1\ \text{mol Cr}} \times \frac{96485\ \text{C}}{\text{mol e}^-} = 1.32 \times 10^6\ \text{C}$$

The time required is then

$$t = \frac{Q}{I} = \frac{1.32 \times 10^6\ \text{C}}{33.46\ \text{C/s}} = 3.95 \times 10^4\ \text{s} = 11.0\ \text{hr}$$

Check your answer: In a long problem like this, a single check is probably not enough. Each of the steps gives a reasonable number, so things are probably correct. Pay careful attention to unit conversions and the stoichiometry.

? Exercise 9.7.2

What mass of zinc is required to galvanize the top of a 3.00 m × 5.50 m sheet of iron to a thickness of 0.100 mm of zinc? If the zinc comes from a solution of $Zn(NO_3)_2$ and the current is 25.5 A, how long will it take to galvanize the top of the iron? The density of zinc is 7.140 g/cm^3.

Answer

231 g Zn required 23,000 minutes.

Summary

Using electricity to force a nonspontaneous process to occur is electrolysis. Electrolytic cells are electrochemical cells with negative cell potentials (meaning a positive Gibbs free energy), and so are nonspontaneous. Electrolysis can occur in electrolytic cells by introducing a power supply, which supplies the energy to force the electrons to flow in the nonspontaneous direction. Electrolysis is done in solutions, which contain enough ions so current can flow. If the solution contains only one material, like the electrolysis of molten sodium chloride, it is a simple matter to determine what is oxidized and what is reduced. In more complicated systems, like the electrolysis of aqueous sodium chloride, more than one species can be oxidized or reduced and the standard reduction potentials are used to determine the most likely oxidation (the half-reaction with the largest [most positive] standard reduction potential) and reduction (the half-reaction with the smallest [least positive] standard reduction potential). Sometimes unexpected half-reactions occur because of overpotential. Overpotential is the difference between the theoretical half-reaction reduction potential and the actual voltage required. When present, the applied potential must be increased, making it possible for a different reaction to occur in the electrolytic cell. The total charge, Q, that passes through an electrolytic cell can be expressed as the current (I) multiplied by time ($Q = It$) or as the moles of electrons (n) multiplied by Faraday's constant ($Q = nF$). These relationships can be used to determine things like the amount of material used or generated during electrolysis, how long the reaction must proceed, or what value of the current is required.

Summary

electrolysis

process using electrical energy to cause a nonspontaneous process to occur

electrolytic cell

electrochemical cell in which electrolysis is used; electrochemical cell with negative cell potentials

electroplating

depositing a thin layer of one metal on top of a conducting surface

overpotential

difference between the theoretical potential and actual potential in an electrolytic cell; the “extra” voltage required to make some nonspontaneous electrochemical reaction to occur

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9.E: Electrochemistry (Exercises)

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