CHEMICAL PRINCIPLES



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Chemical Principles for Medical Students

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This text was compiled on 01/12/2026

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LICENSING

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CHAPTER OVERVIEW

1: ELECTRONIC STRUCTURE OF ATOMS

A general chemistry Libretexts Textmap organized around the textbook

Chemistry: The Central Science

by Brown, LeMay, Bursten, Murphy, and Woodward

Template:HideTOC

In this chapter, we describe how electrons are arranged in atoms and how the spatial arrangements of electrons are related to their energies. We also explain how knowing the arrangement of electrons in an atom enables chemists to predict and explain the chemistry of an element. As you study the material presented in this chapter, you will discover how the shape of the periodic table reflects the electronic arrangements of elements. In this and subsequent chapters, we build on this information to explain why certain chemical changes occur and others do not. After reading this chapter, you will know enough about the theory of the electronic structure of atoms to explain what causes the characteristic colors of neon signs, how laser beams are created, and why gemstones and fireworks have such brilliant colors. In later chapters, we will develop the concepts introduced here to explain why the only compound formed by sodium and chlorine is NaCl, an ionic compound, whereas neon and argon do not form any stable compounds, and why carbon and hydrogen combine to form an almost endless array of covalent compounds, such as CH_4, C_2H_2, C_2H_4, and C_2H_6. You will discover that knowing how to use the periodic table is the single most important skill you can acquire to understand the incredible chemical diversity of the elements.

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1.1: THE WAVE NATURE OF LIGHT

LEARNING OBJECTIVES

- To learn about the characteristics of electromagnetic waves. Light, X-Rays, infrared and microwaves are among the types of electromagnetic waves.

Scientists discovered much of what we know about the structure of the atom by observing the interaction of atoms with various forms of radiant, or transmitted, energy, such as the energy associated with the visible light we detect with our eyes, the infrared radiation we feel as heat, the ultraviolet light that causes sunburn, and the x-rays that produce images of our teeth or bones. All these forms of radiant energy should be familiar to you. We begin our discussion of the development of our current atomic model by describing the properties of waves and the various forms of electromagnetic radiation.



Figure **1.1.1**: A Wave in Water. When a drop of water falls onto a smooth water surface, it generates a set of waves that travel outward in a circular direction.

1.1.1 PROPERTIES OF WAVES

A wave is a periodic oscillation that transmits energy through space. Anyone who has visited a beach or dropped a stone into a puddle has observed waves traveling through water (Figure **1.1.1**). These waves are produced when wind, a stone, or some other disturbance, such as a passing boat, transfers energy to the water, causing the surface to oscillate up and down as the energy travels outward from its point of origin. As a wave passes a particular point on the surface of the water, anything floating there moves up and down.

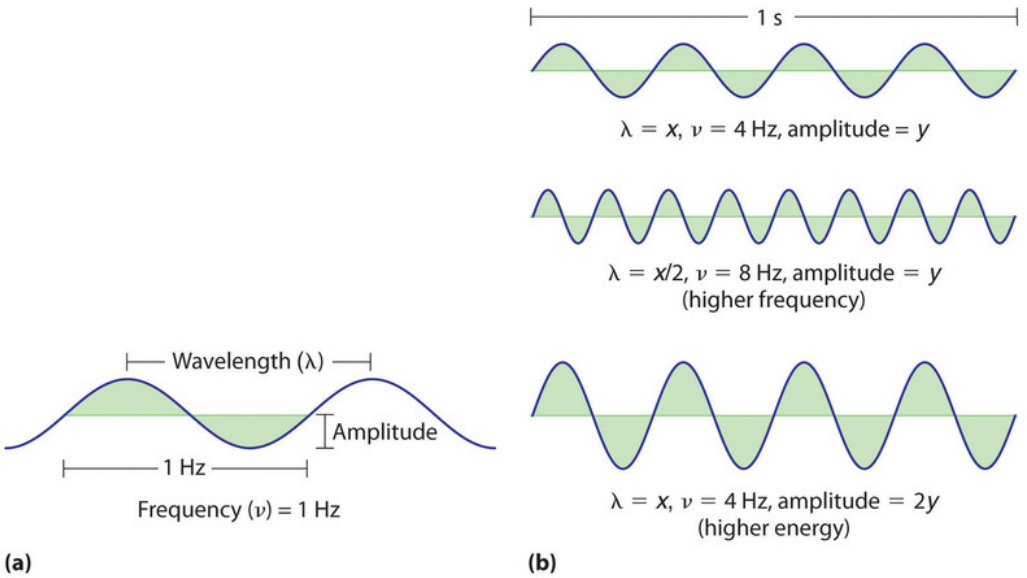


Figure **1.1.2**: Important Properties of Waves (a) Wavelength (λ in meters), frequency (ν, in Hz), and amplitude are indicated on this drawing of a wave. (b) The wave with the shortest wavelength has the greatest number of wavelengths per unit time (i.e., the highest frequency). If two waves have the same frequency and speed, the one with the greater amplitude has the higher energy.

Waves have characteristic properties (Figure **1.1.2**). As you may have noticed in Figure **1.1.1**, waves are periodic, that is, they repeat regularly in both space and time. The distance between two corresponding points in a wave—between the midpoints of two peaks, for example, or two troughs—is the **wavelength** (λ, lowercase Greek lambda). Wavelengths are described by a unit of distance, typically meters. The **frequency** (u, lowercase Greek nu) of a wave is the number of oscillations that pass a particular point in a given period of time. The usual units are oscillations per second (1/s = s^{-1}), which in the SI system is called the hertz (Hz). It is named after German physicist Heinrich Hertz (1857–1894), a pioneer in the field of electromagnetic radiation.

The **amplitude**, or vertical height, of a wave is defined as half the peak-to-trough height; as the amplitude of a wave with a given frequency increases, so does its energy. As you can see in Figure **1.1.2**, two waves can have the same amplitude but different wavelengths and vice versa. The distance traveled by a wave per unit time is its speed (v), which is typically measured in meters per second (m/s). The speed of a wave is equal to the product of its wavelength and frequency:

$$(\text{wavelength})(\text{frequency}) = \text{speed}$$

$$\lambda u = v \tag{1.1.1}$$

$$\left(\frac{\textit{meters}}{\cancel{\textit{wave}}}\right)\left(\frac{\cancel{\text{wave}}}{\text{second}}\right) = \frac{\text{meters}}{\text{second}} \tag{1.1.2}$$

> Be careful not to confuse the symbols for the speed, v, with the frequency, u.

Different types of waves may have vastly different possible speeds and frequencies. Water waves are slow compared to sound waves, which can travel through solids, liquids, and gases. Whereas water waves may travel a few meters per second, the speed of sound in dry air at 20°C is 343.5 m/s. Ultrasonic waves, which travel at an even higher speed (>1500 m/s) and have a greater frequency, are used in such diverse applications as locating underwater objects and the medical imaging of internal organs.

1.1.2 ELECTROMAGNETIC RADIATION

Water waves transmit energy through space by the periodic oscillation of matter (the water). In contrast, energy that is transmitted, or radiated, through space in the form of periodic oscillations of electric and magnetic fields is known as **electromagnetic radiation**. (Figure **1.1.3**). Some forms of electromagnetic radiation are shown in Figure **1.1.4**. In a vacuum, all forms of electromagnetic radiation—whether microwaves, visible light, or gamma rays—travel at the speed of light (c), which turns out to be a fundamental physical constant with a value of 2.99792458 × 10^8 m/s (about 3.00 ×10^8 m/s or 1.86 × 10^5 mi/s). This is about a million times faster than the speed of sound.

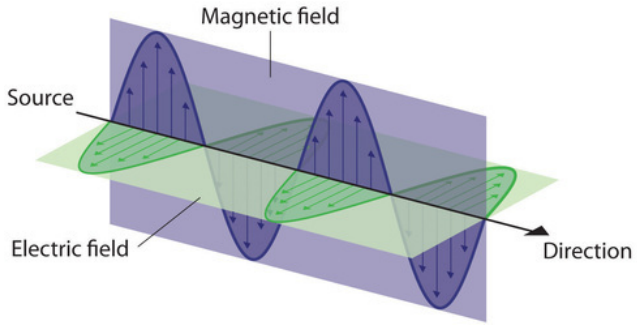


Figure **1.1.3**: The Nature of Electromagnetic Radiation. All forms of electromagnetic radiation consist of perpendicular oscillating electric and magnetic fields.

Because the various kinds of electromagnetic radiation all have the same speed (c), they differ in only wavelength and frequency. As shown in Figure **1.1.4** and Table **1.1.1**, the wavelengths of familiar electromagnetic radiation range from 10^1 m for radio waves to 10^{-12} m for gamma rays, which are emitted by nuclear reactions. By replacing v with \(c\) in Equation 1.1.1, we can show that the frequency of electromagnetic radiation is inversely proportional to its wavelength:

$$c = \lambda u \tag{1.1.3}$$

$$u = \frac{c}{\lambda} \tag{1.1.4}$$

For example, the frequency of radio waves is about 10^8 Hz, whereas the frequency of gamma rays is about 10^{20} Hz. Visible light, which is electromagnetic radiation that can be detected by the human eye, has wavelengths between about 7 × 10^{-7} m (700 nm, or 4.3 × 10^{14} Hz) and 4 × 10^{-7} m (400 nm, or 7.5 × 10^{14} Hz). Note that when frequency increases, wavelength decreases; c being a constant stays the same. Similarly, when frequency decreases, the wavelength increases.

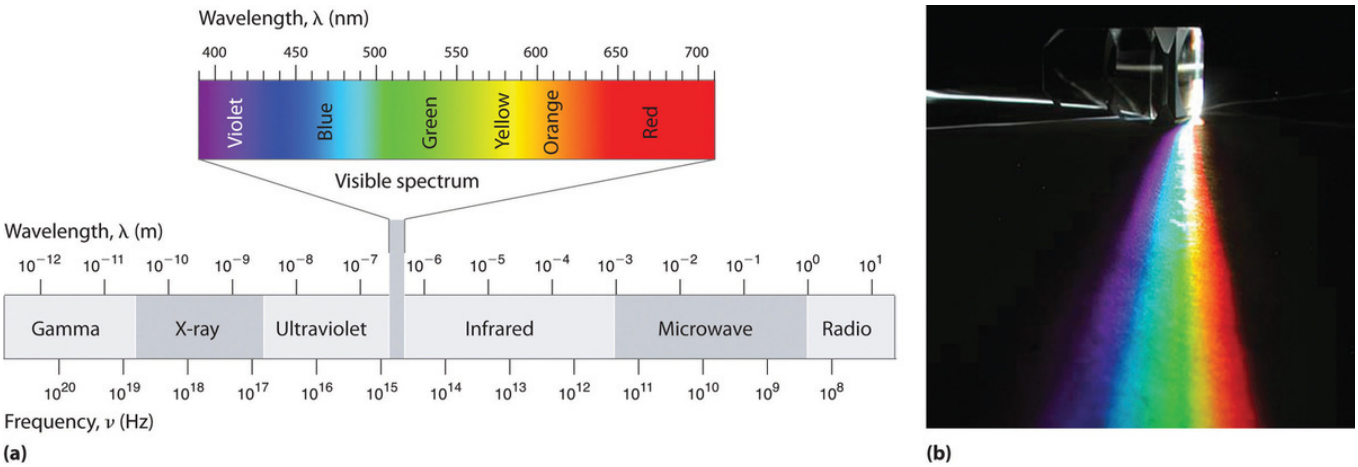


Figure 1.1.4: The Electromagnetic Spectrum. (a) This diagram shows the wavelength and frequency ranges of electromagnetic radiation. The visible portion of the electromagnetic spectrum is the narrow region with wavelengths between about 400 and 700 nm. (b) When white light is passed through a prism, it is split into light of different wavelengths, whose colors correspond to the visible spectrum.

Within the visible range our eyes perceive radiation of different wavelengths (or frequencies) as light of different colors, ranging from red to violet in order of decreasing wavelength. The components of white light—a mixture of all the frequencies of visible light—can be separated by a prism, as shown in part (b) in Figure 1.1.4. A similar phenomenon creates a rainbow, where water droplets suspended in the air act as tiny prisms.

Table 1.1.1: Common Wavelength Units for Electromagnetic Radiation

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

As you will soon see, the energy of electromagnetic radiation is directly proportional to its frequency and inversely proportional to its wavelength:

$$E \propto u \tag{1.1.5}$$

$$\propto \frac{1}{\lambda} \tag{1.1.6}$$

Whereas visible light is essentially harmless to our skin, ultraviolet light, with wavelengths of ≤ 400 nm, has enough energy to cause severe damage to our skin in the form of sunburn. Because the ozone layer of the atmosphere absorbs sunlight with wavelengths less than 350 nm, it protects us from the damaging effects of highly energetic ultraviolet radiation.

> *The energy of electromagnetic radiation increases with increasing frequency and decreasing wavelength.*



Electromagnetic Radiation: https://youtu.be/TZy7a69pP-w

EXAMPLE 1.1.1: WAVELENGTH OF RADIOWAVES

Your favorite FM radio station, WXYZ, broadcasts at a frequency of 101.1 MHz. What is the wavelength of this radiation?

Given: frequency

Asked for: wavelength

Strategy:

Substitute the value for the speed of light in meters per second into Equation 1.1.4 to calculate the wavelength in meters.

Solution:

From Equation 1.1.4, we know that the product of the wavelength and the frequency is the speed of the wave, which for electromagnetic radiation is 2.998×10^8 m/s:

$$\begin{aligned} \lambda\nu &= c \\ &= 2.998 \times 10^8 m/s \end{aligned}$$

Thus the wavelength λ is given by

$$\begin{aligned} \lambda &= \frac{c}{u} \\ &= \left(\frac{2.988 \times 10^8\ m/\cancel{s}}{101.1\ \cancel{MHz}}\right)\left(\frac{1\ \cancel{MHz}}{10^6\ \cancel{s^{-1}}}\right) \\ &= 2.965\ m \end{aligned}$$

EXERCISE 1.1.1

As the police officer was writing up your speeding ticket, she mentioned that she was using a state-of-the-art radar gun operating at 35.5 GHz. What is the wavelength of the radiation emitted by the radar gun?

Answer

8.45 mm

1.1.3 SUMMARY

Understanding the electronic structure of atoms requires an understanding of the properties of waves and electromagnetic radiation. A **wave** is a periodic oscillation by which energy is transmitted through space. All waves are **periodic**, repeating regularly in both space and time. Waves are characterized by several interrelated properties: **wavelength** (λ), the distance between successive waves; **frequency** (u), the number of waves that pass a fixed point per unit time; **speed** (v), the rate at which the wave propagates through space; and **amplitude**, the magnitude of the oscillation about the mean position. The speed of a wave is equal to the product of its wavelength and frequency. **Electromagnetic radiation** consists of two perpendicular waves, one electric and one magnetic, propagating at the **speed of light** (c).

Electromagnetic radiation is radiant energy that includes radio waves, microwaves, visible light, x-rays, and gamma rays, which differ in their frequencies and wavelengths.

1.1.4 CONTRIBUTORS AND ATTRIBUTIONS

- Modified by Joshua Halpern (Howard University)

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1.2: QUANTIZED ENERGY AND PHOTONS

LEARNING OBJECTIVES

- To understand how energy is quantized.

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

1.2.1 BLACKBODY RADIATION

One phenomenon that seemed to contradict the theories of classical physics was blackbody radiation, which is electromagnetic radiation given off by a hot object. The wavelength (i.e. color) of radiant energy emitted by a blackbody depends on only its temperature, not its surface or composition. Hence an electric stove burner or the filament of a space heater glows dull red or orange when heated, whereas the much hotter tungsten wire in an incandescent light bulb gives off a yellowish light.



Figure **1.2.1**: Blackbody Radiation. When heated, all objects emit electromagnetic radiation whose wavelength (and color) depends on the temperature of the object. A relatively low-temperature object, such as a horseshoe forged by a blacksmith, appears red, whereas a higher-temperature object, such as the surface of the sun, appears yellow or white. Images used with permission from Wikipedia.

The *intensity* of radiation is a measure of the energy emitted per unit area. A plot of the intensity of blackbody radiation as a function of wavelength for an object at various temperatures is shown in Figure **1.2.2**. One of the major assumptions of classical physics was that energy increased or decreased in a smooth, continuous manner. For example, classical physics predicted that as wavelength decreased, the intensity of the radiation an object emits should increase in a smooth curve without limit at *all* temperatures, as shown by the broken line for 6000 K in Figure **1.2.2**. Thus classical physics could not explain the sharp *decrease* in the intensity of radiation emitted at shorter wavelengths (primarily in the ultraviolet region of the spectrum), which was referred to as the "ultraviolet catastrophe." In 1900, however, the German physicist Max Planck (1858–1947) explained the ultraviolet catastrophe by proposing (in what he called "an act of despair") that the energy of electromagnetic waves is *quantized* rather than continuous. This means that for each temperature, there is a maximum intensity of radiation that is emitted in a blackbody object, corresponding to the peaks in Figure **1.2.2**, so the intensity does not follow a smooth curve as the temperature increases, as predicted by classical physics. Thus energy could be gained or lost only in integral multiples of some smallest unit of energy, a **quantum**.

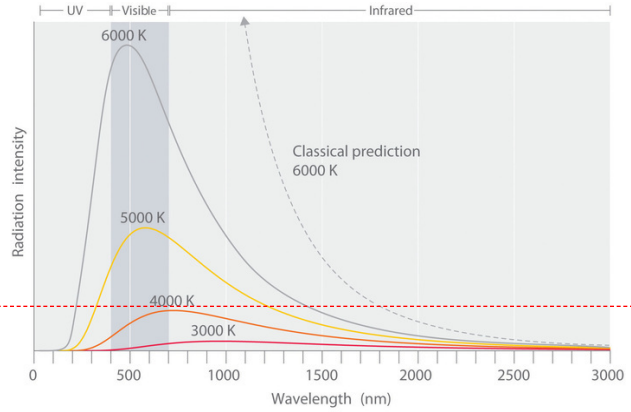
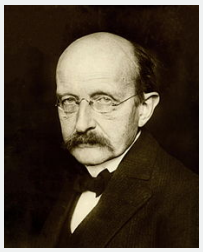


Figure **1.2.2**: Relationship between the Temperature of an Object and the Spectrum of Blackbody Radiation it Emits. At relatively low temperatures, most radiation is emitted at wavelengths longer than 700 nm, which is in the infrared portion of the spectrum. The dull red glow of the electric stove element in Figure **1.2.1** is due to the small amount of radiation emitted at wavelengths less than 700 nm, which the eye can detect. As the temperature of the object increases, the maximum intensity shifts to shorter wavelengths, successively resulting in orange, yellow, and finally white light. At high temperatures, all wavelengths of visible light are emitted with approximately equal intensities. The white light spectrum shown for an object at 6000 K closely approximates the spectrum of light emitted by the sun (Figure **1.2.1**). Note the sharp decrease in the intensity of radiation emitted at wavelengths below 400 nm, which constituted the ultraviolet catastrophe. The classical prediction fails to fit the experimental curves entirely and does not have a maximum intensity.

MAX PLANCK (1858–1947)

In addition to being a physicist, Planck was a gifted pianist, who at one time considered music as a career. During the 1930s, Planck felt it was his duty to remain in Germany, despite his open opposition to the policies of the Nazi government.



One of his sons was executed in 1944 for his part in an unsuccessful attempt to assassinate Hitler, and bombing during the last weeks of World War II destroyed Planck's home. After WWII, the major German scientific research organization was renamed the Max Planck Society.

Although quantization may seem to be an unfamiliar concept, we encounter it frequently. For example, US money is integral multiples of pennies. Similarly, musical instruments like a piano or a trumpet can produce only certain musical notes, such as C or F sharp. Because these instruments cannot produce a continuous range of frequencies, their frequencies are quantized. Even electrical charge is quantized: an ion

may have a charge of −1 or −2 but *not* −1.33 electron charges.

Planck postulated that the energy of a particular quantum of radiant energy could be described by the equation

$$E = hu \tag{1.2.1}$$

where the proportionality constant h is called Planck's constant, one of the most accurately known fundamental constants in science. For our purposes, its value to four significant figures is generally sufficient:

$$h = 6.626 \times 10^{-34}\ J \bullet s\ \text{(joule-segundos)}$$

As the frequency of electromagnetic radiation increases, the magnitude of the associated quantum of radiant energy increases. By assuming that energy can be emitted by an object only in integral multiples of $h\nu$, Planck devised an equation that fit the experimental data shown in Figure **1.2.2**. We can understand Planck's explanation of the ultraviolet catastrophe qualitatively as follows: At low temperatures, radiation with only relatively low frequencies is emitted, corresponding to low-energy quanta. As the temperature of an object increases, there is an increased probability of emitting radiation with higher frequencies, corresponding to higher-energy quanta. At any temperature, however, it is simply more probable for an object to lose energy by emitting a large number of lower-energy quanta than a single very high-energy quantum that corresponds to ultraviolet radiation. The result is a maximum in the plot of intensity of emitted radiation versus wavelength, as shown in Figure **1.2.2**, and a shift in the position of the maximum to lower wavelength (higher frequency) with increasing temperature.

At the time he proposed his radical hypothesis, Planck could not explain *why* energies should be quantized. Initially, his hypothesis explained only one set of experimental data—blackbody radiation. If quantization were observed for a large number of different phenomena, then quantization would become a law. In time, a theory might be developed to explain that law. As things turned out, Planck's hypothesis was the seed from which modern physics grew.



Energy of a Photon: Energy of a Photon, YouTube(opens in new window) [youtu.be]

1.2.2 THE PHOTOELECTRIC EFFECT

Only five years after he proposed it, Planck's quantization hypothesis was used to explain a second phenomenon that conflicted with the accepted laws of classical physics. When certain metals are exposed to light, electrons are ejected from their surface (Figure **1.2.3**). Classical physics predicted that the number of electrons emitted and their kinetic energy should depend on only the intensity of the light, not its frequency. In fact, however, each metal was found to have a characteristic threshold frequency of light; below that frequency, no electrons are emitted regardless of the light's intensity. Above the threshold frequency, the number of electrons emitted was found to be proportional to the intensity of the light, and their kinetic energy was proportional to the frequency. This phenomenon was called the photoelectric effect (A phenomenon in which electrons are ejected from the surface of a metal that has been exposed to light).

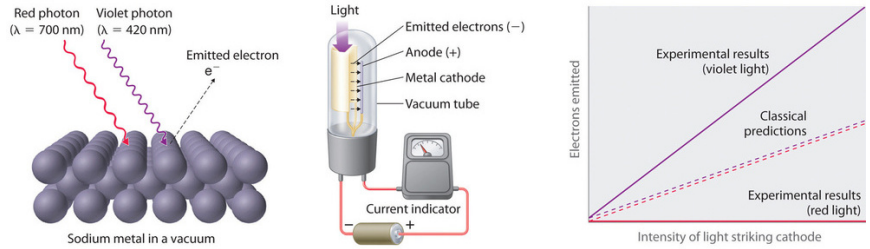


Figure **1.2.3**: The Photoelectric Effect (a) Irradiating a metal surface with photons of sufficiently high energy causes electrons to be ejected from the metal. (b) A photocell that uses the photoelectric effect, similar to those found in automatic door openers. When light strikes the metal cathode, electrons are emitted and attracted to the anode, resulting in a flow of electrical current. If the incoming light is interrupted by, for example, a passing person, the current drops to zero. (c) In contrast to predictions using classical physics, no electrons are emitted when photons of light with energy less than E_o, such as red light, strike the cathode. The energy of violet light is above the threshold frequency, so the number of emitted photons is proportional to the light's intensity.

Albert Einstein (1879–1955; Nobel Prize in Physics, 1921) quickly realized that Planck's hypothesis about the quantization of radiant energy could also explain the photoelectric effect. The key feature of Einstein's hypothesis was the assumption that radiant energy arrives at the metal surface in particles that we now call **photons** (a quantum of radiant energy, each of which possesses a particular energy energy E given by Equation 1.2.1 Einstein postulated that each metal has a particular electrostatic attraction for its electrons that must be overcome before an electron can be emitted from its surface ($E_o = u_o$). If photons of light with energy less than E_o strike a metal surface, no single photon has enough energy to eject an electron, so no electrons are emitted regardless of the intensity of the light. If a photon with energy greater than E_o strikes the metal, then part of its energy is used to overcome the forces that hold the electron to the metal surface, and the excess energy appears as the kinetic energy of the ejected electron:

$$\begin{aligned} \text{kinetic energy of ejected electron} &= E - E_o \\ &= hu - hu_o \\ &= h(u - u_o) \end{aligned} \tag{1.2.2}$$

When a metal is struck by light with energy above the threshold energy E_o, the *number* of emitted electrons is proportional to the *intensity* of the light beam, which corresponds to the *number* of photons per square centimeter, but the *kinetic energy* of the emitted electrons is proportional to the *frequency* of the light. Thus Einstein showed that the energy of the emitted electrons depended on the frequency of the light, contrary to the prediction of classical physics. Moreover, the idea that light could behave not only as a wave but as a particle in the form of photons suggested that matter and energy might not be such unrelated phenomena after all.



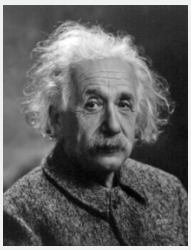
The Photoelectric Effect: The Photoelectric Effect, YouTube(opens in new window) [youtu.be]



Figure **1.2.4**: A Beam of Red Light Emitted by a Helium Neon laser reads a bar code. Originally Helium neon lasers, which emit red light at a wavelength of 632.8 nm, were used to read bar codes. Today, smaller, inexpensive diode lasers are used.

ALBERT EINSTEIN (1879–1955)

In 1900, Einstein was working in the Swiss patent office in Bern. He was born in Germany and throughout his childhood his parents and teachers had worried that he might be developmentally disabled. The patent office job was a low-level civil service position that was not very demanding, but it did allow Einstein to spend a great deal of time reading and thinking about physics.



In 1905, his "miracle year" he published four papers that revolutionized physics. One was on the special theory of relativity, a second on the equivalence of mass and energy, a third on Brownian motion, and the fourth on the photoelectric effect, for which he received the Nobel Prize in 1921, the theory of relativity and energy-matter equivalence being still controversial at the time

Planck's and Einstein's postulate that energy is quantized is in many ways similar to Dalton's description of atoms. Both theories are based on the existence of simple building blocks, atoms in one case and quanta of energy in the other. The work of Planck and Einstein thus suggested a connection between the quantized nature of energy and the properties of individual atoms.

EXAMPLE **1.2.1**

A ruby laser, a device that produces light in a narrow range of wavelengths emits red light at a wavelength of 694.3 nm (Figure **1.2.4**). What is the energy in joules of a single photon?

Given: wavelength

Asked for: energy of single photon.

Strategy:

Use Equation **1.2.1** and the relationship between wavelength and frequency to calculate the energy in joules.

Solution:

The energy of a single photon is given by Equaton **1.2.1**

$$E = h\nu = \frac{hc}{\lambda}.$$

EXERCISE **1.2.1**

An x-ray generator, such as those used in hospitals, emits radiation with a wavelength of 1.544 Å.

a. What is the energy in joules of a single photon?
b. How many times more energetic is a single x-ray photon of this wavelength than a photon emitted by a ruby laser?

Answer a

$1.287 \times 10^{-15}\ J/photon$

Answer b

4497 times

1.2.2.1 EXTERNAL VIDEOS AND EXAMPLES

- Calculating Energy of a Mole of Photons - Johnny Cantrell
- .Photons - ViaScience, an advanced explanation of the Planck radiation law and the photoelectric effect (below) as well as biological interactions with UV light.and the nature of light and quantum weirdness. Probably the first 6 minutes and the last 3 (from 12:00 on) as an introduction to wave particle duality.are useful to a beginning student.
- Quantum Chemistry - Ohio State
- Quantum Chemistry Quizzes - mhe education
- AP Chemistry Chapter 7 Review - Science Geek
- Quantum Theory of the Atom Practice Quiz - Northrup

1.2.3 SUMMARY

The fundamental building blocks of energy are quanta and of matter are atoms. The properties of **blackbody radiation**, the radiation emitted by hot objects, could not be explained with classical physics. Max Planck postulated that energy was quantized and could be emitted or absorbed only in integral multiples of a small unit of energy, known as a **quantum**. The energy of a quantum is proportional to the frequency of the radiation; the proportionality constant h is a fundamental constant (Planck's constant). Albert Einstein used Planck's concept of the quantization of energy to explain the **photoelectric effect**, the ejection of electrons from certain metals when exposed to light. Einstein postulated the existence of what today we call **photons**, particles of light with a particular energy, $E = h\nu$. Both energy and matter have fundamental building blocks: quanta and atoms, respectively.

1.2.4 CONTRIBUTORS AND ATTRIBUTIONS

- Modified by Joshua Halpern (Howard University)

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1.3: LINE SPECTRA AND THE BOHR MODEL

LEARNING OBJECTIVES

- To know the relationship between atomic spectra and the electronic structure of atoms.

The concept of the photon emerged from experimentation with *thermal radiation*, electromagnetic radiation emitted as the result of a source's temperature, which produces a continuous spectrum of energies.The photoelectric effect provided indisputable evidence for the existence of the photon and thus the particle-like behavior of electromagnetic radiation. However, more direct evidence was needed to verify the quantized nature of energy in all matter. In this section, we describe how observation of the interaction of atoms with visible light provided this evidence.

1.3.1 LINE SPECTRA

Although objects at high temperature emit a continuous spectrum of electromagnetic radiation, a different kind of spectrum is observed when pure samples of individual elements are heated. For example, when a high-voltage electrical discharge is passed through a sample of hydrogen gas at low pressure, the resulting individual isolated hydrogen atoms caused by the dissociation of H_2 emit a red light. Unlike blackbody radiation, the color of the light emitted by the hydrogen atoms does not depend greatly on the temperature of the gas in the tube. When the emitted light is passed through a prism, only a few narrow lines of particular wavelengths, called a **line spectrum**, are observed rather than a continuous range of wavelengths (Figure **1.3.1**). The light emitted by hydrogen atoms is red because, of its four characteristic lines, the most intense line in its spectrum is in the red portion of the visible spectrum, at 656 nm. With sodium, however, we observe a yellow color because the most intense lines in its spectrum are in the yellow portion of the spectrum, at about 589 nm.

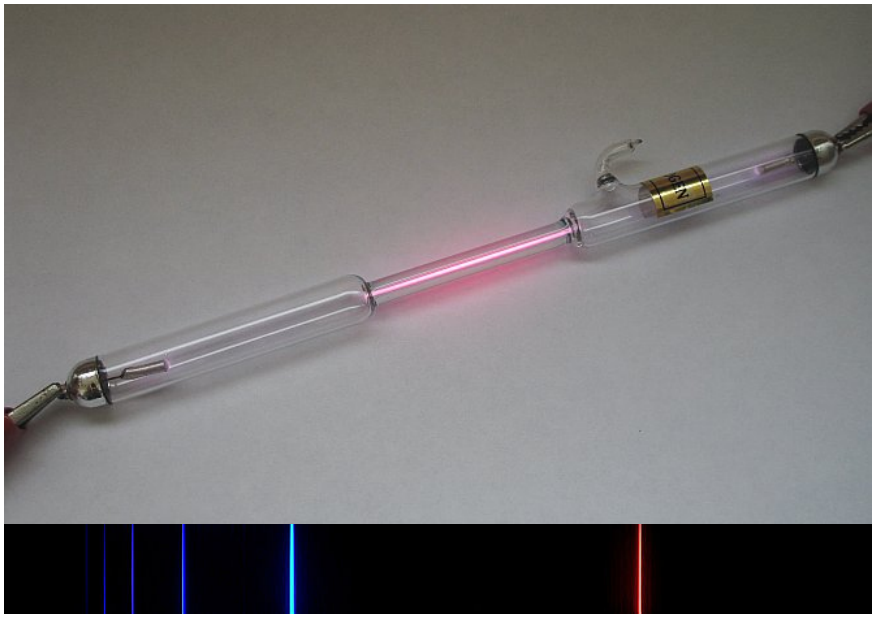


Figure **1.3.1**: The Emission of Light by Hydrogen Atoms. (a) A sample of excited hydrogen atoms emits a characteristic red light. (CC BY-SA 3.0 Unported; Science Made Alive via Wikipedia) (b) When the light emitted by a sample of excited hydrogen atoms is split into its component wavelengths by a prism, four characteristic violet, blue, green, and red emission lines can be observed, the most intense of which is at 656 nm. (CC BY-SA 3.0; Jan Homann via Wikipedia)

Such *emission spectra* were observed for many other elements in the late 19th century, which presented a major challenge because classical physics was unable to explain them. Part of the explanation is provided by Planck's equation: the observation of only a few values of λ (or u) in the line spectrum meant that only a few values of E were possible. Thus *the energy levels of a hydrogen atom had to be quantized*; in other words, only states that had certain values of energy were possible, or *allowed*. If a hydrogen atom could have *any* value of energy, then a continuous spectrum would have been observed, similar to blackbody radiation.

In 1885, a Swiss mathematics teacher, Johann Balmer (1825–1898), showed that the frequencies of the lines observed in the visible region of the spectrum of hydrogen fit a simple equation that can be expressed as follows:

$$u = constant \left(\frac{1}{2^2} - \frac{1}{n^2}\right) \tag{1.3.1}$$

where n = 3, 4, 5, 6. As a result, these lines are known as the *Balmer series*. The Swedish physicist Johannes Rydberg (1854–1919) subsequently restated and expanded Balmer's result in the *Rydberg equation*:

$$\frac{1}{\lambda} = \Re\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \tag{1.3.2}$$

where n_1 and n_2 are positive integers, $n_2 > n_1$, and $\Re$ the *Rydberg constant*, has a value of $1.09737 \times 10^7\ \text{m}^{-1}$.

JOHANN BALMER (1825–1898)

A mathematics teacher at a secondary school for girls in Switzerland, Balmer was 60 years old when he wrote the paper on the spectral lines of hydrogen that made him famous.



Balmer published only one other paper on the topic, which appeared when he was 72 years old.

Like Balmer's equation, Rydberg's simple equation described the wavelengths of the visible lines in the emission spectrum of hydrogen (with n_1 = 2, n_2 = 3, 4, 5,…). More important, Rydberg's equation also predicted the wavelengths of other series of lines that would be observed in the emission spectrum of hydrogen: one in the ultraviolet (n_1 = 1, n_2 = 2, 3, 4,…) and one in the infrared (n_1 = 3, n_2 = 4, 5, 6). Unfortunately, scientists had not yet developed any theoretical justification for an equation of this form.

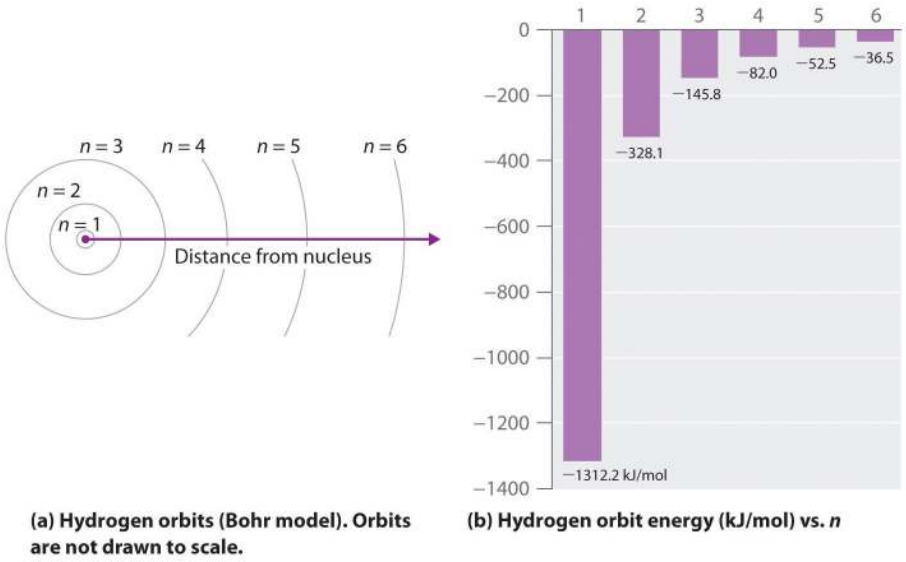
1.3.2 BOHR'S MODEL

In 1913, a Danish physicist, Niels Bohr (1885–1962; Nobel Prize in Physics, 1922), proposed a theoretical model for the hydrogen atom that explained its emission spectrum. Bohr's model required only one assumption: *The electron moves around the nucleus in circular orbits that can have only certain allowed radii.* Rutherford's earlier model of the atom had also assumed that electrons moved in circular orbits around the nucleus and that the atom was held together by the electrostatic attraction between the positively charged nucleus and the negatively charged electron. Although we now know that the assumption of circular orbits was incorrect, Bohr's insight was to propose that *the electron could occupy only certain regions of space*.

Using classical physics, Niels Bohr showed that the energy of an electron in a particular orbit is given by

$$E_n = \frac{-\Re hc}{n^2} \tag{1.3.3}$$

where $\Re$ is the Rydberg constant, h is Planck's constant, c is the speed of light, and n is a positive integer corresponding to the number assigned to the orbit, with n = 1 corresponding to the orbit closest to the nucleus. In this model $n = \infty$ corresponds to the level where the energy holding the electron and the nucleus together is zero. In that level, the electron is unbound from the nucleus and the atom has been separated into a negatively charged (the electron) and a positively charged (the nucleus) ion. In this state the radius of the orbit is also infinite. The atom has been ionized.



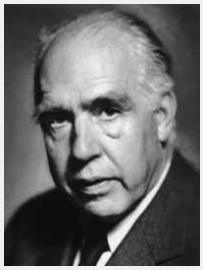
(a) Hydrogen orbits (Bohr model). Orbits are not drawn to scale.

(b) Hydrogen orbit energy (kJ/mol) vs. *n*

Figure **1.3.2**: The Bohr Model of the Hydrogen Atom (a) The distance of the orbit from the nucleus increases with increasing *n*. (b) The energy of the orbit becomes increasingly less negative with increasing *n*.

NIELS BOHR (1885–1962)

During the Nazi occupation of Denmark in World War II, Bohr escaped to the United States, where he became associated with the Atomic Energy Project.



In his final years, he devoted himself to the peaceful application of atomic physics and to resolving political problems arising from the development of atomic weapons.

As n decreases, the energy holding the electron and the nucleus together becomes increasingly negative, the radius of the orbit shrinks and more energy is needed to ionize the atom. The orbit with n = 1 is the lowest lying and most tightly bound. The negative sign in Equation 1.3.3 indicates that the electron-nucleus pair is more tightly bound (i.e. at a lower potential energy) when they are near each other than when they are far apart. Because a hydrogen atom with its one electron in this orbit has the lowest possible energy, this is the **ground state** (the most stable arrangement of electrons for an element or a compound) for a hydrogen atom. As n increases, the radius of the orbit increases; the electron is farther from the proton, which results in a less stable arrangement with higher potential energy (Figure **1.3.2*a***). A hydrogen atom with an electron in an orbit with n > 1 is therefore in an **excited state**, defined as any arrangement of electrons that is higher in energy than the ground state. When an atom in an excited state undergoes a transition to the ground state in a process called decay, it loses energy by emitting a photon whose energy corresponds to the *difference* in energy between the two states (Figure **1.3.1**).

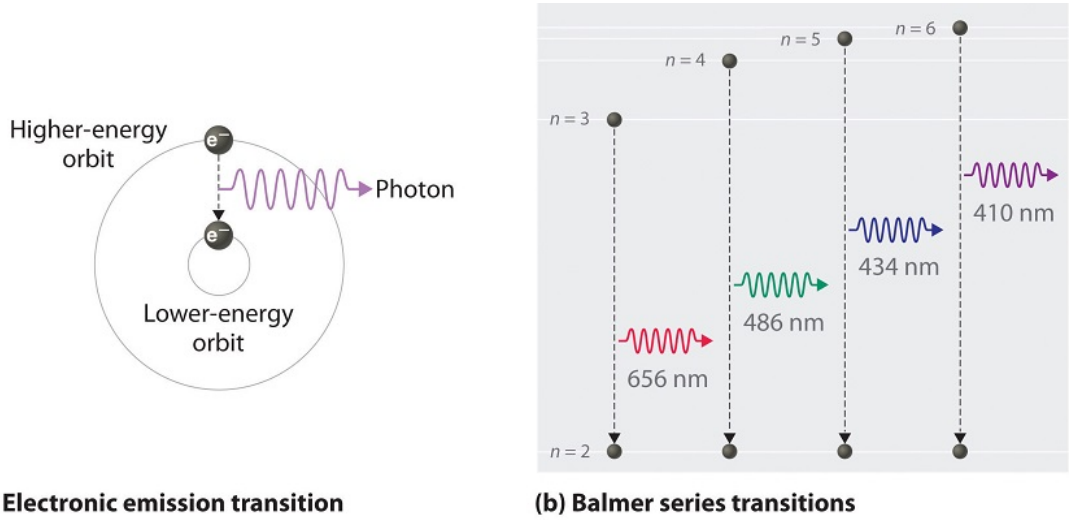


Figure **1.3.3**: The Emission of Light by a Hydrogen Atom in an Excited State. (a) Light is emitted when the electron undergoes a transition from an orbit with a higher value of n (at a higher energy) to an orbit with a lower value of n (at lower energy). (b) The Balmer series of emission lines is due to transitions from orbits with $n \geq 3$ to the orbit with $n = 2$. The differences in energy between these levels corresponds to light in the visible portion of the electromagnetic spectrum.

So the difference in energy (ΔE) between any two orbits or energy levels is given by $\Delta E = E_{n_1} - E_{n_2}$ where n_1 is the final orbit and n_2 the initial orbit. Substituting from Bohr's equation (Equation 1.3.3) for each energy value gives

$$\begin{aligned}\Delta E &= E_{final} - E_{initial} \\ &= -\frac{\Re hc}{n_2^2} - \left(-\frac{\Re hc}{n_1^2}\right) \\ &= -\Re hc\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)\end{aligned}$$

If $n_2 > n_1$, the transition is from a higher energy state (larger-radius orbit) to a lower energy state (smaller-radius orbit), as shown by the dashed arrow in part (a) in Figure **1.3.3**. Substituting hc/λ for ΔE gives

$$\Delta E = \frac{hc}{\lambda} = -\Re hc\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \tag{1.3.4}$$

Canceling hc on both sides gives

$$\frac{1}{\lambda} = -\Re\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \tag{1.3.5}$$

Except for the negative sign, this is the same equation that Rydberg obtained experimentally. The negative sign in Equations 1.3.4 and 1.3.5 indicates that energy is released as the electron moves from orbit n_2 to orbit n_1 because orbit n_2 is at a higher energy than orbit n_1. Bohr calculated the value of $\Re$ from fundamental constants such as the charge and mass of the electron and Planck's constant and obtained a value of $1.0974 \times 10^7\ m^{-1}$, the same number Rydberg had obtained by analyzing the emission spectra.

We can now understand the physical basis for the Balmer series of lines in the emission spectrum of hydrogen (**1.3.3***b*); the lines in this series correspond to transitions from higher-energy orbits (n > 2) to the second orbit (n = 2). Thus the hydrogen atoms in the sample have absorbed energy from the electrical discharge and decayed from a higher-energy excited state (n > 2) to a lower-energy state (n = 2) by emitting a photon of electromagnetic radiation whose energy corresponds exactly to the difference in energy between the two states (Figure **1.3.3***a*). The n = 3 to n = 2 transition gives rise to the line at 656 nm (red), the n = 4 to n = 2 transition to the line at 486 nm (green), the n = 5 to n = 2 transition to the line at 434 nm (blue), and the n = 6 to n = 2 transition to the line at 410 nm (violet). Because a sample of hydrogen contains a large number of atoms, the intensity of the various lines in a line spectrum depends on the number of atoms in each excited state. At the temperature in the gas discharge tube, more atoms are in the n = 3 than the n ≥ 4 levels. Consequently, the n = 3 to n = 2 transition is the most intense line, producing the characteristic red color of a hydrogen discharge (Figure **1.3.1***a*). Other families of lines are produced by transitions from excited states with n > 1 to the orbit with n = 1 or to orbits with n ≥ 3. These transitions are shown schematically in Figure **1.3.4**



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

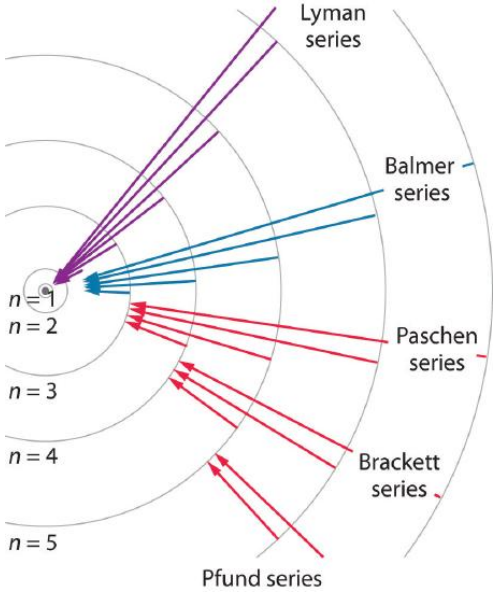


Figure **1.3.4**: Electron Transitions Responsible for the Various Series of Lines Observed in the Emission Spectrum of Hydrogen. The Lyman series of lines is due to transitions from higher-energy orbits to the lowest-energy orbit (n = 1); these transitions release a great deal of energy, corresponding to radiation in the ultraviolet portion of the electromagnetic spectrum. The Paschen, Brackett, and Pfund series of lines are due to transitions from higher-energy orbits to orbits with n = 3, 4, and 5, respectively; these transitions release substantially less energy, corresponding to infrared radiation. (Orbits are not drawn to scale.)

USING ATOMS TO TIME

In contemporary applications, electron transitions are used in timekeeping that needs to be exact. Telecommunications systems, such as cell phones, depend on timing signals that are accurate to within a millionth of a second per day, as are the devices that control the US power grid. Global positioning system (GPS) signals must be accurate to within a billionth of a second per day, which is equivalent to gaining or losing no more than one second in 1,400,000 years. Quantifying time requires finding an event with an interval that repeats on a regular basis.

To achieve the accuracy required for modern purposes, physicists have turned to the atom. The current standard used to calibrate clocks is the cesium atom. Supercooled cesium atoms are placed in a vacuum chamber and bombarded with microwaves whose frequencies are carefully controlled. When the frequency is exactly right, the atoms absorb enough energy to undergo an electronic transition to a higher-energy state. Decay to a lower-energy state emits radiation. The microwave frequency is continually adjusted, serving as the clock's pendulum.

In 1967, the second was defined as the duration of 9,192,631,770 oscillations of the resonant frequency of a cesium atom, called the *cesium clock*. Research is currently under way to develop the next generation of atomic clocks that promise to be even more accurate. Such devices would allow scientists to monitor vanishingly faint electromagnetic signals produced by nerve pathways in the brain and

geologists to measure variations in gravitational fields, which cause fluctuations in time, that would aid in the discovery of oil or minerals.

EXAMPLE 1.3.1: THE LYMAN SERIES

The so-called Lyman series of lines in the emission spectrum of hydrogen corresponds to transitions from various excited states to the n = 1 orbit. Calculate the wavelength of the lowest-energy line in the Lyman series to three significant figures. In what region of the electromagnetic spectrum does it occur?

Given: lowest-energy orbit in the Lyman series

Asked for: wavelength of the lowest-energy Lyman line and corresponding region of the spectrum

Strategy:

A. Substitute the appropriate values into Equation 1.3.2 (the Rydberg equation) and solve for λ.

B. Use Figure 2.2.1 to locate the region of the electromagnetic spectrum corresponding to the calculated wavelength.

Solution:

We can use the Rydberg equation to calculate the wavelength:

$$\frac{1}{\lambda} = -\Re\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

A For the Lyman series, n_1 = 1. The lowest-energy line is due to a transition from the n = 2 to n = 1 orbit because they are the closest in energy.

$$\frac{1}{\lambda} = -\Re\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) = 1.097 \times m^{-1}\left(\frac{1}{1} - \frac{1}{4}\right) = 8.228 \times 10^6\ m^{-1}$$

It turns out that spectroscopists (the people who study spectroscopy) use cm^{-1} rather than m^{-1} as a common unit. Wavelength is inversely proportional to energy but frequency is directly proportional as shown by Planck's formula, $E = hu$.

Spectroscopists often talk about energy and frequency as equivalent. The cm^{-1} unit is particularly convenient. The infrared range is roughly 200 - 5,000 cm^{-1}, the visible from 11,000 to 25.000 cm^{-1} and the UV between 25,000 and 100,000 cm^{-1}. The units of cm^{-1} are called wavenumbers, although people often verbalize it as inverse centimeters. We can convert the answer in part A to cm^{-1}.

$$\tilde{u} = \frac{1}{\lambda} = 8.228 \times 10^6\ \cancel{m^{-1}}\left(\frac{\cancel{m}}{100\ cm}\right) = 82,280\ cm^{-1}$$

and

$$\lambda = 1.215 \times 10^{-7}\ m = 122\ nm$$

This emission line is called Lyman alpha. It is the strongest atomic emission line from the sun and drives the chemistry of the upper atmosphere of all the planets, producing ions by stripping electrons from atoms and molecules. It is completely absorbed by oxygen in the upper stratosphere, dissociating O_2 molecules to O atoms which react with other O_2 molecules to form stratospheric ozone.

B This wavelength is in the ultraviolet region of the spectrum.

EXERCISE 1.3.1: THE PFUND SERIES

The Pfund series of lines in the emission spectrum of hydrogen corresponds to transitions from higher excited states to the n = 5 orbit. Calculate the wavelength of the *second* line in the Pfund series to three significant figures. In which region of the spectrum does it lie?

Answer

4.65×10^3 nm; infrared

Bohr's model of the hydrogen atom gave an exact explanation for its observed emission spectrum. The following are his key contributions to our understanding of atomic structure:

Unfortunately, Bohr could not explain *why* the electron should be restricted to particular orbits. Also, despite a great deal of tinkering, such as assuming that orbits could be ellipses rather than circles, his model could not quantitatively explain the emission spectra of any element

other than hydrogen (Figure 1.3.5). In fact, Bohr's model worked only for species that contained just one electron: H, He^{+}, Li^{2+}, and so forth. Scientists needed a fundamental change in their way of thinking about the electronic structure of atoms to advance beyond the Bohr model.

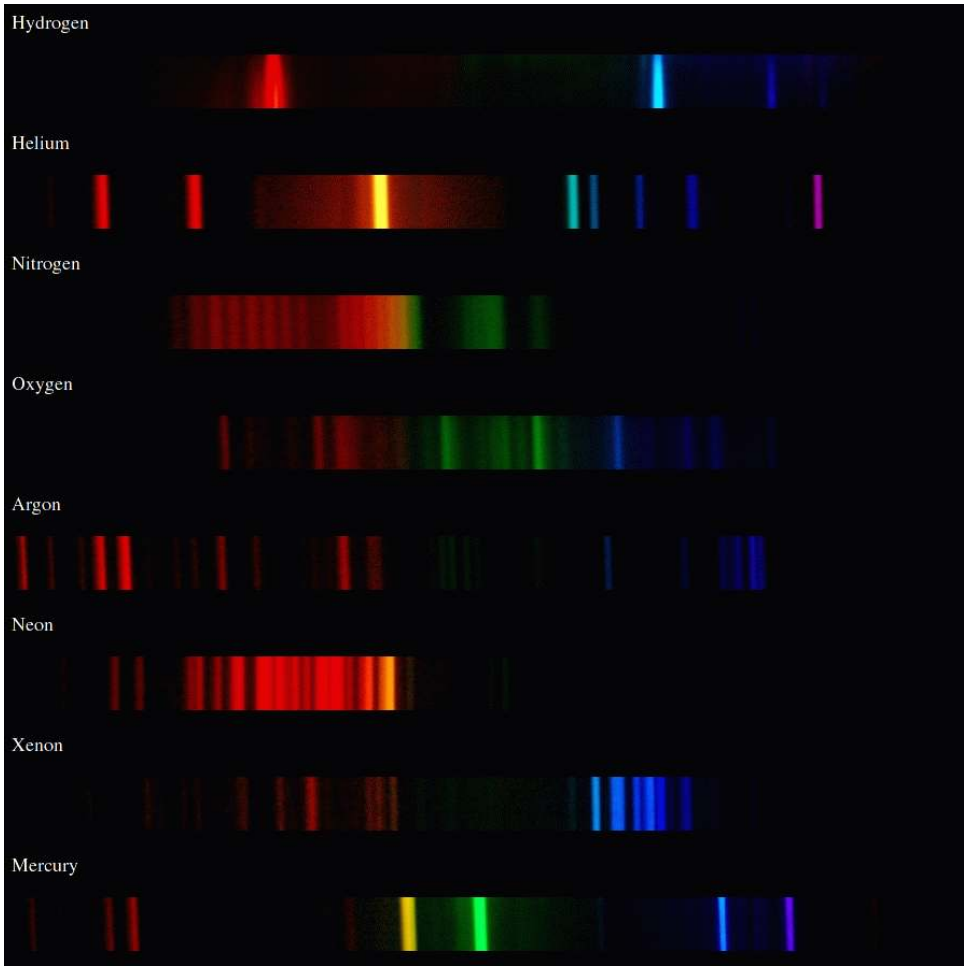


Figure 1.3.5: The atomic emission spectra for various elements. Each thin band in each spectrum corresponds to a single, unique transition between energy levels in an atom. Astronomical spectra image(opens in new window) from the Rochester Institute of Technology, CC BY-NC-SA 2.0(opens in new window).

1.3.3 THE ENERGY STATES OF THE HYDROGEN ATOM

Thus far we have explicitly considered only the emission of light by atoms in excited states, which produces an emission spectrum (a spectrum produced by the emission of light by atoms in excited states). The converse, absorption of light by ground-state atoms to produce an excited state, can also occur, producing an absorption spectrum (a spectrum produced by the absorption of light by ground-state atoms).

> When an atom emits light, it decays to a lower energy state; when an atom absorbs light, it is excited to a higher energy state.

If white light is passed through a sample of hydrogen, hydrogen atoms absorb energy as an electron is excited to higher energy levels (orbits with $n \geq 2$). If the light that emerges is passed through a prism, it forms a continuous spectrum with *black* lines (corresponding to no light passing through the sample) at 656, 468, 434, and 410 nm. These wavelengths correspond to the $n = 2$ to $n = 3$, $n = 2$ to $n = 4$, $n = 2$ to $n = 5$, and $n = 2$ to $n = 6$ transitions. Any given element therefore has both a characteristic emission spectrum and a characteristic absorption spectrum, which are essentially complementary images.

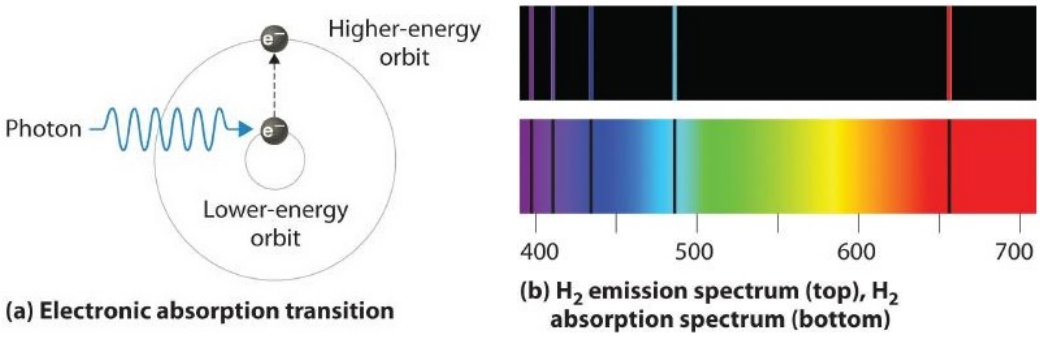


Figure 1.3.6: Absorption and Emission Spectra. Absorption of light by a hydrogen atom. (a) When a hydrogen atom absorbs a photon of light, an electron is excited to an orbit that has a higher energy and larger value of n. (b) Images of the emission and absorption spectra of hydrogen are shown here. (CC BY-NC-SA 3.0; anonymous)

Emission and absorption spectra form the basis of *spectroscopy*, which uses spectra to provide information about the structure and the composition of a substance or an object. In particular, astronomers use emission and absorption spectra to determine the composition of stars and interstellar matter. As an example, consider the spectrum of sunlight shown in Figure 1.3.7 Because the sun is very hot, the light it emits is in the form of a continuous emission spectrum. Superimposed on it, however, is a series of dark lines due primarily to the absorption of specific frequencies of light by cooler atoms in the outer atmosphere of the sun. By comparing these lines with the spectra of elements measured on Earth, we now know that the sun contains large amounts of hydrogen, iron, and carbon, along with smaller amounts of other elements. During the solar eclipse of 1868, the French astronomer Pierre Janssen (1824–1907) observed a set of lines that did not match those of any known element. He suggested that they were due to the presence of a new element, which he named *helium*, from the Greek *helios*, meaning "sun." Helium was finally discovered in uranium ores on Earth in 1895. Alpha particles are helium nuclei. Alpha particles emitted by the radioactive uranium pick up electrons from the rocks to form helium atoms.

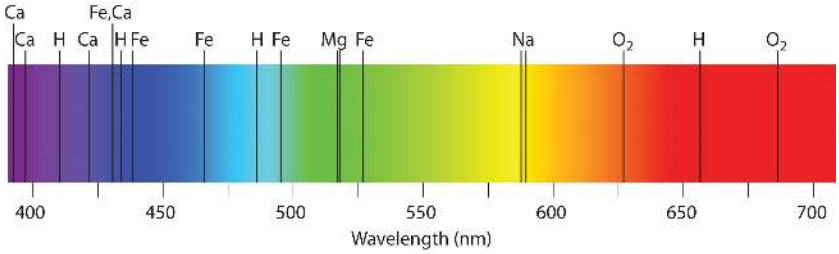


Figure 1.3.7: The Visible Spectrum of Sunlight. The characteristic dark lines are mostly due to the absorption of light by elements that are present in the cooler outer part of the sun's atmosphere; specific elements are indicated by the labels. The lines at 628 and 687 nm, however, are due to the absorption of light by oxygen molecules in Earth's atmosphere. (CC BY-NC-SA 3.0; anonymous)

The familiar red color of neon signs used in advertising is due to the emission spectrum of neon shown in part (b) in Figure 1.3.5. Similarly, the blue and yellow colors of certain street lights are caused, respectively, by mercury and sodium discharges. In all these cases, an electrical discharge excites neutral atoms to a higher energy state, and light is emitted when the atoms decay to the ground state. In the case of mercury, most of the emission lines are below 450 nm, which produces a blue light (part (c) in Figure 1.3.5). In the case of sodium, the most intense emission lines are at 589 nm, which produces an intense yellow light.

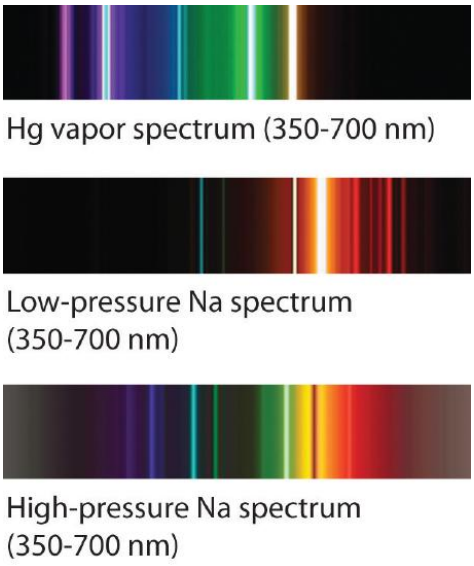


Figure **1.3.8**: The emission spectra of sodium and mercury. Sodium and mercury spectra. Many street lights use bulbs that contain sodium or mercury vapor. Due to the very different emission spectra of these elements, they emit light of different colors. The lines in the sodium lamp are broadened by collisions. The dark line in the center of the high pressure sodium lamp where the low pressure lamp is strongest is cause by absorption of light in the cooler outer part of the lamp.

1.3.4 SUMMARY

There is an intimate connection between the atomic structure of an atom and its spectral characteristics. Atoms of individual elements emit light at only specific wavelengths, producing a **line spectrum** rather than the continuous spectrum of all wavelengths produced by a hot object. Niels Bohr explained the line spectrum of the hydrogen atom by assuming that the electron moved in circular orbits and that orbits with only certain radii were allowed. Lines in the spectrum were due to transitions in which an electron moved from a higher-energy orbit with a larger radius to a lower-energy orbit with smaller radius. The orbit closest to the nucleus represented the **ground state** of the atom and was most stable; orbits farther away were higher-energy **excited states**. Transitions from an excited state to a lower-energy state resulted in the emission of light with only a limited number of wavelengths. Atoms can also absorb light of certain energies, resulting in a transition from the ground state or a lower-energy excited state to a higher-energy excited state. This produces an **absorption spectrum**, which has dark lines in the same position as the bright lines in the **emission spectrum** of an element. Bohr's model revolutionized the understanding of the atom but could not explain the spectra of atoms heavier than hydrogen.

1.3.5 KEY CONCEPTS

- Electrons can occupy only certain regions of space, called *orbits*.
- Orbits closer to the nucleus are lower in energy.
- Electrons can move from one orbit to another by absorbing or emitting energy, giving rise to characteristic spectra.

1.3.6 CONTRIBUTORS AND ATTRIBUTIONS

- Modified by Joshua Halpern (Howard University)

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1.4: THE WAVE BEHAVIOR OF MATTER

LEARNING OBJECTIVES

- To understand the wave–particle duality of matter.

Einstein's photons of light were individual packets of energy having many of the characteristics of particles. Recall that the collision of an electron (a particle) with a sufficiently energetic photon can eject a *photoelectron* from the surface of a metal. Any excess energy is transferred to the electron and is converted to the kinetic energy of the ejected electron. Einstein's hypothesis that energy is concentrated in localized bundles, however, was in sharp contrast to the classical notion that energy is spread out uniformly in a wave. We now describe Einstein's theory of the relationship between energy and mass, a theory that others built on to develop our current model of the atom.

1.4.1 THE WAVE CHARACTER OF MATTER

Einstein initially assumed that photons had zero mass, which made them a peculiar sort of particle indeed. In 1905, however, he published his special theory of relativity, which related energy and mass according to the famous equation:

$$E = h\nu = h\frac{c}{\lambda} = mc^2 \tag{1.4.1}$$

According to this theory, a photon of wavelength λ and frequency ν has a nonzero mass, which is given as follows:

$$m = \frac{E}{c^2} = \frac{h\nu}{c^2} = \frac{h}{\lambda c} \tag{1.4.2}$$

That is, light, which had always been regarded as a wave, also has properties typical of particles, a condition known as wave–particle duality (a principle that matter and energy have properties typical of both waves and particles). Depending on conditions, light could be viewed as either a wave or a particle.

In 1922, the American physicist Arthur Compton (1892–1962) reported the results of experiments involving the collision of x-rays and electrons that supported the particle nature of light. At about the same time, a young French physics student, Louis de Broglie (1892–1972), began to wonder whether the converse was true: Could particles exhibit the properties of waves? In his PhD dissertation submitted to the Sorbonne in 1924, de Broglie proposed that a particle such as an electron could be described by a wave whose wavelength is given by

$$\lambda = \frac{h}{mv} \tag{1.4.3}$$

where

- h is Planck's constant,
- m is the mass of the particle, and
- v is the velocity of the particle.

This revolutionary idea was quickly confirmed by American physicists Clinton Davisson (1881–1958) and Lester Germer (1896–1971), who showed that beams of electrons, regarded as particles, were diffracted by a sodium chloride crystal in the same manner as x-rays, which were regarded as waves. It was proven experimentally that electrons do exhibit the properties of waves. For his work, de Broglie received the Nobel Prize in Physics in 1929.

If particles exhibit the properties of waves, why had no one observed them before? The answer lies in the numerator of de Broglie's equation, which is an extremely small number. As you will calculate in Example **1.4.1**, Planck's constant (6.63×10^{-34} J•s) is so small that the wavelength of a particle with a large mass is too short (less than the diameter of an atomic nucleus) to be noticeable.



The de Broglie Equation: The de Broglie Equation, YouTube(opens in new window) [youtu.be]

EXAMPLE 1.4.1: WAVELENGTH OF A BASEBALL IN MOTION

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

Given: mass and speed of object

Asked for: wavelength

Strategy:

A. Convert the speed of the baseball to the appropriate SI units: meters per second.

B. Substitute values into Equation 1.4.3 and solve for the wavelength.

Solution:

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

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

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

$$\lambda = \frac{6.626 \times 10^{-34}\ J \cdot s}{(0.149\ kg)\,(44.69\ m \cdot s)} = \frac{6.626 \times 10^{-34}\ \cancel{kg} \cdot m^2 \cdot \cancel{s}^{-2} \cdot \cancel{s}}{\left(0.149\ \cancel{kg}\right)\left(44.69\ \cancel{m} \cdot \cancel{s}^{-1}\right)} = 9.95 \times 10^{-35}\ m$$

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

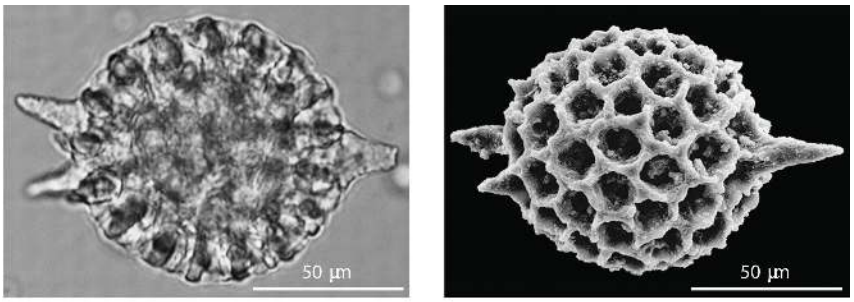
EXERCISE 1.4.1: WAVELENGTH OF A NEUTRON IN MOTION

Calculate the wavelength of a neutron that is moving at 3.00 × 10^3 m/s.

Answer

1.32 Å, or 132 pm

As you calculated in Example **1.4.1**, objects such as a baseball or a neutron have such short wavelengths that they are best regarded primarily as particles. In contrast, objects with very small masses (such as photons) have large wavelengths and can be viewed primarily as waves. Objects with intermediate masses, however, such as electrons, exhibit the properties of both particles *and* waves. Although we still usually think of electrons as particles, the wave nature of electrons is employed in an *electron microscope*, which has revealed most of what we know about the microscopic structure of living organisms and materials. Because the wavelength of an electron beam is much shorter than the wavelength of a beam of visible light, this instrument can resolve smaller details than a light microscope can (Figure **1.4.1**).



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

Figure **1.4.1**: A Comparison of Images Obtained Using a Light Microscope and an Electron Microscope. Because of their shorter wavelength, high-energy electrons have a higher resolving power than visible light. Consequently, an electron microscope (b) is able to resolve finer details than a light microscope (a). (Radiolaria, which are shown here, are unicellular planktonic organisms.)

AN IMPORTANT WAVE PROPERTY: PHASE AND INTERFERENCE

A wave is a disturbance that travels in space. The magnitude of the wave at any point in space and time varies sinusoidally. While the absolute value of the magnitude of one wave at any point is not very important, the *relative* displacement of two waves, called the phase difference, is vitally important because it determines whether the waves reinforce or interfere with each other. Figure **1.4.2*A*** shows an arbitrary phase difference between two wave and Figure **1.4.2*B*** shows what happens when the two waves are 180 degrees out of phase. The green line is their sum. Figure **1.4.2*C*** shows what happens when the two lines are in phase, exactly superimposed on each other. Again, the green line is the sum of the intensities. A pattern of constructive and destructive interference is obtained when two (or more) diffracting waves interact with each other. This principle of diffraction and interference was used to prove the wave properties of electrons and is the basis for how electron microscopes work.

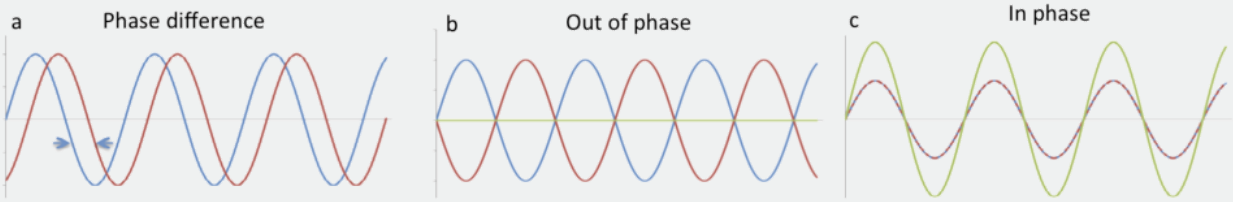
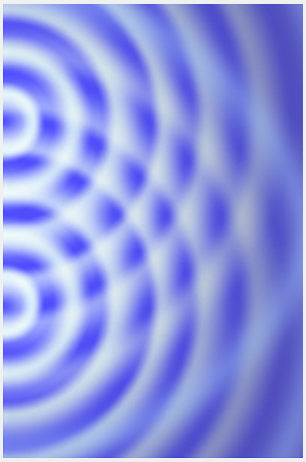


Figure **1.4.2**: Phase. Two waves traveling together are displaced by a phase difference. If the phase difference is 0° then they lay on top of each other and reinforce. If the phase difference is 180° they completely cancel each other out.

A shows two waves with a phase difference where the peaks are slightly misaligned. B shows two waves out of phase, the two waves are opposite of each other. C shows two waves in phase, the two waves peak at the same time.



The waves are the white circles that start from the left side. The waves intersect at multiple points.

Photograph of an interference pattern produced by circular water waves in a ripple tank.

For a mathematical analysis of phase aspects in sinusoids, check the math Libretexts library.

1.4.1.1 STANDING WAVES

De Broglie also investigated why only certain orbits were allowed in Bohr's model of the hydrogen atom. He hypothesized that the electron behaves like a **standing wave** (a wave that does not travel in space). An example of a standing wave is the motion of a string of a violin or guitar. When the string is plucked, it vibrates at certain fixed frequencies because it is fastened at both ends (Figure **1.4.3**). If the length of the string is L, then the lowest-energy vibration (the fundamental) has wavelength

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

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

$$\lambda = \frac{2L}{n} \tag{1.4.4}$$

where n has any integral value. When plucked, all other frequencies die out immediately. Only the resonant frequencies survive and are heard. Thus, we can think of the resonant frequencies of the string as being quantized. Notice in Figure **1.4.3** that all overtones have one or more nodes, points where the string does not move. The amplitude of the wave at a node is zero.

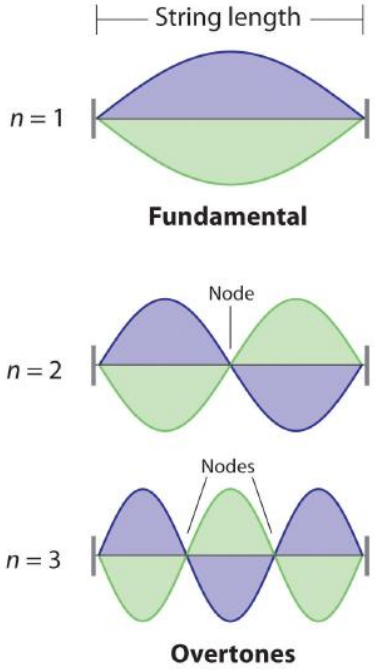


Figure **1.4.3**: Standing Waves on a Vibrating String. The vibration with \(n = 1\) is the fundamental and contains no nodes. Vibrations with higher values of n are called overtones; they contain \(n − 1\) nodes.

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

$$2\pi r = n\lambda \tag{1.4.5}$$

where r is the radius of the circle. De Broglie argued that Bohr's allowed orbits could be understood if the electron behaved like a *standing circular wave* (Figure **1.4.4**). The standing wave could exist only if the circumference of the circle was an integral multiple of the wavelength such that the propagated waves were all in phase, thereby increasing the net amplitudes and causing *constructive interference*. Otherwise, the propagated waves would be out of phase, resulting in a net decrease in amplitude and causing *destructive interference*. The nonresonant waves interfere with themselves! De Broglie's idea explained Bohr's allowed orbits and energy levels nicely: in the lowest energy level, corresponding to $n = 1$ in Equation 1.4.5, one complete wavelength would close the circle. Higher energy levels would have successively higher values of n with a corresponding number of nodes.

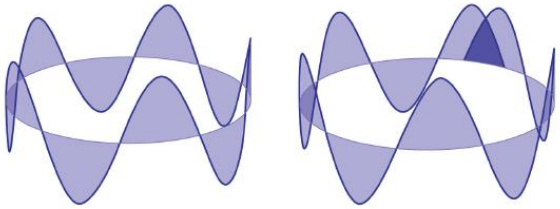


Figure **1.4.4**: Standing Circular Wave and Destructive Interference. (a) In a standing circular wave with \(n = 5\), the circumference of the circle corresponds to exactly five wavelengths, which results in constructive interference of the wave with itself when overlapping occurs. (b) If the circumference of the circle is not equal to an integral multiple of wavelengths, then the wave does not overlap exactly with itself, and the resulting destructive interference will result in cancellation of the wave. Consequently, a standing wave cannot exist under these conditions.

Like all analogies, although the standing wave model helps us understand much about why Bohr's theory worked, it also, if pushed too far, can mislead. As you will see, some of de Broglie's ideas are retained in the modern theory of the electronic structure of the atom: the wave behavior of the electron and the presence of nodes that increase in number as the energy level increases. Unfortunately, his (and Bohr's) explanation also contains one major feature that we now know to be incorrect: in the currently accepted model, the electron in a given orbit is *not* always at the same distance from the nucleus.

1.4.2 THE HEISENBERG UNCERTAINTY PRINCIPLE

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

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

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

$$(\Delta x)\,(\Delta\,[mv]) \geq \frac{h}{4\pi} \tag{1.4.6}$$

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

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

$$(\Delta\,[mv]) = \frac{h}{4\pi\,(\Delta x)} = \frac{h}{4\pi\,(0)} = \infty \tag{1.4.7}$$

Because the mass of the electron at rest (m) is both constant and accurately known, the uncertainty in $\Delta(mv)$ must be due to the Δv term, which would have to be infinitely large for $\Delta(mv)$ to equal infinity. That is, according to Equation 1.4.7, the more accurately we know the exact position of the electron (as $\Delta x \rightarrow 0$), the less accurately we know the speed and the kinetic energy of the electron ($1/2\ mv^2$) because $\Delta(mv) \rightarrow \infty$. Conversely, the more accurately we know the precise momentum (and the energy) of the electron [as $\Delta(mv) \rightarrow 0$], then $\Delta x \rightarrow \infty$ and we have no idea where the electron is.

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

EXAMPLE 1.4.1: QUANTUM NATURE OF BASEBALLS

Calculate the minimum uncertainty in the position of the pitched baseball from Example 1.4.1 that has a mass of exactly 149 g and a speed of 100 ± 1 mi/h.

Given: mass and speed of object

Asked for: minimum uncertainty in its position

Strategy:

A. Rearrange the inequality that describes the Heisenberg uncertainty principle (Equation 1.4.6) to solve for the minimum uncertainty in the position of an object (Δx).
B. Find Δv by converting the velocity of the baseball to the appropriate SI units: meters per second.
C. Substitute the appropriate values into the expression for the inequality and solve for Δx.

Solution:

A The Heisenberg uncertainty principle (Equation 1.4.6) tells us that

$$(\Delta x)(\Delta(mv)) = h/4\pi$$

. Rearranging the inequality gives

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

B We know that $h = 6.626 \times 10^{-34}$ J•s and $m = 0.149$ kg. Because there is no uncertainty in the mass of the baseball, $\Delta(mv) = m\Delta v$ and $\Delta v = \pm 1$ mi/h. We have

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

C Therefore,

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

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

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

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

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

EXERCISE 1.4.2

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

Answer

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

1.4.2.1 VIDEOS AND EXAMPLES

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

- Quantum Chemistry - Ohio State
- Quantum Chemistry Quizzes - mhe education
- AP Chemistry Chapter 7 Review - Science Geek

Answers for these quizzes are included.

1.4.3 SUMMARY

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

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

The electron in Bohr's circular orbits could thus be described as a **standing wave**, one that does not move through space. Standing waves are familiar from music: the lowest-energy standing wave is the **fundamental** vibration, and higher-energy vibrations are **overtones** and have successively more **nodes**, points where the amplitude of the wave is always zero. Werner Heisenberg's **uncertainty principle** states that it is impossible to precisely describe both the location and the speed of particles that exhibit wavelike behavior.

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

1.4.4 CONTRIBUTORS AND ATTRIBUTIONS

- Modified by Joshua Halpern (Howard University)

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1.5: QUANTUM MECHANICS AND WAVEFUNCTIONS

LEARNING OBJECTIVES

1. Understand the Relationship Between the Schrödinger Equation and the Wavefunction
2. Grasp the Mathematical Significance of the Wavefunction Ψ for an Atom
3. Interpret the Physical Meaning of the Square of the Wavefunction ($|\Psi|^2$) for an Atom

The paradox described by Heisenberg's uncertainty principle and the wavelike nature of subatomic particles such as the electron made it impossible to use the equations of classical physics to describe the motion of electrons in atoms. Scientists needed a new approach that took the wave behavior of the electron into account. In 1926, an Austrian physicist, Erwin Schrödinger (1887–1961; Nobel Prize in Physics, 1933), developed *wave mechanics*, a mathematical technique that describes the relationship between the motion of a particle that exhibits wavelike properties (such as an electron) and its allowed energies.

ERWIN SCHRÖDINGER (1887–1961)

Schrödinger's unconventional approach to atomic theory was typical of his unconventional approach to life. He was notorious for his intense dislike of memorizing data and learning from books. When Hitler came to power in Germany, Schrödinger escaped to Italy. He then worked at Princeton University in the United States but eventually moved to the Institute for Advanced Studies in Dublin, Ireland, where he remained until his retirement in 1955.

1.5.1 1D EXAMPLE OF THE TIME-INDEPENDENT SCHRÖDINGER EQUATION

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

$$-\frac{\hbar}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\,\psi(x) = E\cdot\psi(x) \tag{1.5.1}$$

Caution

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

There are 3 components to this equation

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

Example 1.5.1: The wavefunction of a particle in a 1-D box

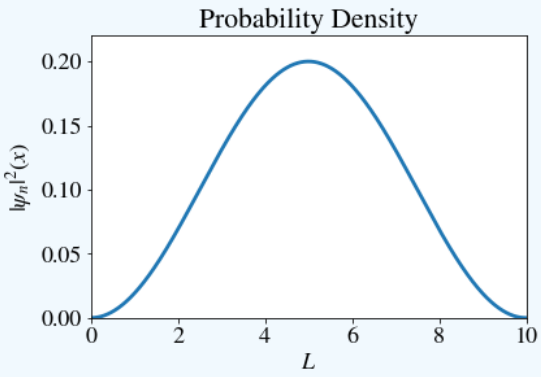
Consider an electron that can move in one-dimensional space (moving within a line). If this electron is confined within a 1-D box of length 10 Å its state will be described by

$$\psi_1(x) = \sqrt{\frac{2}{10\text{Å}}}sin(\frac{\pi}{10\text{Å}}\cdot x) \tag{1.5.2}$$

Solution

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

$$|\psi_1(x)|^2 = \frac{2}{10\text{Å}}\left(sin(\frac{\pi}{10\text{Å}}\cdot x)\right)^2 \tag{1.5.3}$$



If we were to measure in the lab the position of this particle, there would be a 0.07 probability to find it at $x = 8\mathring{A}$. The energy of state 1 is given by $E = 6.025 \cdot 10^{-20} Joules$

To describe particle-waves that can move in 3 dimensions (for example, the H atom, with 1 electron and 1 proton), we use a 3-dimensional wavefunction $\psi(x, y, z)$ with the Schrödinger equation also written for 3 dimensions. The probability density would be plotted in 4 dimensions (one for each coordinate x, y, z, and a 4th for the value of Probability Density at each point in space $|\psi(x, y, z)|^2$.

1.5.2 UNDERSTANDING 3D WAVEFUNCTIONS

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

- **A wavefunction uses three variables to describe the position of an electron.** A fourth variable is usually required to fully describe the location of objects in motion. Three specify the position in space (as with the Cartesian coordinates *x*, *y*, and *z*), and one specifies the time at which the object is at the specified location. For example, if you were the captain of a ship trying to intercept an enemy submarine, you would need to know its latitude, longitude, and depth, as well as the time at which it was going to be at this position (Figure 1.5.1). For electrons, we can ignore the time dependence because we will be using standing waves, which by definition do not change with time, to describe the position of an electron.

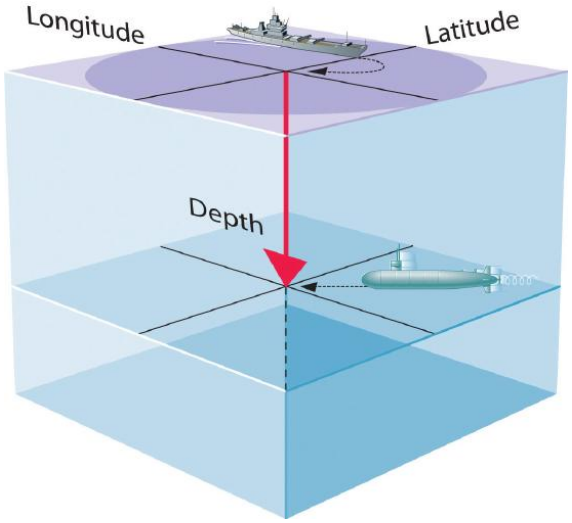


Figure 1.5.1: The Four Variables (Latitude, Longitude, Depth, and Time) required to precisely locate an object

- **The magnitude of the wavefunction at a particular point in space is proportional to the amplitude of the wave at that point.** Many wavefunctions are complex functions, which is a mathematical term indicating that they contain $\sqrt{-1}$, represented as i. Hence the amplitude of the wave has no real physical significance. In contrast, the sign of the wavefunction (either positive or negative) corresponds to the phase of the wave, which will be important in our discussion of chemical bonding. The sign of the wavefunction should *not* be confused with a positive or negative electrical charge.

- **The square of the wavefunction at a given point is proportional to the probability of finding an electron at that point, which leads to a distribution of probabilities in space.** The square of the wavefunction (Ψ^2) is always a real quantity [recall that that $\sqrt{-1}^2 = -1$] and is proportional to the probability of finding an electron at a given point. More accurately, the probability is given by the product of the wavefunction Ψ and its complex conjugate Ψ*, in which all terms that contain *i* are replaced by $-i$. We use probabilities because, according to Heisenberg's uncertainty principle, we cannot precisely specify the position of an electron. The probability of finding an electron at any point in space depends on several factors, including the distance from the nucleus and, in many cases, the atomic equivalent of latitude and longitude. As one way of graphically representing the probability distribution, the probability of finding an electron is indicated by the density of colored dots, as shown for the ground state of the hydrogen atom in Figure 1.5.2.
- **Describing the electron distribution as a standing wave leads to sets of *quantum numbers* that are characteristic of each wavefunction.** From the patterns of one- and two-dimensional standing waves shown previously, you might expect (correctly) that the patterns of three-dimensional standing waves would be complex. Fortunately, however, in the 18th century, a French mathematician, Adrien Legendre (1752–1783), developed a set of equations to describe the motion of tidal waves on the surface of a flooded planet. Schrödinger incorporated Legendre's equations into his wavefunctions. The requirement that the waves must be in phase with one another to avoid cancellation and produce a standing wave results in a limited number of solutions (wavefunctions), each of which is specified by a set of numbers called quantum numbers.
- **Each wavefunction is associated with a particular energy.** As in Bohr's model, the energy of an electron in an atom is quantized; it can have only certain allowed values. The major difference between Bohr's model and Schrödinger's approach is that Bohr had to impose the idea of quantization arbitrarily, whereas in Schrödinger's approach, quantization is a natural consequence of describing an electron as a standing wave.

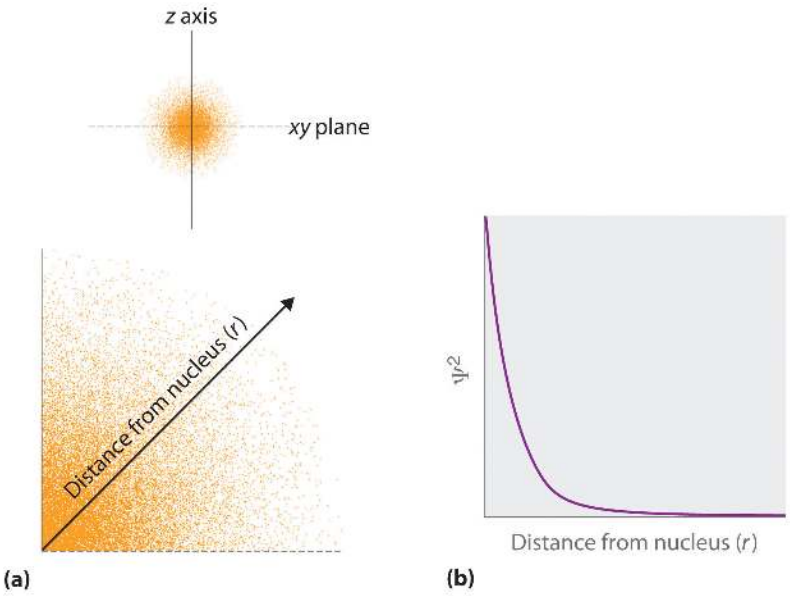


Figure 1.5.2: Probability of Finding the Electron in the Ground State of the Hydrogen Atom at Different Points in Space. (a) The density of the dots shows electron probability. (b) In this plot of Ψ^2 versus *r* for the ground state of the hydrogen atom, the electron probability density is greatest at $r = 0$ (the nucleus) and falls off with increasing *r*. Because the line never actually reaches the horizontal axis, the probability of finding the electron at very large values of *r* is very small but *not* zero.

1.5.3 SUMMARY

- **Relationship Between the Schrödinger Equation and the Wavefunction** The Schrödinger Equation is a fundamental equation in quantum mechanics that describes how the quantum state of a physical system changes over time. When applied to atoms, solving this equation yields the wavefunction (Ψ), which encapsulates all the information about an electron's state within the atom.
- **Mathematical Significance of the Wavefunction for an Atom** Mathematically, the wavefunction Ψ is a complex function that depends on the electron coordinates. For a hydrogen atom, Ψ is called an **orbital**.
- **Physical Significance of the Square of the Wavefunction for an Atom** Physically, the square of the wavefunction's magnitude, $|\Psi|^2$, represents the probability density of finding an electron in a particular region around the nucleus. This probabilistic interpretation replaces the classical notion of electrons following fixed orbits, highlighting the inherent uncertainties in the electron's position within the atom.

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1.6: The Schrödinger Wave Equation for the Hydrogen Atom

Learning Objectives

1. Understand the Application of the Schrödinger Equation to the Hydrogen Atom
2. Interpret the Physical Significance of the Hydrogen Atom's Wavefunctions
3. Recognize the Role of 4 Quantum Numbers in Describing Atomic Orbitals

The hydrogen atom, consisting of an electron and a proton, is a two-particle system, and the internal motion of two particles around their center of mass is equivalent to the motion of a single particle with a reduced mass. This reduced particle is located at r, where r is the vector specifying the position of the electron relative to the position of the proton. The length of r is the distance between the proton and the electron, and the direction of r and the direction of r is given by the orientation of the vector pointing from the proton to the electron. Since the proton is much more massive than the electron, we will assume throughout this chapter that the reduced mass equals the electron mass and the proton is located at the center of mass.

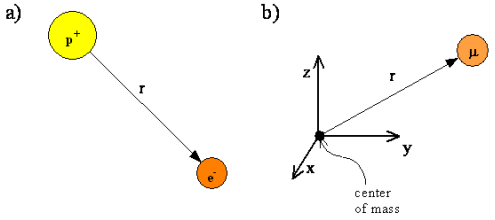


Figure **1.6.1**: a) The proton (p^+) and electron (e^-) of the hydrogen atom. b) Equivalent reduced particle with reduced mass μ at distance r from center of mass.

Since the internal motion of any two-particle system can be represented by the motion of a single particle with a reduced mass, the description of the hydrogen atom has much in common with the description of a diatomic molecule discussed previously. The Schrödinger Equation for the hydrogen atom

$$\hat{H}(r,\theta,\varphi)\psi(r,\theta,\varphi) = E\psi(r,\theta,\varphi) \tag{1.6.1}$$

employs the same kinetic energy operator, $\hat{T}$, written in spherical coordinates. For the hydrogen atom, however, the distance, r, between the two particles can vary, unlike the diatomic molecule where the bond length was fixed, and the rigid rotor model was used. The hydrogen atom Hamiltonian also contains a potential energy term, $\hat{V}$, to describe the attraction between the proton and the electron. This term is the Coulomb potential energy,

$$\hat{V}(r) = -\frac{e^2}{4\pi\epsilon_0 r} \tag{1.6.2}$$

where r is the distance between the electron and the proton. The Coulomb potential energy depends inversely on the distance between the electron and the nucleus and does not depend on any angles. Such a potential is called a central potential.

It is convenient to switch from Cartesian coordinates x, y, z to spherical coordinates in terms of a radius r, as well as angles ϕ, which is measured from the positive x axis in the xy plane and may be between 0 and 2π, and θ, which is measured from the positive z axis towards the xy plane and may be between 0 and π.

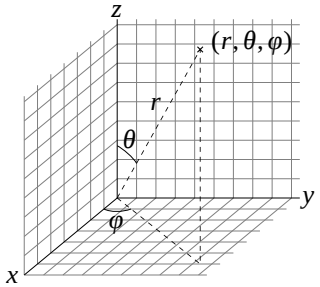


Figure **1.6.2**: Spherical Coordinates

The time-indepdent Schrödinger equation (in spherical coordinates) for a electron around a positively charged nucleus is then

$$\left\{-\frac{\hbar^2}{2\mu r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]-\frac{e^2}{4\pi\epsilon_0 r}\right\}\psi(r,\theta,\varphi) = E\psi(r,\theta,\varphi) \tag{1.6.3}$$

Since the angular momentum operator does not involve the radial variable, r, we can separate variables in Equation 1.6.3 by using a **product wavefunction**. We know that the eigenfunctions of the angular momentum operator are the Spherical Harmonic functions (Table M4), $Y(\theta,\varphi)$, so a good choice for a product function is

$$\psi(r,\theta,\varphi) = R(r)Y(\theta,\varphi) \tag{1.6.4}$$

The Spherical Harmonic functions $Y(\theta,\varphi)$, the angular components of $\psi(r,\theta,\phi)$, provide information about where the electron is around the proton, and the radial function $R(r)$, the radial components of $\psi(r,\theta,\phi)$, describes how far the electron is away from the proton. A solution for both $R(r)$ and $Y(\theta,\varphi)$ with E_n that depends on only one quantum number n, although others are required for the proper description of the wavefunction:

$$E_n = -\frac{m_e e^4}{8\epsilon_0^2 h^2 n^2} \tag{1.6.5}$$

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

The hydrogen atom wavefunctions, $\psi(r,\theta,\phi)$, are called atomic orbitals. An atomic orbital is a function that describes one electron in an atom. The wavefunction with n = 1, l l = 0 is called the 1s orbital, and an electron that is described by this function is said to be “in” the ls orbital, i.e. have a 1s orbital state. The constraints on n, l l), and m_l that are imposed during the solution of the hydrogen atom Schrödinger equation explain why there is a single 1s orbital, why there are three 2p orbitals, five 3d orbitals, etc. We will see when we consider multi-electron atoms, these constraints explain the features of the Periodic Table. In other words, the Periodic Table is a manifestation of the Schrödinger model and the physical constraints imposed to obtain the solutions to the Schrödinger equation for the hydrogen atom.

The Three Quantum Numbers

Schrödinger’s approach requires three quantum numbers (n, l, and m_l) to specify a wavefunction for the electron. The quantum numbers provide information about the spatial distribution of an electron. Although n can be any positive integer (NOT zero), only certain values of l and m_l are allowed for a given value of \(n).

The principal quantum number (n): One of three quantum numbers that tells the average relative distance of an electron from the nucleus. indicates the energy of the electron and the average distance of an electron from the nucleus

$$n = 1,\ 2,\ 3,\ 4,\ \ldots \tag{1.6.6}$$

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

The Azimuthal Quantum Number (also known as angular momentum quantum number): The second quantum number is often called the azimuthal quantum number (l). One of three quantum numbers that describes the shape of the region of space occupied by an electron.. The value of l describes the shape of the region of space occupied by the electron. The allowed values of l depend on the value of n and can range from 0 to n − 1:

$$l = 0,\ 1,.,2,\ 3,\ ..\ (n-1) \tag{1.6.7}$$

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

The Magnetic Quantum Number: The third quantum number is the magnetic quantum number (m_l). One of three quantum numbers that describes the orientation of the region of space occupied by an electron with respect to an applied magnetic field.. The value of m_l describes the orientation of the region in space occupied by an electron with respect to an applied magnetic field. The allowed values of m_l depend on the value of l: m_l can range from −l to l in integral steps:

$$m = -l,\ -l+1, \ldots 0,\ \ldots l-1, l \tag{1.6.8}$$

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

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

Example 1.6.1: Number of subshells

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

Given: value of n

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

Strategy:

A Given n = 4, calculate the allowed values of l. From these allowed values, count the number of subshells.

B For each allowed value of l, calculate the allowed values of ml. The sum of the number of orbitals in each subshell is the number of orbitals in the principal shell.

Solution

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

B For l = 0, ml can be only 0, and thus the l = 0 subshell has only one orbital. For l = 1, ml can be 0 or ±1; thus the l = 1 subshell has three orbitals. For l = 2, ml can be 0, ±1, or ±2, so there are five orbitals in the l = 2 subshell. The last allowed value of l is l = 3, for which ml can be 0, ±1, ±2, or ±3, resulting in seven orbitals in the l = 3 subshell. The total number of orbitals in the n = 4 principal shell is the sum of the number of orbitals in each subshell and is equal to n2:

$$\underset{(l=0)}{1} + \underset{(l=1)}{3} + \underset{(l=2)}{5} + \underset{(l=3)}{7} = 16 \text{ orbitals} = (4 \text{ principal shells})^2$$

Exercise 1.6.1

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

Answer: three subshells; nine orbitals

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

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

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

We can summarize the relationships between the quantum numbers and the number of subshells and orbitals as follows (Table **1.6.1**):

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

Note

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

Table **1.6.1**: Allowed values of n, l, and m_l through n = 4

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

The Radial Functions and Radial Probability Density Functions

The first six radial functions are provided in Table **1.6.2**. Note that the functions in the table exhibit a dependence on Z, the atomic number of the nucleus. Other one electron systems have electronic states analogous to those for the hydrogen atom, and inclusion of the charge on the nucleus allows the same wavefunctions to be used for all one-electron systems. For hydrogen, $Z = 1$ and for helium, $Z = 2$.

Table **1.6.2**: Hydrogen-like radial wavefunctions for n values $1, 2, 3$: Z is the atomic number of the nucleus, and $\rho = \frac{Zr}{a_0}$, where a_0 is the Bohr radius and r is the radial variable.

n	ℓ	Radial Function
$n=1$	$\ell=0$	$R_{10}=2\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}e^{-\rho}$
$n=2$	$\ell=0$	$R_{20}=\frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}(2-\rho)e^{\frac{-\rho}{2}}$
	$\ell=1$	$R_{21}=\frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\rho e^{-\rho/2}$
$n=3$	$\ell=0$	$R_{30}=\frac{2}{81\sqrt{3}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}(27-18\rho+2\rho^2)e^{-\rho/3}$
	$\ell=1$	$R_{31}=\frac{4}{81\sqrt{6}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}(6\rho-\rho^2)e^{-\rho/3}$
	$\ell=2$	$R_{32}=\frac{4}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\rho^2e^{-\rho/3}$
$n=4$	$\ell=0$	$R_{40}=\frac{1}{96}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}(24-36\rho+12\rho^2-\rho^3)e^{-\rho/4}$

Visualizing the variation of an electronic wavefunction with r,θ, and ϕ is important because the absolute square of the wavefunction depicts the charge distribution (electron probability density) in an atom or molecule. The charge distribution is central to chemistry because it is related to chemical reactivity. For example, an electron deficient part of one molecule is attracted to an electron rich region of another molecule, and such interactions play a major role in chemical interactions ranging from substitution and addition reactions to protein folding and the interaction of substrates with enzymes.

Methods for separately examining the radial portions of atomic orbitals provide useful information about the distribution of charge density within the orbitals. Graphs of the radial functiondensity, $R_{n\ell}(r)$, for the 1s, 2s, and 2p orbitals plotted in Figure **1.6.2** (left). The radial probability density function, $P_{n\ell}(r) = r^2[R_{n\ell}(r)^2]$, represents the probability of locating the electron within a spherical

shell of thickness dr at a radial distance r from the nucleus. Radial probability density functions for three types of atomic orbitals are plotted in Figure **1.6.2** (right).

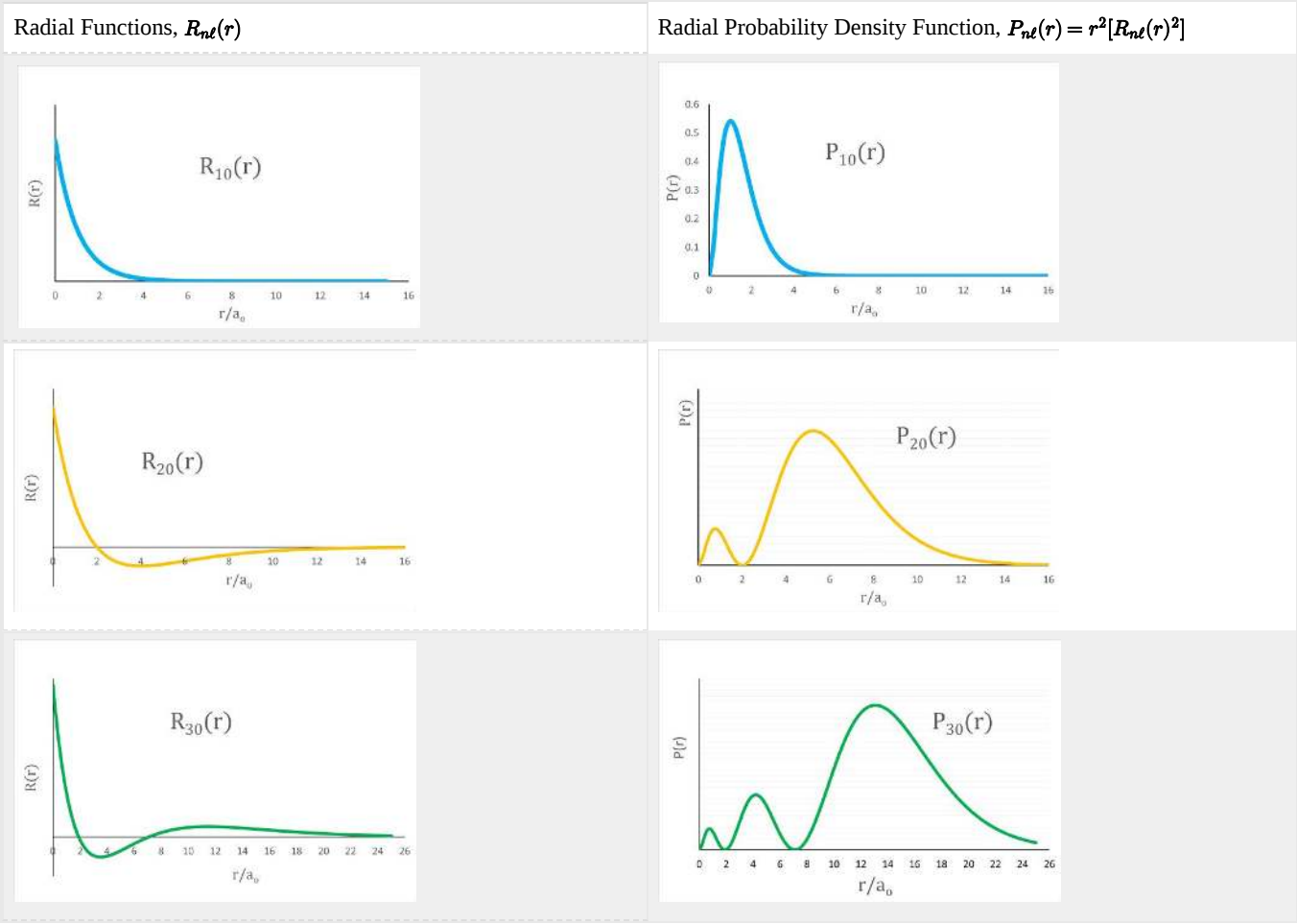
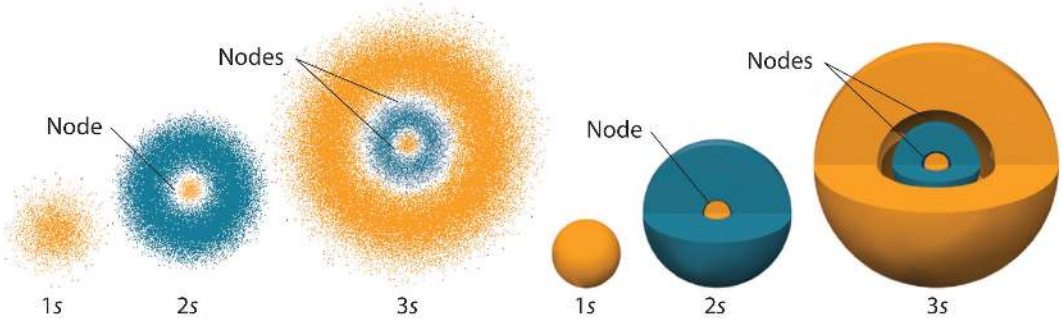
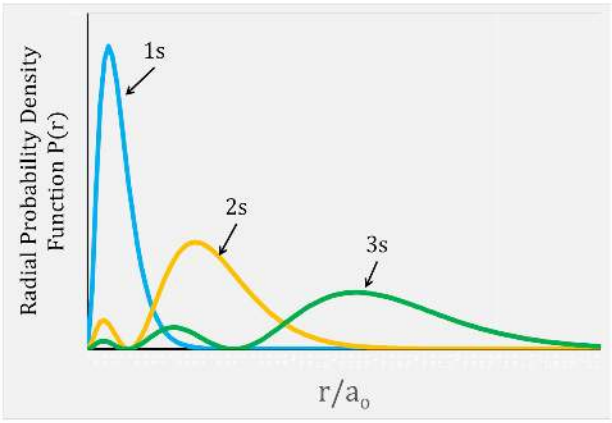


Figure 1.6.2: (left) **Radial functions**, R(r), for the 1s, 2s, and 2p orbitals. (right) **Radial probability density functions** for the 1s, 2s, and 2p orbitals. (CC BY 4.0 ; Ta-Wei Li)

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

Figure **1.6.3** compares the electron probability densities for the hydrogen 1*s*, 2*s*, and 3*s* orbitals. Note that all three are spherically symmetrical. For the 2*s* and 3*s* orbitals, however (and for all other *s* orbitals as well), the electron probability density does not fall off smoothly with increasing *r*. Instead, a series of minima and maxima are observed in the radial probability plots (part (c) in Figure **1.6.3**). The minima correspond to **radial nodes** (Nodes are regions where the electron probability density is zero, $\psi(r, \theta, \varphi) = 0$, and radial nodes are spherical surfaces at specific distances from the nucleus where the radial probability density function equals to zero, $P_{n\ell}(r) = 0$), which alternate with spherical regions of nonzero electron probability.





(c) **Radial probability Density Function**

Figure **1.6.3**: Probability Densities for the 1 s, 2 s, and 3*s* Orbitals of the Hydrogen Atom. (a) The electron probability density in any plane that contains the nucleus is shown. Note the presence of circular regions, or nodes, where the probability density is zero. (b) Contour surfaces enclose 90% of the electron probability, which illustrates the different sizes of the 1*s*, 2*s*, and 3*s* orbitals. The cutaway drawings give partial views of the internal radial nodes. The orange color corresponds to regions of space where the phase of the wave function is positive, and the blue color corresponds to regions of space where the phase of the wave function is negative. (c) In these plots of electron probability as a function of distance from the nucleus (*r*) in all directions (radial probability density function P(r)), the most probable radius increases as*n* increases, but the 2*s* and 3*s* orbitals have regions of significant electron probability at small values of *r*.

The Angular Component

The angular component of the wavefunction $Y(\theta,\phi)$ in Equation 1.6.4 does much to give an orbital its distinctive shape. $Y(\theta,\phi)$ is typically normalized so the the integral of $Y^2(\theta,\phi)$ over the unit sphere is equal to one. In this case, $Y^2(\theta,\phi)$ serves as a probability function. The probability function can be interpreted as the probability that the electron will be found on the ray emitting from the origin that is at angles (θ,ϕ) from the axes. The probability function can also be interpreted as the probability distribution of the electron being at position (θ,ϕ) on a sphere of radius *r*, given that it is *r* distance from the nucleus. $Y_{l,m_l}(\theta,\phi)$ are also the wavefunction solutions to Schrödinger's equation for a rigid rotor consisting of rotating bodies, for example a diatomic molecule. These are called Spherical Harmonic functions (Table M4).

s Orbitals (l=0)

Three things happen to *s* orbitals as *n* increases (Figure 6.6.2):

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

Orbitals are generally drawn as three-dimensional surfaces that enclose 90% of the electron density. Although such drawings show the relative sizes of the orbitals, they do not normally show the radial nodes in the 2*s* and 3*s* orbitals because the radial nodes lie inside the 90% surface. Fortunately, the positions of the radial nodes are not important for chemical bonding.

p Orbitals (l=1)

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

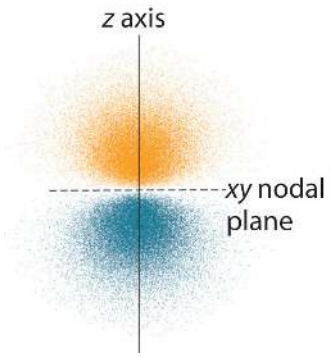


Figure **1.6.4**: The colors correspond to regions of space where the phase of the wave function is positive (orange) and negative (blue).

The electron probability distribution for one of the hydrogen 2*p* orbitals is shown in Figure **1.6.4**. Because this orbital has two lobes of electron density arranged along the *z* axis, with an electron density of zero in the *xy* plane (i.e., the *xy* plane is a nodal plane), it is a $2p_z$ orbital. As shown in Figure **1.6.5**, the other two 2*p* orbitals have identical shapes, but they lie along the *x* axis ($2p_x$) and *y* axis ($2p_y$), respectively. Note that each *p* orbital has just one nodal plane. In each case, the phase of the wave function for each of the 2*p* orbitals is positive for the lobe that points along the positive axis and negative for the lobe that points along the negative axis. It is important to emphasize that these signs correspond to the *phase* of the wave that describes the electron motion, *not* to positive or negative charges.

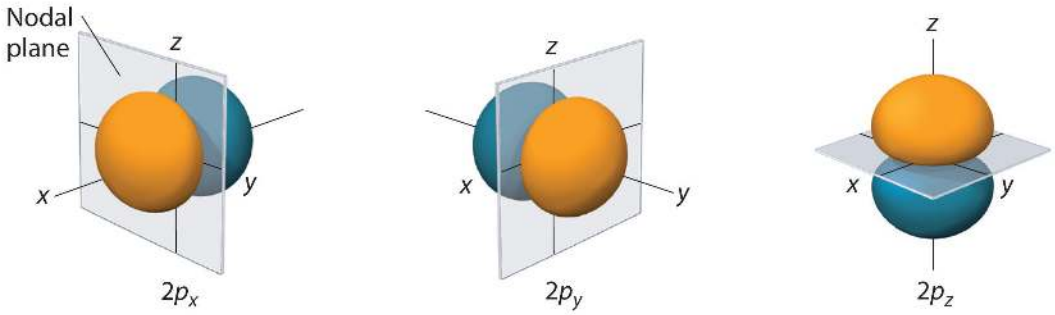


Figure **1.6.5**: The Three Equivalent 2 p Orbitals of the Hydrogen Atom

The surfaces shown enclose 90% of the total electron probability for the $2p_x$, $2p_y$, and $2p_z$ orbitals. Each orbital is oriented along the axis indicated by the subscript and a nodal plane that is perpendicular to that axis bisects each 2*p* orbital. The phase of the wave function is positive (orange) in the region of space where *x*, *y*, or *z* is positive and negative (blue) where *x*, *y*, or *z* is negative. Just as with the *s* orbitals, the size and complexity of the *p* orbitals for any atom increase as the principal quantum number *n* increases. The shapes of the 90% probability surfaces of the 3*p*, 4*p*, and higher-energy *p* orbitals are, however, essentially the same as those shown in Figure Figure **1.6.5**.

d Orbitals (l=2)

Subshells with $l = 2$ have five *d* orbitals; the first principal shell to have a *d* subshell corresponds to $n = 3$. The five *d* orbitals have m_l values of −2, −1, 0, +1, and +2 (Figure **1.6.6**).

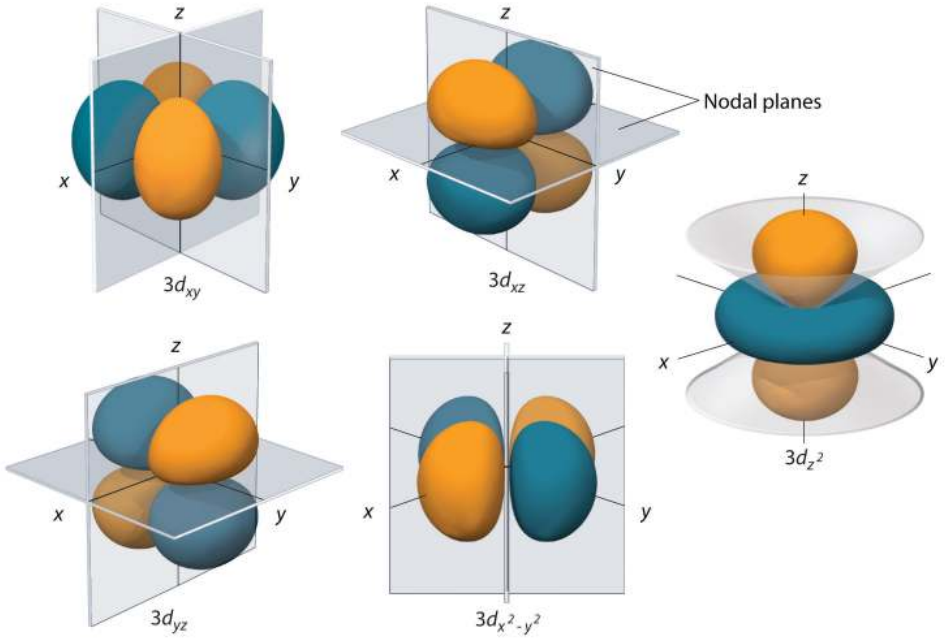


Figure **1.6.6**: The Five Equivalent 3d Orbitals of the Hydrogen Atom. The surfaces shown enclose 90% of the total electron probability for the five hydrogen 3d orbitals. Four of the five 3d orbitals consist of four lobes arranged in a plane that is intersected by two perpendicular nodal planes. These four orbitals have the same shape but different orientations. The fifth 3d orbital, $3d_{z^2}$, has a distinct shape even though it is mathematically equivalent to the others. The phase of the wave function for the different lobes is indicated by color: orange for positive and blue for negative.

The hydrogen 3d orbitals have more complex shapes than the 2p orbitals. All five 3d orbitals contain two nodal surfaces, as compared to one for each p orbital and zero for each s orbital. In three of the d orbitals, the lobes of electron density are oriented between the x and y, x and z, and y and z planes; these orbitals are referred to as the $3d_{xy}$, \)3d_{xz}_, and \)3d_{yz}\) orbitals, respectively. A fourth d orbital has lobes lying along the x and y axes; this is the 3dx2−y2 orbital. The fifth 3d orbital, called the $3d_{z^2}$ orbital, has a unique shape: it looks like a $2p_z$ orbital combined with an additional doughnut of electron probability lying in the xy plane. Despite its peculiar shape, the $3d_{z^2}$ orbital is mathematically equivalent to the other four and has the same energy. In contrast to p orbitals, the phase of the wave function for d orbitals is the same for opposite pairs of lobes. As shown in Figure **1.6.6**, the phase of the wave function is positive for the two lobes of the dz^2 orbital that lie along the z axis, whereas the phase of the wave function is negative for the doughnut of electron density in the xy plane. Like the s and p orbitals, as n increases, the size of the d orbitals increases, but the overall shapes remain similar to those depicted in Figure 6.6.5.

f Orbitals (l=3)

Principal shells with $n = 4$ can have subshells with $l = 3$ and m_l values of −3, −2, −1, 0, +1, +2, and +3. These subshells consist of seven *f* orbitals. Each *f* orbital has three nodal surfaces, so their shapes are complex (not shown).

Energies

The constraint that n be greater than or equal to $l + 1$ also turns out to quantize the energy, producing the same quantized expression for hydrogen atom energy levels that was obtained from the Bohr model of the hydrogen atom.

$$E = -\frac{Z^2}{n^2} Rhc \tag{1.6.9}$$

or

$$E_n = -\frac{Z^2 \mu e^4}{8\epsilon_0^2 h^2 n^2} \tag{1.6.10}$$

The relative energies of the atomic orbitals with $n \leq 4$ for a hydrogen atom are plotted in Figure **1.6.7** ; note that the orbital energies depend on *only* the principal quantum number *n*. Consequently, the energies of the 2*s* and 2*p* orbitals of hydrogen are the same; the

energies of the 3*s*, 3*p*, and 3*d* orbitals are the same; and so forth. The orbital energies obtained for hydrogen using quantum mechanics are exactly the same as the allowed energies calculated by Bohr. In contrast to Bohr's model, however, which allowed only one orbit for each energy level, quantum mechanics predicts that there are *4* orbitals with different electron density distributions in the $n = 2$ principal shell (one 2*s* and three 2*p* orbitals), *9* in the $n = 3$ principal shell, and *16* in the $n = 4$ principal shell.

Note

For a single electron system, the energy of that electron is a function of only the principal quantum number (Equation 1.6.9).

The different values of l and m_l for the individual orbitals within a given principal shell are not important for understanding the emission or absorption spectra of the hydrogen atom under most conditions, but they do explain the splittings of the main lines that are observed when hydrogen atoms are placed in a magnetic field. As we have just seen, however, quantum mechanics also predicts that in the hydrogen atom, all orbitals with the same value of n (e.g., the three 2*p* orbitals) are degenerate, meaning that they have the same energy. Figure **1.6.7** shows that the energy levels become closer and closer together as the value of n increases, as expected because of the $1/n^2$ dependence of orbital energies.

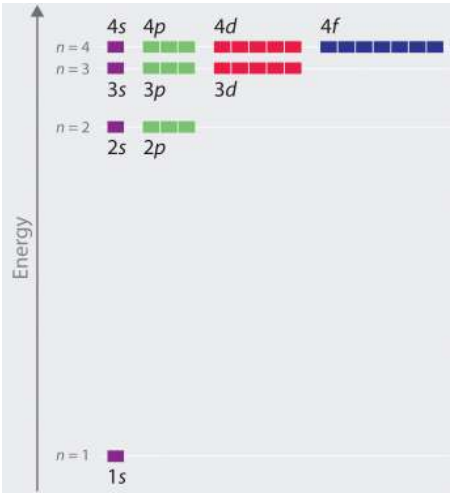


Figure **1.6.7**: Orbital Energy Level Diagram for the Hydrogen Atom. Each box corresponds to one orbital. Note that the difference in energy between orbitals decreases rapidly with increasing values of n.

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

Note: Bohr vs. Schrödinger

It is interesting to compare the results obtained by solving the Schrödinger equation with Bohr's model of the hydrogen atom. There are several ways in which the Schrödinger model and Bohr model differ.

1. First, and perhaps most strikingly, the Schrödinger model does not produce well-defined orbits for the electron. The wavefunctions only give us the probability for the electron to be at various directions and distances from the proton.
2. Second, the quantization of angular momentum is different from that proposed by Bohr. Bohr proposed that the angular momentum is quantized in integer units of $\hbar$, while the Schrödinger model leads to an angular momentum of $(l(l+1)\hbar^2)\frac{1}{2}$.
3. Third, the quantum numbers appear naturally during solution of the Schrödinger equation while Bohr had to postulate the existence of quantized energy states. Although more complex, the Schrödinger model leads to a better correspondence between theory and experiment over a range of applications that was not possible for the Bohr model.

Electron Spin: The Fourth Quantum Number

The quantum numbers n, l, m are not sufficient to fully characterize the physical state of the electrons in an atom. In 1926, Otto Stern and Walther Gerlach carried out an experiment that could not be explained in terms of the three quantum numbers n, l, m and showed that there is, in fact, another quantum-mechanical degree of freedom that needs to be included in the theory. The experiment is illustrated in the Figure 1.6.8. A beam of atoms (e.g. hydrogen or silver atoms) is sent through a spatially inhomogeneous magnetic field with a definite field gradient toward one of the poles. It is observed that the beam splits into two beams as it passes through the field region.

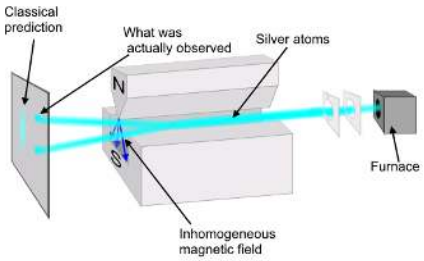


Figure 1.6.8: The Stern-Gerlach apparatus. from Wikipedia

The fact that the beam splits into 2 beams suggests that the electrons in the atoms have a degree of freedom capable of coupling to the magnetic field. That is, an electron has an *intrinsic magnetic moment* M arising from a degree of freedom that has no classical analog. The magnetic moment must take on only 2 values according to the Stern-Gerlach experiment. The intrinsic property that gives rise to the magnetic moment must have some analog to a *spin*, S; unlike position and momentum, which have clear classical analogs, spin does not. The implication of the Stern-Gerlach experiment is that we need to include a fourth quantum number, m_s in our description of the physical state of the electron. That is, in addition to give its principle, angular, and magnetic quantum numbers, we also need to say if it is a spin-up electron or a spin-down electron.

Note: Spin is a Quantum Phenomenon

Unlike position and momentum, which have clear classical analogs, spin does not.

In 1925, two graduate students in physics in the Netherlands, George Uhlenbeck (1900–1988) and Samuel Goudsmit (1902–1978), proposed that the splittings were caused by an electron spinning about its axis, much as Earth spins about its axis. When an electrically charged object spins, it produces a magnetic moment parallel to the axis of rotation, making it behave like a magnet. Although the electron cannot be viewed solely as a particle, spinning or otherwise, it is indisputable that it does have a magnetic moment. This magnetic moment is called electron spin.

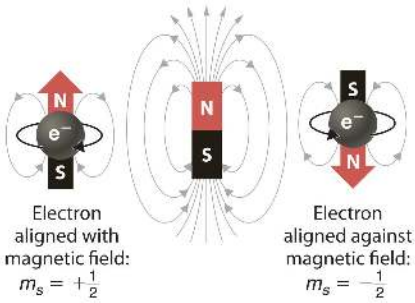


Figure 1.6.9: Electron Spin. In a magnetic field, an electron has two possible orientations with different energies, one with spin up, aligned with the magnetic field, and one with spin down, aligned against it. All other orientations are forbidden.

In the presence of an external magnetic field, an electron can adopt one of two possible orientations (Figure 1.6.9). These orientations are described by a fourth quantum number, the **spin quantum number** (msm_sms), which can have only two possible values: +½ (spin-up) and −½ (spin-down). The subscript "s" stands for **spin**, reflecting the intrinsic angular momentum of the electron. This property causes an electron to behave like a tiny magnet, capable of aligning either with or against the external magnetic field.

The concept of electron spin had significant implications for chemistry, recognized early on by Austrian physicist **Wolfgang Pauli** (1900–1958), who was awarded the Nobel Prize in Physics in 1945. He formulated the **Pauli Exclusion Principle**, which states that no two electrons in the same atom can have identical sets of quantum numbers. As a result, each orbital can hold a maximum of two electrons, and they must have opposite spins. This principle will be explored in more detail in the following sections.

Contributors and Attributions

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1.7: Many-Electron Atoms - Penetration and Shielding

Learning Objectives

- Explain how electron shielding and penetration affect the effective nuclear charge, Z_{eff}, across different subshells.
- Describe how orbital energy levels are determined in many-electron atoms.
- Write the electron configuration of any element and relate it to the element's position on the periodic table.

In hydrogen atoms, the energy of an electron orbital depends solely on the principal quantum number n. However, in many-electron atoms, orbital energy is influenced by additional quantum numbers - n, l, and m_l. This results in significant differences in energy levels compared to hydrogen. For example, while the 3s and 3p orbitals in hydrogen have the same energy (they are *degenerate*), they differ in energy in atoms with more than one electron.

This difference arises due to two key concepts: **electron shielding** and **penetration**. These effects alter the effective nuclear charge Z_{eff} experienced by electrons in different subshells. For instance, electrons in the 3s orbital experience a higher Z_{eff} than those in 3p because they penetrate closer to the nucleus and are less shielded. Radial probability density functions are useful tools for visualizing how penetration varies among orbitals.

Introduction to Shielding and Penetration

Electrons, being negatively charged, are attracted to the positively charged nucleus. However, they also repel each other. The balance between these attractive and repulsive forces leads to **shielding**—where inner electrons partially block the nuclear charge from being fully felt by outer electrons.

The specific orbital and subshell an electron occupies determine how close it can get to the nucleus. This ability to approach the nucleus is called **penetration**. The closer an electron can get, the stronger the electrostatic attraction it experiences from the nucleus.

This concept can be described using **Coulomb's Law**:

$$F = k\frac{q_i \cdot q_j}{r^2} \tag{1.7.1}$$

Here, F is the electrostatic force between two charges, q_i and q_j , separated by a distance r and k is Coulomb's constant. In atoms, this means that the force experienced by an electron depends on its distance from other charges (electrons or the nucleus) and the magnitude of those charges.

In an idealized model, all electrons would experience the full nuclear charge equally. For example, in a lithium atom (Li), each of its three electrons might be thought to feel the full +3 charge from the nucleus. In reality, the inner (core) electrons shield the outer (valence) electrons, reducing the nuclear charge they effectively experience. This reduced attraction is referred to as the **effective nuclear charge**, or Z_{eff} .

Core electrons, being closer to the nucleus, experience a Z_{eff} close to the actual nuclear charge. Valence electrons, on the other hand, experience a significantly reduced Z_{eff} due to both the shielding effect of core electrons and mutual repulsion from other valence electrons.

The force on an electron due to the nucleus is given by:

$$F_{electron-nucleus} = k\frac{Z \cdot e^2}{r^2} \tag{1.7.2}$$

Where

- Z is the atomic number (nuclear charge)
- e is the charge of an electron
- r is the distance from the nucleus

In multi-electron atoms, due to shielding, we use Z_{eff} instead of Z:

$$F_{eff} = k\frac{Z_{eff} \cdot e^2}{r^2} \tag{1.7.3}$$

Understand Shielding and Penetration - Radial Probability Density Functions

The **radial probability density function** shows how electron density is distributed as a function of distance from the nucleus. These graphs help visualize shielding and penetration.

As shown in Figure **1.7.1**, the inner 1s electrons shield outer electrons from the nucleus, reducing the effective nuclear charge Z_{eff} of the outer electrons. In the hydrogen atom, the 2s and 2p orbitals are degenerate, as the single electron experiences the full nuclear charge without shielding. However, in multi-electron atoms, the shielding effect of the inner 1s electrons reduces Z_{eff} of 2s and 2p both. However, the 2s orbital penetrates closer to the nucleus due to its inner radial peak as shown in Figure **1.7.2** , so it experiences less shielding and feels a stronger nuclear attraction. In contrast, the 2p orbital has less penetration and is more shielded. As a result, the 2s orbital is lower in energy than the 2p in multi-electron atoms. This difference in shielding and penetration explains why 2s and 2p orbitals split in energy. The graphs show these differences: the 2s radial probability has a small inner peak indicating penetration, while 2p lacks this, confirming its weaker attraction to the nucleus. Thus, energy splitting arises from electron-electron interactions and orbital shape.

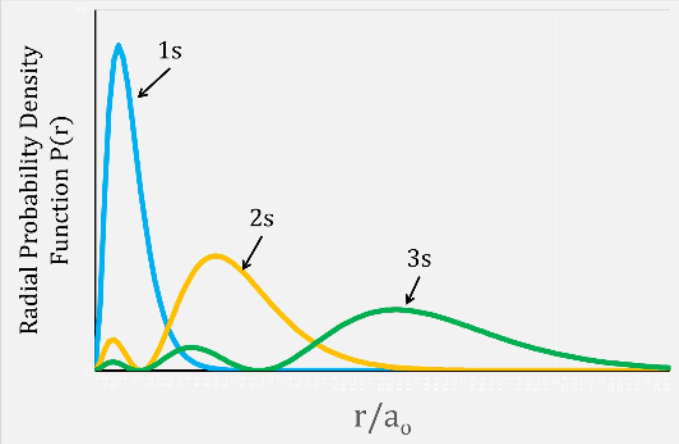


Figure **1.7.1**: P(r) for 1s, 2s, and 3s of the Hydrogen Atom.

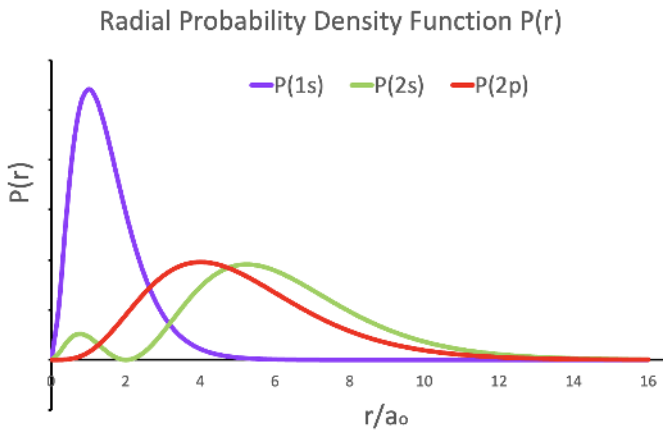


Figure **1.7.2**: P(r) for 1s, 2s and 2p of the Hydrogen Atom.

Figure **1.7.1** shows the inner 1s electrons shield outer electrons from the nucleus, reducing the effective nuclear charge Z_{eff} of the outer electrons. Figure **1.7.2** shows shows that the 2*s* orbital penetrates inside the 1*s* orbital more than the 2*p* orbital does. Consequently, when an electron is in the small inner lobe of the 2*s* orbital, it experiences a relatively large value of Z_{eff}, which causes the energy of the 2*s* orbital to be lower than the energy of the 2*p* orbital. (CC BY 4.0 ; Ta-Wei Li)

Orbital Penetration

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

Within the same shell value (*n*), the penetrating power of an electron follows this trend in subshells (l):

$$s > p > d > f$$

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

$$1s > 2s > 2p > 3s > 3p > 4s > 3d > 4p > 5s > 4d > 5p > 6s > 4f....$$

and the energy of an electron for each shell and subshell goes as follows...

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p....$$

The electron probability density for s-orbitals is highest in the center of the orbital, or at the nucleus. If we imagine a dartboard that represents the circular shape of the s-orbital and if the darts landed in correlation to the probability of where an electron would be

found, the greatest dart density would be at the 50 points region, but most of the darts would be at the 30 point region. When considering the 1s-orbital, the spherical shell of 53 pm is represented by the 30 point ring.

Electrons which experience greater penetration experience stronger attraction to the nucleus, less shielding, and therefore experience a larger *Effective Nuclear Charge* (Z_{eff}), but shield other electrons more effectively.

Orbitals and their Energies

Unlike in hydrogen-like atoms with only one electron, in multielectron atoms the values of quantum numbers *n and l* determine the energies of an orbital. The energies of the different orbitals for a typical multielectron atom are shown in Figure **1.7.3**. Within a given principal shell of a multielectron atom, the orbital energies increase with increasing *l*. An *ns* orbital always lies below the corresponding *np* orbital, which in turn lies below the *nd* orbital.



Figure **1.7.3**: Orbital Energy Level Diagram for a Typical Multielectron Atom

These energy differences are caused by the effects of *shielding* and *penetration*, the extent to which a given orbital lies inside other filled orbitals. For example, an electron in the 2*s* orbital penetrates inside a filled 1*s* orbital more than an electron in a 2*p* orbital does. Since electrons, all being negatively charged, repel each other, an electron closer to the nucleus partially *shields* an electron farther from the nucleus from the attractive effect of the positively charged nucleus. Hence in an atom with a filled 1*s* orbital, the effective nuclear charge (Z_{eff}) experienced by a 2*s* electron is greater than the Z_{eff} experienced by a 2*p* electron. Consequently, the 2*s* electron is more tightly bound to the nucleus and has a lower energy, consistent with the order of energies shown in Figure **1.7.1**.

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

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Notice in Figure **1.7.1** that the difference in energies between subshells can be so large that the energies of orbitals from different principal shells can become approximately equal. For example, the energy of the 3*d* orbitals in most atoms is actually *between* the energies of the 4*s* and the 4*p* orbitals.

The Pauli Exclusion Principle

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

By giving the values of n, l, and m_l, we also specify a particular orbital (e.g., 1*s* with $n = 1$, $l = 0$, $m_l = 0$). Because m_s has only two possible values (+½ or −½), two electrons, *and only two electrons*, can occupy any given orbital, one with spin up and one with spin down. With this information, we can proceed to construct the entire periodic table, which was originally based on the physical and chemical properties of the known elements.

✔ Example 1.7.1

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

Given: orbital

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

Strategy:

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

Solution:

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

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

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

? Exercise 1.7.1

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

Answer

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

Summary

In many-electron atoms, orbital energy levels are affected by both shielding and penetration, unlike hydrogen, where energy depends only on the principal quantum number n. **Penetration** refers to how close an electron can approach the nucleus; s orbitals penetrate more than p or d orbitals, leading to a stronger effective nuclear charge Z_{eff}. **Shielding** occurs when inner electrons block the attraction between the nucleus and outer electrons, reducing Z_{eff} for those farther out. As a result, subshells in the same

principal level (e.g., 3s, 3p, 3d) have different energies. Radial probability density graphs show these effects visually—for example, 2s electrons are closer to the nucleus than 2p electrons. These concepts explain trends in atomic size and ionization energy across the periodic table. Additionally, the **Pauli exclusion principle** states that each orbital can hold a maximum of two electrons with opposite spins, which helps define the electron configurations of elements.

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1.8: ELECTRON CONFIGURATIONS

LEARNING OBJECTIVES

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

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

1.8.1 THE AUFBAU PRINCIPLE

We construct the periodic table by following the aufbau principle (from German, meaning "building up"). First we determine the number of electrons in the atom; then we add electrons one at a time to the lowest-energy orbital available *without violating the Pauli principle*. We use the orbital energy diagram of Figure **1.8.1**, recognizing that each orbital can hold two electrons, one with spin up ↑, corresponding to m_s = +½, which is arbitrarily written first, and one with spin down ↓, corresponding to m_s = −½. A filled orbital is indicated by ↑↓, in which the electron spins are said to be *paired*. Here is a schematic orbital diagram for a hydrogen atom in its ground state:

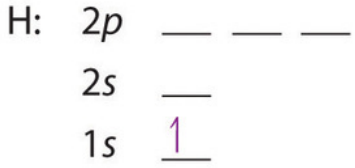
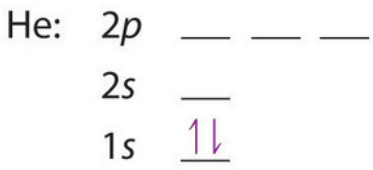


Figure **1.8.1**: One electron in.

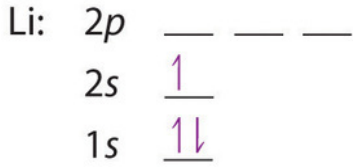
From the orbital diagram, we can write the electron configuration in an abbreviated form in which the occupied orbitals are identified by their principal quantum number *n* and their value of *l* (*s*, *p*, *d*, or *f*), with the number of electrons in the subshell indicated by a superscript. For hydrogen, therefore, the single electron is placed in the 1*s* orbital, which is the orbital lowest in energy (Figure **1.8.1**), and the electron configuration is written as $1s^1$ and read as "one-s-one."

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



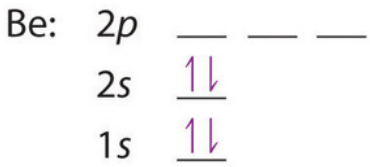
written as $1s^2$, where the superscript 2 implies the pairing of spins. Otherwise, our configuration would violate the Pauli principle.

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

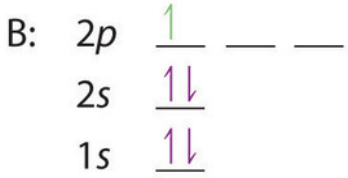


This electron configuration is written as $1s^22s^1$.

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

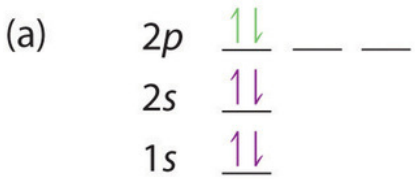


When we reach boron, with $Z = 5$ and five electrons, we must place the fifth electron in one of the 2*p* orbitals. Because all three 2*p* orbitals are degenerate, it doesn't matter which one we select. The electron configuration of boron is $1s^2 2s^2 2p^1$:

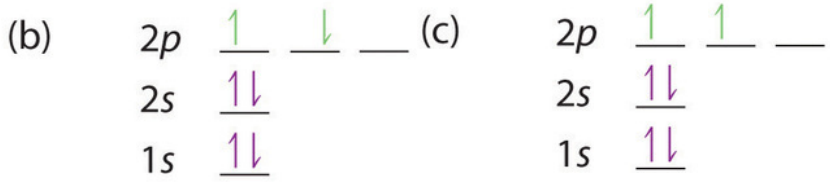


Boron has one electron pair in the 1 s orbital, one electron pair in the 2 s orbital, and one electron in the 2 p orbital.

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



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



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

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

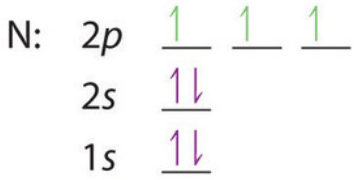
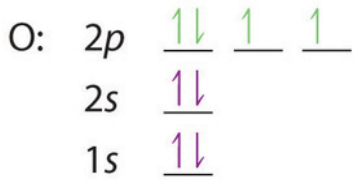


Figure **1.8.1**: Copy and Paste Caption here. (Copyright; author via source)

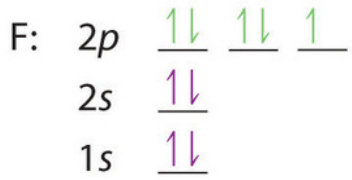
with three unpaired electrons. The electron configuration of nitrogen is thus $1s^2 2s^2 2p^3$.

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



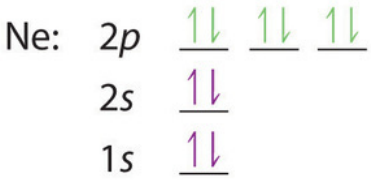
Oxygen has one electron pair in the 1 s orbital, one electron pair in the 2 s pair, and one electron pair, and 2 unpaired electrons in the 2 p orbitals.

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



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

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



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

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



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

1.8.2 VALENCE ELECTRONS

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

Electron Configuration of Neon and Sodium

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

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

Electron Configuration of Sodium and Lithium

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

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

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

EXAMPLE 1.8.1: ELECTRONIC CONFIGURATION OF PHOSPHORUS

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

Given: atomic number

Asked for: orbital diagram and valence electron configuration for phosphorus

Strategy:

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

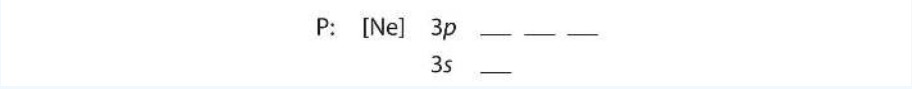
B. Referring to Figure **1.8.1**, draw an orbital diagram to represent those valence orbitals. Following Hund's rule, place the valence electrons in the available orbitals, beginning with the orbital that is lowest in energy. Write the electron configuration from your orbital diagram.

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

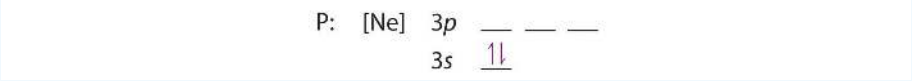
Solution:

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

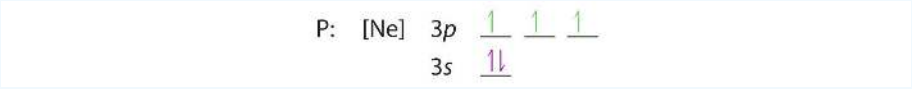
B The additional five electrons are placed in the next available orbitals, which Figure **1.8.1** tells us are the 3*s* and 3*p* orbitals:



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



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



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

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

EXERCISE 1.8.1

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

Answer

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



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

The general order in which orbitals are filled is depicted in Figure **1.8.2**. Subshells corresponding to each value of *n* are written from left to right on successive horizontal lines, where each row represents a row in the periodic table. The order in which the orbitals are filled is indicated by the diagonal lines running from the upper right to the lower left. Accordingly, the 4*s* orbital is filled prior to the 3*d* orbital because of shielding and penetration effects. Consequently, the electron configuration of potassium, which begins the fourth period, is [Ar]$4s^1$, and the configuration of calcium is [Ar]$4s^2$. Five 3*d* orbitals are filled by the next 10 elements, the transition metals, followed by three 4*p* orbitals. Notice that the last member of this row is the noble gas krypton (Z = 36), [Ar]$4s^2 3d^{10} 4p^6$ = [Kr], which has filled 4*s*, 3*d*, and 4*p* orbitals. The fifth row of the periodic table is essentially the same as the fourth, except that the 5*s*, 4*d*, and 5*p* orbitals are filled sequentially.

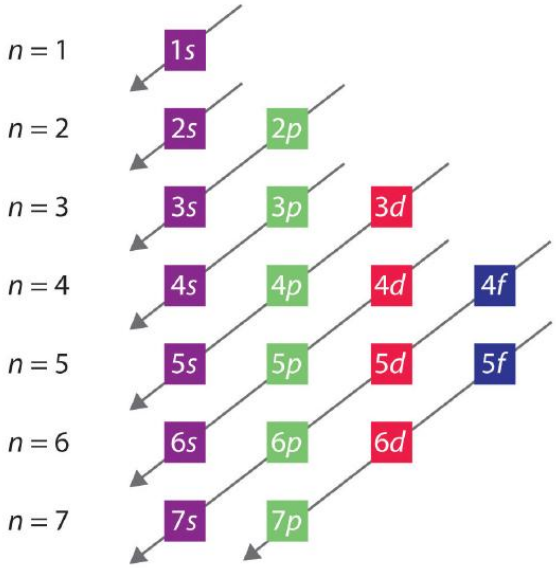


Figure **1.8.2**: Predicting the Order in Which Orbitals Are Filled in Multielectron Atoms. If you write the subshells for each value of the principal quantum number on successive lines, the observed order in which they are filled is indicated by a series of diagonal lines running from the upper right to the lower left.

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

EXAMPLE 1.8.2: ELECTRON CONFIGURATION OF MERCURY

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

Given: atomic number

Asked for: complete electron configuration

Strategy:

Using the orbital diagram in Figure **1.8.1** and the periodic table as a guide, fill the orbitals until all 80 electrons have been placed.

Solution:

By placing the electrons in orbitals following the order shown in Figure **1.8.2** and using the periodic table as a guide, we obtain

Solution to Example 6.8.2

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

After filling the first five rows, we still have 80 − 54 = 26 more electrons to accommodate. According to Figure **1.8.2**, we need to fill the 6*s* (2 electrons), 4*f* (14 electrons), and 5*d* (10 electrons) orbitals. The result is mercury's electron configuration:

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

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

EXERCISE 1.8.2: ELECTRON CONFIGURATION OF FLEROVIUM

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

Answer

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

The electron configurations of the elements are presented in Figure **1.8.2**, which lists the orbitals in the order in which they are filled. In several cases, the ground state electron configurations are different from those predicted by Figure **1.8.1**. Some of these anomalies occur as the 3*d* orbitals are filled. For example, the observed ground state electron configuration of chromium is $[\text{Ar}]4s^1 3d^5$ rather than the predicted $[\text{Ar}]4s^2 3d^4$. Similarly, the observed electron configuration of copper is $[\text{Ar}]4s^1 3d^{10}$ instead of $[\text{Ar}]s^2 3d^9$. The actual electron configuration may be rationalized in terms of an added stability associated with a half-filled (ns^1, np^3, nd^5, nf^7) or filled (ns^2, np^6, nd^{10}, nf^{14}) subshell. (In fact, this "special stability" is really another consequence of the *instability* caused by pairing an electron with another in the same orbital, as illustrated by Hund's rule.) Given the small differences between higher energy levels, this added stability is enough to shift an electron from one orbital to another. In heavier elements, other more complex effects can also be important, leading to many additional anomalies. For example, cerium has an electron configuration of $[\text{Xe}]6s^2 4f^1 5d^1$, which is impossible to rationalize in simple terms. In most cases, however, these apparent anomalies do not have important chemical consequences.

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



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

1.8.3 SUMMARY

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

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1.9: ELECTRON CONFIGURATIONS AND THE PERIODIC TABLE

LEARNING OBJECTIVES

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

As you have learned, the electron configurations of the elements explain the otherwise peculiar shape of the periodic table. Although the table was originally organized on the basis of physical and chemical similarities between the elements within groups, these similarities are ultimately attributable to orbital energy levels and the Pauli principle, which cause the individual subshells to be filled in a particular order. As a result, the periodic table can be divided into "blocks" corresponding to the type of subshell that is being filled, as illustrated in Figure **1.9.1**. For example, the two columns on the left, known as the *s* block, consist of elements in which the *ns* orbitals are being filled. The six columns on the right, elements in which the *np* orbitals are being filled, constitute the *p* block. In between are the 10 columns of the *d* block, elements in which the $(n - 1)d$ orbitals are filled. At the bottom lie the 14 columns of the *f* block, elements in which the $(n - 2)f$ orbitals are filled. Because two electrons can be accommodated per orbital, the number of columns in each block is the same as the maximum electron capacity of the subshell: 2 for *ns*, 6 for *np*, 10 for $(n - 1)d$, and 14 for $(n - 2)f$. Within each column, each element has the same valence electron configuration—for example, ns^1 (group 1) or ns^2np^1 (group 13). As you will see, this is reflected in important similarities in the chemical reactivity and the bonding for the elements in each column.

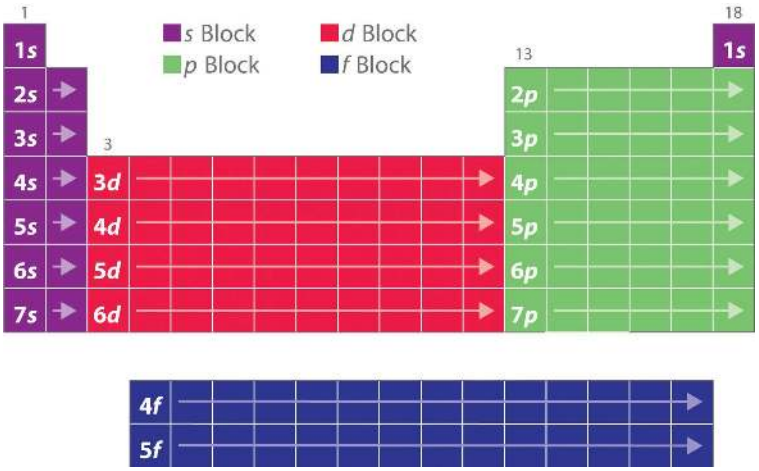


Figure **1.9.1**: The Periodic Table, Showing How the Elements Are Grouped According to the Kind of Subshell (*s*, *p*, *d*, *f*) Being Filled with Electrons in the Valence Shell of Each Element. The electron configurations of the elements are in Figure 6.9.2.

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

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

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

Figure **1.9.2**: Electron Configurations of the Elements. The electron configurations of elements indicated in red are exceptions due to the added stability associated with half-filled and filled subshells. The electron configurations of the elements indicated in blue are also anomalous, but the reasons for the observed configurations are more complex. For elements after No, the electron configurations are tentative.

EXAMPLE 1.9.1

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

Given: series of elements

Asked for: valence electron configurations

Strategy:

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

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

Solution:

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

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

? EXERCISE 1.9.1

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

Answer

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

1.9.1 SUMMARY

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

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1.E: ELECTRONIC STRUCTURE OF ATOMS (EXERCISES)

1.E.1 THE WAVE NATURE OF LIGHT

1.E.1.1 CONCEPTUAL PROBLEMS

1. What are the characteristics of a wave? What is the relationship between electromagnetic radiation and wave energy?
2. At constant wavelength, what effect does increasing the frequency of a wave have on its speed? its amplitude?
3. List the following forms of electromagnetic radiation in order of increasing wavelength: x-rays, radio waves, infrared waves, microwaves, ultraviolet waves, visible waves, and gamma rays. List them in order of increasing frequency. Which has the highest energy?
4. A large industry is centered on developing skin-care products, such as suntan lotions and cosmetics, that cannot be penetrated by ultraviolet radiation. How does the wavelength of visible light compare with the wavelength of ultraviolet light? How does the energy of visible light compare with the energy of ultraviolet light? Why is this industry focused on blocking ultraviolet light rather than visible light?

1.E.1.2 NUMERICAL PROBLEMS

5. The human eye is sensitive to what fraction of the electromagnetic spectrum, assuming a typical spectral range of 10^4 to 10^{20} Hz? If we came from the planet Krypton and had x-ray vision (i.e., if our eyes were sensitive to x-rays in addition to visible light), how would this fraction be changed?
6. What is the frequency in megahertz corresponding to each wavelength?
    1. 755 m
    2. 6.73 nm
    3. 1.77×10^3 km
    4. 9.88 Å
    5. 3.7×10^{-10} m
7. What is the frequency in megahertz corresponding to each wavelength?
    1. 5.8×10^{-7} m
    2. 2.3 Å
    3. 8.6×10^7 m
    4. 6.2 mm
    5. 3.7 nm
8. Line spectra are also observed for molecular species. Given the following characteristic wavelengths for each species, identify the spectral region (ultraviolet, visible, etc.) in which the following line spectra will occur. Given 1.00 mol of each compound and the wavelength of absorbed or emitted light, how much energy does this correspond to?
    1. NH_3, 1.0×10^{-2} m
    2. CH_3CH_2OH, 9.0 μm
    3. Mo atom, 7.1 Å
9. What is the speed of a wave in meters per second that has a wavelength of 1250 m and a frequency of 2.36×10^5 s^{-1}?
10. A wave travels at 3.70 m/s with a frequency of 4.599×10^7 Hz and an amplitude of 1.0 m. What is its wavelength in nanometers?
11. An AM radio station broadcasts with a wavelength of 248.0 m. What is the broadcast frequency of the station in kilohertz? An AM station has a broadcast range of 92.6 MHz. What is the corresponding wavelength range in meters for this reception?
12. An FM radio station broadcasts with a wavelength of 3.21 m. What is the broadcast frequency of the station in megahertz? An FM radio typically has a broadcast range of 82–112 MHz. What is the corresponding wavelength range in meters for this reception?
13. A microwave oven operates at a frequency of approximately 2450 MHz. What is the corresponding wavelength? Water, with its polar molecules, absorbs electromagnetic radiation primarily in the infrared portion of the spectrum. Given this fact, why are microwave ovens used for cooking food?

1.E.2 QUANTIZED ENERGY AND PHOTONS

1.E.2.1 CONCEPTUAL PROBLEMS

14. Describe the relationship between the energy of a photon and its frequency.
15. How was the ultraviolet catastrophe explained?
16. If electromagnetic radiation with a continuous range of frequencies above the threshold frequency of a metal is allowed to strike a metal surface, is the kinetic energy of the ejected electrons continuous or quantized? Explain your answer.
17. The vibrational energy of a plucked guitar string is said to be quantized. What do we mean by this? Are the sounds emitted from the 88 keys on a piano also quantized?
18. Which of the following exhibit quantized behavior: a human voice, the speed of a car, a harp, the colors of light, automobile tire sizes, waves from a speedboat?

1.E.2.2 CONCEPTUAL ANSWERS

14. The energy of a photon is directly proportional to the frequency of the electromagnetic radiation.
15.
16.
17.
18. Quantized: harp, tire size, speedboat waves; continuous: human voice, colors of light, car speed.

1.E.2.3 NUMERICAL PROBLEMS

19. What is the energy of a photon of light with each wavelength? To which region of the electromagnetic spectrum does each wavelength belong?
    1. 4.33×10^5 m
    2. 0.065 nm
    3. 786 pm
20. How much energy is contained in each of the following? To which region of the electromagnetic spectrum does each wavelength belong?
    1. 250 photons with a wavelength of 3.0 m
    2. 4.2×10^6 photons with a wavelength of 92 μm
    3. 1.78×10^{22} photons with a wavelength of 2.1 Å
21. A 6.023×10^{23} photons are found to have an energy of 225 kJ. What is the wavelength of the radiation?
22. Use the data in Table 2.1.1 to calculate how much more energetic a single gamma-ray photon is than a radio-wave photon. How many photons from a radio source operating at a frequency of 8×10^5 Hz would be required to provide the same amount of energy as a single gamma-ray photon with a frequency of 3×10^{19} Hz?
23. Use the data in Table 2.1.1 to calculate how much more energetic a single x-ray photon is than a photon of ultraviolet light.
24. A radio station has a transmitter that broadcasts at a frequency of 100.7 MHz with a power output of 50 kW. Given that 1 W = 1 J/s, how many photons are emitted by the transmitter each second?

1.E.2.4 NUMERICAL ANSWERS

19.
    1. 4.59×10^{-31} J/photon, radio
    2. 3.1×10^{-15} J/photon, gamma ray
    3. 2.53×10^{-16} J/photon, gamma ray
20.
21. 532 nm

1.E.3 LINE SPECTRA AND THE BOHR MODEL

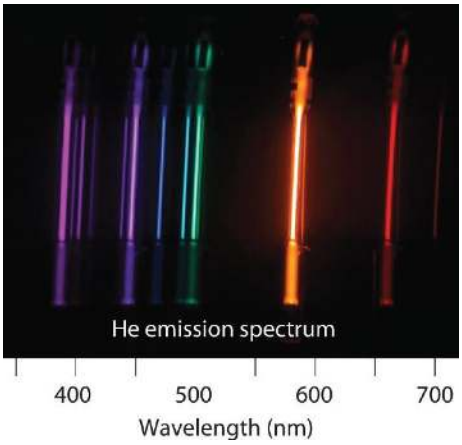
1.E.3.1 CONCEPTUAL PROBLEMS

25. Is the spectrum of the light emitted by isolated atoms of an element discrete or continuous? How do these spectra differ from those obtained by heating a bulk sample of a solid element? Explain your answers.

26. Explain why each element has a characteristic emission and absorption spectra. If spectral emissions had been found to be continuous rather than discrete, what would have been the implications for Bohr's model of the atom?
27. Explain the differences between a ground state and an excited state. Describe what happens in the spectrum of a species when an electron moves from a ground state to an excited state. What happens in the spectrum when the electron falls from an excited state to a ground state?
28. What phenomenon causes a neon sign to have a characteristic color? If the emission spectrum of an element is constant, why do some neon signs have more than one color?
29. How is light from a laser different from the light emitted by a light source such as a light bulb? Describe how a laser produces light.

1.E.3.2 NUMERICAL PROBLEMS

30. Using a Bohr model and the transition from $n = 2$ to $n = 3$ in an atom with a single electron, describe the mathematical relationship between an emission spectrum and an absorption spectrum. What is the energy of this transition? What does the sign of the energy value represent in this case? What range of light is associated with this transition?
31. If a hydrogen atom is excited from an $n = 1$ state to an $n = 3$ state, how much energy does this correspond to? Is this an absorption or an emission? What is the wavelength of the photon involved in this process? To what region of the electromagnetic spectrum does this correspond?
32. The hydrogen atom emits a photon with a 486 nm wavelength, corresponding to an electron decaying from the $n = 4$ level to which level? What is the color of the emission?
33. An electron in a hydrogen atom can decay from the $n = 3$ level to $n = 2$ level. What is the color of the emitted light? What is the energy of this transition?
34. Calculate the wavelength and energy of the photon that gives rise to the third line in order of increasing energy in the Lyman series in the emission spectrum of hydrogen. In what region of the spectrum does this wavelength occur? Describe qualitatively what the absorption spectrum looks like.
35. The wavelength of one of the lines in the Lyman series of hydrogen is 121 nm. In what region of the spectrum does this occur? To which electronic transition does this correspond?
36. The emission spectrum of helium is shown. Estimate what change in energy (ΔE) gives rise to each line?



37. Removing an electron from solid potassium requires 222 kJ/mol. Would you expect to observe a photoelectric effect for potassium using a photon of blue light ($\lambda = 485$ nm)? What is the longest wavelength of energy capable of ejecting an electron from potassium? What is the corresponding color of light of this wavelength?
38. The binding energy of an electron is the energy needed to remove an electron from its lowest energy state. According to Bohr's postulates, calculate the binding energy of an electron in a hydrogen atom. There are 6.02×10^{23} atoms in 1g of hydrogen atoms What wavelength in nanometers is required to remove such an electron from one hydrogen atom?
39. As a radio astronomer, you have observed spectral lines for hydrogen corresponding to a state with $n = 320$, and you would like to produce these lines in the laboratory. Is this feasible? Why or why not?

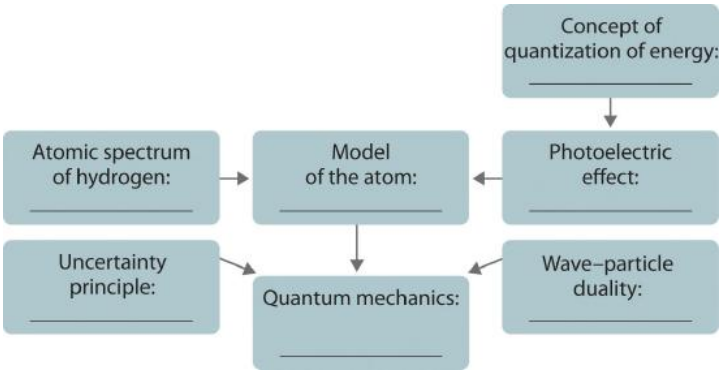
1.E.3.3 NUMERICAL ANSWERS

30. 656 nm; red light
31.
32. $n = 2$, blue-green light
33.
34. 97.2 nm, 2.04×10^{-18} J/photon, ultraviolet light, absorption spectrum is a single dark line at a wavelength of 97.2 nm
35.
36. Violet: 390 nm, 307 kJ/mol photons; Blue-purple: 440 nm, 272 kJ/mol photons; Blue-green: 500 nm, 239 kJ/mol photons; Orange: 580 nm, 206 kJ/mol photons; Red: 650 nm, 184 kJ/mol photons
37.
38. 1313 kJ/mol, $\lambda \leq 91.1$ nm

1.E.4 THE WAVE BEHAVIOR OF MATTER

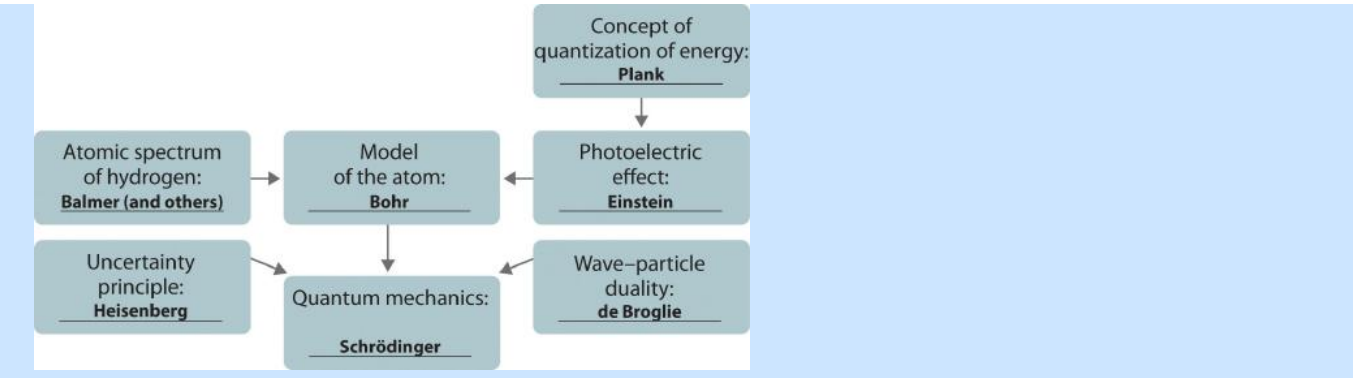
1.E.4.1 CONCEPTUAL PROBLEMS

40. Explain what is meant by each term and illustrate with a sketch:
    1. standing wave
    2. fundamental
    3. overtone
    4. node
41. How does Einstein's theory of relativity illustrate the wave–particle duality of light? What properties of light can be explained by a wave model? What properties can be explained by a particle model?
42. In the modern theory of the electronic structure of the atom, which of de Broglie's ideas have been retained? Which proved to be incorrect?
43. According to Bohr, what is the relationship between an atomic orbit and the energy of an electron in that orbit? Is Bohr's model of the atom consistent with Heisenberg's uncertainty principle? Explain your answer.
44. The development of ideas frequently builds on the work of predecessors. Complete the following chart by filling in the names of those responsible for each theory shown.



1.E.4.2 CONCEPTUAL ANSWER

40.
41.
42.
43.
44.



1.E.4.3 NUMERICAL PROBLEMS

45. How much heat is generated by shining a carbon dioxide laser with a wavelength of 1.065 μm on a 68.95 kg sample of water if 1.000 mol of photons is absorbed and converted to heat? Is this enough heat to raise the temperature of the water by 4°C?
46. Show the mathematical relationship between energy and mass and between wavelength and mass. What is the effect of doubling the
    1. mass of an object on its energy?
    2. mass of an object on its wavelength?
    3. frequency on its mass?
47. What is the de Broglie wavelength of a 39 g bullet traveling at 1020 m/s ± 10 m/s? What is the minimum uncertainty in the bullet's position?
48. What is the de Broglie wavelength of a 6800 tn aircraft carrier traveling at 18 ± 0.1 knots (1 knot = 1.15 mi/h)? What is the minimum uncertainty in its position?
49. Calculate the mass of a particle if it is traveling at 2.2×10^6 m/s and has a frequency of 6.67×10^7 Hz. If the uncertainty in the velocity is known to be 0.1%, what is the minimum uncertainty in the position of the particle?
50. Determine the wavelength of a 2800 lb automobile traveling at 80 mi/h ± 3%. How does this compare with the diameter of the nucleus of an atom? You are standing 3 in. from the edge of the highway. What is the minimum uncertainty in the position of the automobile in inches?

1.E.4.4 NUMERICAL ANSWERS

45. E = 112.3 kJ, ΔT = 0.3893°C, over ten times more light is needed for a 4.0°C increase in temperature
46.
47. 1.7×10^{-35} m, uncertainty in position is $\geq 1.4 \times 10^{-34}$ m
48.
49. 9.1×10^{-39} kg, uncertainty in position ≥ 2.6 m

1.E.5 QUANTUM MECHANICS AND ATOMIC ORBITALS

1.E.5.1 CONCEPTUAL PROBLEMS

51. Why does an electron in an orbital with n = 1 in a hydrogen atom have lower energy than a free electron ($n = \infty$)?
52. What four variables are required to fully describe the position of any object in space? In quantum mechanics, one of these variables is not explicitly considered. Which one and why?
53. Chemists generally refer to the square of the wave function rather than to the wave function itself. Why?
54. Orbital energies of species with only one electron are defined by only one quantum number. Which one? In such a species, is the energy of an orbital with n = 2 greater than, less than, or equal to the energy of an orbital with n = 4? Justify your answer.
55. In each pair of subshells for a hydrogen atom, which has the higher energy? Give the principal and the azimuthal quantum number for each pair.
    1. 1*s*, 2*p*
    2. 2*p*, 2*s*
    3. 2*s*, 3*s*

4. 3*d*, 4*s*

56. What is the relationship between the energy of an orbital and its average radius? If an electron made a transition from an orbital with an average radius of 846.4 pm to an orbital with an average radius of 476.1 pm, would an emission spectrum or an absorption spectrum be produced? Why?
57. In making a transition from an orbital with a principal quantum number of 4 to an orbital with a principal quantum number of 7, does the electron of a hydrogen atom emit or absorb a photon of energy? What would be the energy of the photon? To what region of the electromagnetic spectrum does this energy correspond?
58. What quantum number defines each of the following?
    1. the overall shape of an orbital
    2. the orientation of an electron with respect to a magnetic field
    3. the orientation of an orbital in space
    4. the average energy and distance of an electron from the nucleus
59. In an attempt to explain the properties of the elements, Niels Bohr initially proposed electronic structures for several elements with orbits holding a certain number of electrons, some of which are in the following table:

Element	Number of Electrons	Electrons in orbits with n =
		4 3 2 1
H	1	1
He	2	2
Ne	10	8 2
Ar	18	8 8 2
Li	3	1 2
Na	11	1 8 2
K	19	1 8 8 2
Be	4	2 2

    a. Draw the electron configuration of each atom based only on the information given in the table. What are the differences between Bohr's initially proposed structures and those accepted today?
    b. Using Bohr's model, what are the implications for the reactivity of each element?
    c. Give the actual electron configuration of each element in the table.

1.E.5.2 NUMERICAL PROBLEMS

60. How many subshells are possible for $n = 3$? What are they?
61. How many subshells are possible for $n = 5$? What are they?
62. What value of l corresponds to a *d* subshell? How many orbitals are in this subshell?
63. What value of l corresponds to an *f* subshell? How many orbitals are in this subshell?
64. State the number of orbitals and electrons that can occupy each subshell.
    1. 2*s*
    2. 3*p*
    3. 4*d*
    4. 6*f*
65. State the number of orbitals and electrons that can occupy each subshell.
    1. 1*s*
    2. 4*p*
    3. 5*d*
    4. 4*f*
66. How many orbitals and subshells are found within the principal shell $n = 6$? How do these orbital energies compare with those for $n = 4$?
67. How many nodes would you expect a 4*p* orbital to have? A 5*s* orbital?

68. A *p* orbital is found to have one node in addition to the nodal plane that bisects the lobes. What would you predict to be the value of *n*? If an *s* orbital has two nodes, what is the value of *n*?

1.E.5.3 NUMERICAL ANSWERS

60. Three subshells, with $l = 0$ (*s*), $l = 1$ (*p*), and $l = 2$ (*d*).
61.
62. A *d* subshell has $l = 2$ and contains 5 orbitals.
63.
64.
    1. 2 electrons; 1 orbital
    2. 6 electrons; 3 orbitals
    3. 10 electrons; 5 orbitals
    4. 14 electrons; 7 orbitals
65.
66. A principal shell with $n = 6$ contains six subshells, with $l = 0$, 1, 2, 3, 4, and 5, respectively. These subshells contain 1, 3, 5, 7, 9, and 11 orbitals, respectively, for a total of 36 orbitals. The energies of the orbitals with $n = 6$ are higher than those of the corresponding orbitals with the same value of l for $n = 4$.

1.E.6 REPRESENTATION OF ORBITALS

1.E.7 MANY-ELECTRON ATOMS

1.E.7.1 CONCEPTUAL PROBLEMS

69. A set of four quantum numbers specifies each wave function. What information is given by each quantum number? What does the specified wave function describe?
70. List two pieces of evidence to support the statement that electrons have a spin.
71. The periodic table is divided into blocks. Identify each block and explain the principle behind the divisions. Which quantum number distinguishes the horizontal rows?
72. Identify the element with each ground state electron configuration.
    1. $[He]2s^2 2p^3$
    2. $[Ar]4s^2 3d^1$
    3. $[Kr]5s^2 4d^{10} 5p^3$
    4. $[Xe]6s^2 4f^6$
73. Identify the element with each ground state electron configuration.
    1. $[He]2s^2 2p^1$
    2. $[Ar]4s^2 3d^8$
    3. $[Kr]5s^2 4d^{10} 5p^4$
    4. $[Xe]6s^2$
74. Propose an explanation as to why the noble gases are inert.

1.E.7.2 NUMERICAL PROBLEMS

75. How many magnetic quantum numbers are possible for a 4*p* subshell? A 3*d* subshell? How many orbitals are in these subshells?
76. How many magnetic quantum numbers are possible for a 6*s* subshell? A 4*f* subshell? How many orbitals does each subshell contain?
77. If $l = 2$ and $m_l = 2$, give all the allowed combinations of the four quantum numbers (n, l, m_l, m_s) for electrons in the corresponding 3*d* subshell.
78. Give all the allowed combinations of the four quantum numbers (n, l, m_l, m_s) for electrons in a 4*d* subshell. How many electrons can the 4*d* orbital accommodate? How would this differ from a situation in which there were only three quantum numbers (n, l, m)?
79. Given the following sets of quantum numbers (n, l, m_l, m_s), identify each principal shell and subshell.
    1. 1, 0, 0, ½
    2. 2, 1, 0, ½

3. 3, 2, 0, ½
4. 4, 3, 3, ½

80. Is each set of quantum numbers allowed? Explain your answers.
    1. $n = 2$; $l = 1$; $m_l = 2$; $m_s = +½$
    2. $n = 3$, $l = 0$; $m_l = −1$; $m_s = −½$
    3. $n = 2$; $l = 2$; $m_l = 1$; $m_s = +½$
    4. $n = 3$; $l = 2$; $m_l = 2$; $m_s = +½$
81. List the set of quantum numbers for each electron in the valence shell of each element.
    1. beryllium
    2. xenon
    3. lithium
    4. fluorine
82. List the set of quantum numbers for each electron in the valence shell of each element.
    1. carbon
    2. magnesium
    3. bromine
    4. sulfur
83. Sketch the shape of the periodic table if there were three possible values of m_s for each electron (+½, −½, and 0); assume that the Pauli principle is still valid.
84. Predict the shape of the periodic table if eight electrons could occupy the *p* subshell.
85. If the electron could only have spin +½, what would the periodic table look like?
86. If three electrons could occupy each *s* orbital, what would be the electron configuration of each species?
    1. sodium
    2. titanium
    3. fluorine
    4. calcium
87. If Hund's rule were not followed and maximum pairing occurred, how many unpaired electrons would each species have? How do these numbers compare with the number found using Hund's rule?
    1. phosphorus
    2. iodine
    3. manganese
88. Write the electron configuration for each element in the ground state.
    1. aluminum
    2. calcium
    3. sulfur
    4. tin
    5. nickel
    6. tungsten
    7. neodymium
    8. americium
89. Write the electron configuration for each element in the ground state.
    1. boron
    2. rubidium
    3. bromine
    4. germanium
    5. vanadium
    6. palladium
    7. bismuth
    8. europium

90. Give the complete electron configuration for each element.
    1. magnesium
    2. potassium
    3. titanium
    4. selenium
    5. iodine
    6. uranium
    7. germanium

91. Give the complete electron configuration for each element.
    1. tin
    2. copper
    3. fluorine
    4. hydrogen
    5. thorium
    6. yttrium
    7. bismuth

92. Write the valence electron configuration for each element:
    1. samarium
    2. praseodymium
    3. boron
    4. cobalt

93. Using the Pauli exclusion principle and Hund's rule, draw valence orbital diagrams for each element.
    1. barium
    2. neodymium
    3. iodine

94. Using the Pauli exclusion principle and Hund's rule, draw valence orbital diagrams for each element.
    1. chlorine
    2. silicon
    3. scandium

95. How many unpaired electrons does each species contain?
    1. lead
    2. cesium
    3. copper
    4. silicon
    5. selenium

96. How many unpaired electrons does each species contain?
    1. helium
    2. oxygen
    3. bismuth
    4. silver
    5. boron

97. For each element, give the complete electron configuration, draw the valence electron configuration, and give the number of unpaired electrons present.
    1. lithium
    2. magnesium
    3. silicon
    4. cesium
    5. lead

98. Use an orbital diagram to illustrate the aufbau principle, the Pauli exclusion principle, and Hund's rule for each element.

1. carbon
2. sulfur

1.E.7.3 NUMERICAL ANSWERS

75. For a 4*p* subshell, $n = 4$ and $l = 1$. The allowed values of the magnetic quantum number, m_l, are therefore +1, 0, −1, corresponding to three 4*p* orbitals. For a 3*d* subshell, $n = 3$ and $l = 2$. The allowed values of the magnetic quantum number, m_l, are therefore +2, +1, 0, −1, −2, corresponding to five 3*d* orbitals.

1.E.8 ELECTRON CONFIGURATIONS

1.E.9 ELECTRON CONFIGURATIONS AND THE PERIODIC TABLE

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1.S: ELECTRONIC STRUCTURE OF ATOMS (SUMMARY)

Understanding the electronic structure of atoms requires an understanding of the properties of waves and electromagnetic radiation. A basic knowledge of the electronic structure of atoms requires an understanding of the properties of waves and electromagnetic radiation. A wave is a periodic oscillation by which energy is transmitted through space. All waves are periodic, repeating regularly in both space and time. Waves are characterized by several interrelated properties.

- **Electronic structure**: arrangement of electrons in atoms
- **Electromagnetic radiation**: aka **radiant energy**; form of energy that has wave characteristics and carries energy through space. *All types of electromagnetic radiation move through a vacuum at a speed of 3.00 X 10^8 m/s (speed of light).*
- **Wavelength**: the distance between identical points on successive waves
- **Frequency**: the number of complete wavelengths that pass a given point in 1s

$$\nu\lambda = c$$

where ν = frequency, λ= wavelength, and c = speed of light

Wavelength is expressed in units of length.

- **Electromagnetic spectrum**: various types of electromagnetic radiations arranged in order of increasing wavelength.

Frequency is expressed in Hertz (Hz), also denoted by s^{-1} or /s

Quantum Effects and Photons

- **Quantum**: smallest quantity of energy that can be emitted or absorbed as electromagnetic radiation

$$E = h\nu$$

where E = energy, h = Planck's constant, ν = frequency

Planck's constant = 6.63 X 10^{-34} J•s

According to Planck's theory, energy is always emitted or absorbed in whole-number multiples of *hv*, for example, *hv*, *2hv*, *3hv*, and so forth. We say that the allowed energies are *quantized* (that is, their values are restricted to certain quantities).

1.S.1 6.2: QUANTIZED ENERGY AND PHOTONS

Blackbody radiation is the radiation emitted by hot objects and could not be explained with classical physics. Max Planck postulated that energy was quantized and may be emitted or absorbed only in integral multiples of a small unit of energy, known as a quantum. The energy of a quantum is proportional to the frequency of the radiation; the proportionality constant h is a fundamental constant (Planck's constant). Albert Einstein used the quantization of energy to explain the photoelectric effect

- The photoelectric effect: when photons of sufficiently high energy strike a metal surface, electrons are emitted from the metal. The emitted electrons are drawn toward the other electrode, which is a positive terminal. As a result, current flows in a circuit.
- **Photon***:* smallest increment (a *quantum*) of radiant energy; a photon of light with frequency v has an energy equal to *hv*.
- When a photon strikes the metal, its energy is transferred to an electron in the metal. A certain amount of energy is required for the electron to overcome the attractive forces that hold it within the metal. If the photons have less energy that this energy threshold, the electrons cannot escape from the metal surface. If a photon has sufficient energy, an electron is emitted. If the photon has more energy than necessary, the excess appears as kinetic energy of the emitted electron.

1.S.2 6.3: LINE SPECTRA AND THE BOHR MODEL

There is an intimate connection between the atomic structure of an atom and its spectral characteristics. Most light is polychromatic and contains light of many wavelengths. Light that has only a single wavelength is monochromatic and is produced by devices called lasers, which use transitions between two atomic energy levels to produce light in a very narrow range of wavelengths. Atoms can also absorb light of certain energies, resulting in a transition from the ground state or a lower-energy e

Line Spectra

Radiation composed of a single wavelength is said to be *monochromatic*.

- **Spectrum**: distribution among various wavelengths of the radiant energy emitted or absorbed by an object
- **Continuous spectrum**: rainbow of colors, containing light of all wavelengths. *Not all radiation sources produce a continuous spectrum*
- **Line spectrum**: spectrum containing radiation of only specific wavelengths

Bohr's Model

Electrons in a permitted orbit have a specific energy and are said to be in an "allowed" energy state. An electron in an allowed energy state will not radiate energy and therefore will not spiral into the nucleus.

$$E_n = -R_H \frac{1}{n^2}$$

- R_H = Rydberg constant: 2.18 X 10^{-18} J
- n = principal quantum number, corresponds to the different allowed orbits for the electron

All energies given by this equation will be negative. The lower (more negative) the energy is, the more stable the atom is. The lowest energy state is that for which n=1.

- **Ground state:** lowest energy state of an atom, n=1
- **Excited state:** when the electron is in higher energy orbit (less negative), n=2 or higher

If n becomes infinitely large (∞), the electron is completely separated from the nucleus:

$$E_\infty = (-2.18 \times 10^{-18} J)\left(\frac{1}{\infty^2}\right) = 0$$

Thus, the state in which the electron is removed from the nucleus is the reference, or zero-energy, state of the hydrogen atom. It is important to remember that this zero-energy state is higher in energy than the states with negative energies

Electrons can change from one energy state to another by absorbing or emitting radiant energy. Radiant energy must be absorbed for an electron to move to a higher energy state, but is emitted when the electron moves to a lower energy state. .

$$\Delta E = E_f - E_i$$

- If $n_f > n_i$, then ΔE is positive, radiant energy is absorbed
- If $n_f < n_i$, then ΔE is negative, radiant energy is emitted

1.S.3 6.4: THE WAVE BEHAVIOR OF MATTER

An electron possesses both particle and wave properties. Louis de Broglie showed that the wavelength of a particle is equal to Planck's constant divided by the mass times the velocity of the particle. The electron in Bohr's circular orbits could thus be described as a standing wave, one that does not move through space. Werner Heisenberg's uncertainty principle states that it is impossible to precisely describe both the location and the speed of particles that exhibit wavelike behavior.

- **Momentum**: the product of the mass, *m*, and the velocity, *v*, of a particle
- **Matter waves**: term used to describe the wave characteristics of a particle

$$\lambda = h/mv$$

λ = wavelength, h = Planck's constant, m = mass, v = velocity

The Uncertainty Principle

- **Uncertainty principle**: theory first put forth by Heisenberg, states that is it impossible to determine both the exact momentum of the electron and its exact location.

1.S.4 6.5: QUANTUM MECHANICS AND ATOMIC ORBITALS

There is a relationship between the motions of electrons in atoms and molecules and their energies that is described by quantum mechanics. Because of wave–particle duality, scientists must deal with the probability of an electron being at a particular point in space. To do so required the development of quantum mechanics, which uses wavefunctions to describe the mathematical relationship between the motion of electrons in atoms and molecules and their energies.

- **Wave functions**: represented by ψ, square of wave function, ψ^2, provides information about an electron's location when it is in an allowed energy state.
- **Probability density**: represented by ψ^2, value that represents the probability that an electron will be found at a given point in space
- **Electron density**: the probability of finding and electron at any particular point in an atom. Equals ψ^2.

Orbitals and Quantum Numbers

-Orbital: allowed energy state of an electron in the quantum-mechanical model of the atom; also used to describe the spatial distribution of an electron. Defined by the value of 3 quantum numbers; *n, l, and* m_l.

value of 3 quantum numbers; n, l, and ml.

Value of l	0	1	2	3
Letter used	s	p	d	f

1. The principal quantum number, *n*, can have integral values of 1, 2, 3 and so forth. As *n* increases, the orbital becomes larger; the electron has a higher energy and is farther away from the nucleus.
2. The second quantum number, *l*, can have integral values from 0 to *n* – 1 for each value of *n*. This quantum number defines the shape of the orbital. Generally designated by the letters *s*, *p*, *d*, and *f*. These correspond to values ranging from 0 to 3.
3. The magnetic quantum number, m_l, can have integral values between *l* and –*l*, including zero. This quantum number describes the orientation of the orbital in space.

Electron shell: collection of orbitals with the same value of *n*

Subshell: one or more orbitals with the same set of *n* and *l* values

1. Each shell is divided into the number of subshells equal to the principal quantum number, *n*, for that shell. The first shell consists of only the 1s subshell; the second shell consists of two subshells, 2s and 2p; the third of three subshell, 3s, 3p and 3d, and so forth.
2. Each subshell is divided into orbitals. Each *s* subshell consists of one orbital; each *p* subshell of three orbitals, each *d* subshell of five, and each *f* subshell of seven orbitals.

1.S.5 6.6: 3D REPRESENTATION OF ORBITALS

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

The s Orbitals: 1s orbital: most stable, spherically symmetric, figure indicates that the probability decreases as we move away from the nucleus. ALL *s* ORBITALS ARE SPHERICALLY SYMMETRIC.

- **Nodal surfaces (nodes)**: intermediate regions where ψ^2 goes to zero. The number of nodes increases with increasing value for the principal quantum number, *n*.

The *p* Orbitals: Electron density is concentrated on two sides of the nucleus, separated by a node at the nucleus. The orbitals of a given subshell have the same size and shape but differ from each other in orientation. The axis along which the orbital is oriented is not related to m_l.

1.S.6 6.7: MANY-ELECTRON ATOMS

In addition to the three quantum numbers (n, l, ml) dictated by quantum mechanics, a fourth quantum number is required to explain certain properties of atoms. This is the electron spin quantum number (ms), which can have values of +½ or −½ for any electron, corresponding to the two possible orientations of an electron in a magnetic field. This is important for chemistry because the Pauli exclusion principle implies that no orbital can contain more than two electrons (with opposite spin).

Although the shapes of the orbitals for many-electron atoms are the same as those for hydrogen, the presence of more than one electron greatly changes the energies of the orbitals. In hydrogen, the energy of an orbital depends only on its principal quantum number, however, in many-electron atoms, electron-electron repulsions cause different subshells to be at different energies

Effective Nuclear Charge

- *Effective nuclear charge*: net positive charge attracting electrons

$$Z_{eff} = Z–S$$

- Z_{eff} = effective nuclear charge
- Z = number of protons in the nucleus
- S = average number of electrons between the nucleus and electron in question
- *Screening effect*: effect of inner electrons in decreasing the nuclear charge experienced by outer electrons

Energies of Orbitals

The extent to which an electron will be screened by the other electrons depends on its electron distribution as we move outward from the nucleus.

- *In a many-electron atom, for a given value of n, Z_{eff} decreases with increasing value of l.*

- *In a many-electron atom, for a given value of n, the energy of an orbital increases with increasing value of l.*

Degenerate: orbitals that have the same energy

Electron Spin and the Pauli Exclusion Principle

- **Electron spin**: property of the electron that makes it behave as though it were a tiny magnet. The electron behaves as if it were spinning on its axis; electron spin is quantized.
- **Electron spin quantum number**: denoted as m_s. It can only have two possible values, +½ and –½, which we can interpret as indicating the two opposite directions in which the electron can spin.
- **Pauli exclusion principle**: states that no two electrons in an atom can have the same set of four quantum numbers n, l, m_l, m_s. This means that if we wish to put two electrons in an orbital and satisfy Pauli's exclusion principle, our only choice is to assign different m_s values to the electrons. Because there are only two values, *we can conclude that an electron can hold a maximum of two electrons and they must have opposite spins*.

1.S.7 6.8: ELECTRON CONFIGURATIONS

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

- **Electron configuration**: the way in which the electrons are distributed among the various orbitals. The most stable, or ground, electron configuration of an atom is that in which the electrons are in the lowest possible energy level
- **Orbital diagram**: representation of electron configuration in which each orbital is represented by a box and each electron by a half-arrow. A half-arrow pointing upward represents an electron with positive spin; one pointing downward represents an electron with a negative spin.

Writing Electron Configurations

- **Hund's rule**: rule stating that electrons occupy degenerate orbitals in such a way as to maximize the number of electrons with the same spin. In other words, each orbital has one electron placed in it before paring of electron in orbitals occurs. Note that this rule applies to orbitals that are *degenerate*, which means that they have the same energy.
- **Valence electrons**: electrons in the outer shells
- **Core electrons**: electrons in the inner shells
- **Transition elements**: aka **Transition metals**; elements of the *d* orbitals
- **Lanthanide elements**: aka **Rare-earth elements**; 14 elements of the 4f orbitals, # 58-71
- **Actinide elements**: 14 elements of 5f orbitals, # 90-103. Most are not found in nature.

1.S.8 6.9: ELECTRON CONFIGURATIONS AND THE PERIODIC TABLE

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

- **Main group elements**: aka **Representatives**; *s* and *p* block elements
- **F-block metals**: 28 elements located below the table, *f* block elements

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CHAPTER OVERVIEW

2: PERIODIC PROPERTIES OF THE ELEMENTS

A general chemistry Libretexts Textmap organized around the textbook

Chemistry: The Central Science

by Brown, LeMay, Bursten, Murphy, and Woodward

Template:HideTOC

Last chapter, we presented the contemporary quantum mechanical model of the atom. In using this model to describe the electronic structures of the elements in order of increasing atomic number, we saw that periodic similarities in electron configuration correlate with periodic similarities in properties, which is the basis for the structure of the periodic table. For example, the noble gases have what is often called filled or closed-shell valence electron configurations. These closed shells are actually filled *s* and *p* subshells with a total of eight electrons, which are called *octets*; helium is an exception, with a closed 1*s* shell that has only two electrons. Because of their filled valence shells, the noble gases are generally unreactive. In contrast, the alkali metals have a single valence electron outside a closed shell and readily lose this electron to elements that require electrons to achieve an octet, such as the halogens. Thus because of their periodic similarities in electron configuration, atoms in the same column of the periodic table tend to form compounds with the same oxidation states and stoichiometries. Last chapter ended with the observation that, because all the elements in a column have the same valence electron configuration, the periodic table can be used to find the electron configuration of most of the elements at a glance.

In this chapter, we explore the relationship between the electron configurations of the elements, as reflected in their arrangement in the periodic table, and their physical and chemical properties. In particular, we focus on the similarities between elements in the same column and on the trends in properties that are observed across horizontal rows or down vertical columns. By the end of this chapter, your understanding of these trends and relationships will provide you with clues as to why argon is used in incandescent light bulbs, why coal and wood burst into flames when they come in contact with pure F_2, why aluminum was discovered so late despite being the third most abundant element in Earth's crust, and why lithium is commonly used in batteries. We begin by expanding on the brief discussion of the history of the periodic table and describing how it was created many years before electrons had even been discovered, much less discussed in terms of shells, subshells, orbitals, and electron spin.

2.1: Development of the Periodic Table

2.2: Shielding and Effective Nuclear Charge

2.3: Sizes of Atoms and Ions

2.4: Ionization Energy

2.5: Electron Affinities

2.E: Periodic Properties of the Elements (Exercises)

2.S: Periodic Properties of the Elements (Summary)

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2.1: DEVELOPMENT OF THE PERIODIC TABLE

LEARNING OBJECTIVES

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

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

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

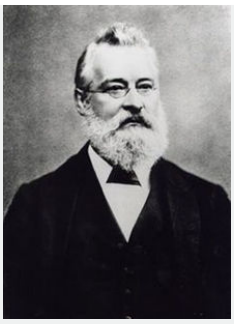
NOTE. Where two elements happen to have the same equivalent, both are designated by the same number.

Figure **2.1.1**: The Arrangement of the Elements into Octaves as Proposed by Newlands. The table shown here accompanied a letter from a 27-year-old Newlands to the editor of the journal *Chemical News* in which he wrote: "If the elements are arranged in the order of their equivalents, with a few slight transpositions, as in the accompanying table, it will be observed that elements belonging to the same group usually appear on the same horizontal line. It will also be seen that the numbers of analogous elements generally differ either by 7 or by some multiple of seven; in other words, members of the same group stand to each other in the same relation as the extremities of one or more octaves in music. Thus, in the nitrogen group, between nitrogen and phosphorus there are 7 elements; between phosphorus and arsenic, 14; between arsenic and antimony, 14; and lastly, between antimony and bismuth, 14 also. This peculiar relationship I propose to provisionally term the *Law of Octaves*. I am, &c. John A. R. Newlands, F.C.S. Laboratory, 19, Great St. Helen's, E.C., August 8, 1865."

By the mid-19th century, the atomic masses of many of the elements had been determined. The English chemist John Newlands (1838–1898), hypothesizing that the chemistry of the elements might be related to their masses, arranged the known elements in order of increasing atomic mass and discovered that every seventh element had similar properties (Figure **2.1.1**). Newlands therefore suggested that the elements could be classified into octaves. He described octaves as a group of seven elements which correspond to the horizontal rows in the main groups of today's periodic table. There were seven elements because the noble gases were not known at the time. Unfortunately, Newlands's "law of octaves" did not seem to work for elements heavier than calcium, and his idea was publicly ridiculed. At one scientific meeting, Newlands was asked why he didn't arrange the elements in alphabetical order instead of by atomic mass, since that would make just as much sense! Actually, Newlands was on the right track—with only a few exceptions, atomic mass does increase with atomic number, and similar properties occur every time a set of ns^2np^6 subshells is filled. Despite the fact that Newlands's table had no logical place for the *d*-block elements, he was honored for his idea by the Royal Society of London in 1887.

JOHN NEWLANDS (1838–1898)

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



The periodic table achieved its modern form through the work of the German chemist Julius Lothar Meyer (1830–1895) and the Russian chemist Dimitri Mendeleev (1834–1907), both of whom focused on the relationships between atomic mass and various physical and chemical properties. In 1869, they independently proposed essentially identical arrangements of the elements. Meyer aligned the elements in his table according to periodic variations in simple atomic properties, such as "atomic volume" (Figure **2.1.2**), which he obtained by dividing the atomic mass (molar mass) in grams per mole by the density (ρ) of the element in grams per cubic centimeter. This property is equivalent to what is today defined as molar volume, the molar mass of an element divided by its density, (measured in cubic centimeters per mole):

$$\frac{molar\ mass\ \left(g/mol\right)}{density\ \left(g/cm^3\right)} = molar\ volume\ \left(cm^3/mol\right) \tag{2.1.1}$$

As shown in Figure **2.1.2**, the alkali metals have the highest molar volumes of the solid elements. In Meyer's plot of atomic volume versus atomic mass, the nonmetals occur on the rising portion of the graph, and metals occur at the peaks, in the valleys, and on the downslopes.

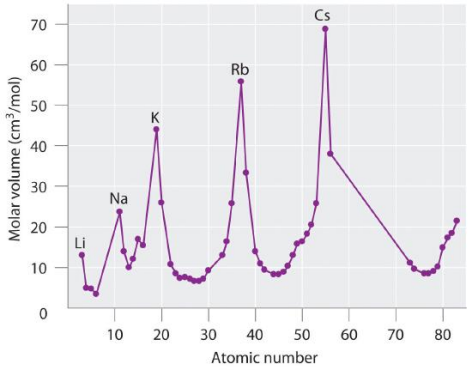
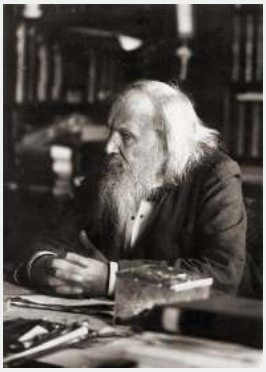


Figure **2.1.2**: Variation of Atomic Volume with Atomic Number, Adapted from Meyer's Plot of 1870. Note the periodic increase and decrease in atomic volume. Because the noble gases had not yet been discovered at the time this graph was formulated, the peaks correspond to the alkali metals (Group 1).

DIMITRI MENDELEEV (1834–1907)

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



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

2.1.1 MENDELEEV'S PERIODIC TABLE

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2.2: SHIELDING AND EFFECTIVE NUCLEAR CHARGE

LEARNING OBJECTIVES

- To understand the basics of electron shielding and penetration

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

2.2.1 ELECTRON SHIELDING AND EFFECTIVE NUCLEAR CHARGE

If an electron is far from the nucleus (i.e., if the distance r between the nucleus and the electron is large), then at any given moment, many of the other electrons will be *between* that electron and the nucleus (Figure **2.2.1**). Hence the electrons will cancel a portion of the positive charge of the nucleus and thereby decrease the attractive interaction between it and the electron farther away. As a result, the electron farther away experiences an effective nuclear charge (Z_{eff}) that is less than the actual nuclear charge Z. This effect is called **electron shielding**.

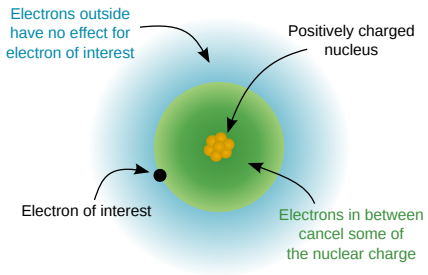


Figure **2.2.1**: This image shows how inner electrons can shield outer electrons from the nuclear charge. (CC BY-SA 3.0; NikNaks via Wikipedia).

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

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

Notice that $Z_{eff} = Z$ only for hydrogen (Figure **2.2.2**).

DEFINITION: SHIELDING

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

Z_{eff} can be calculated by subtracting the magnitude of shielding from the total nuclear charge and the effective nuclear charge of an atom is given by the equation:

$$Z_{eff} = Z - S \tag{2.2.1}$$

where Z is the atomic number (number of protons in nucleus) and S is the shielding constant and is approximated by number of electrons between the nucleus and the electron in question (*the number of nonvalence electrons*). The value of Z_{eff} will provide information on how much of a charge an electron actually experiences.

We can see from Equation 2.2.1 that the effective nuclear charge of an atom increases as the number of protons in an atom increases (Figure **2.2.2**). As we will discuss later on in the chapter, this phenomenon can explain the decrease in atomic radii we see as we go across the

periodic table as electrons are held closer to the nucleus due to increase in number of protons and increase in effective nuclear charge.

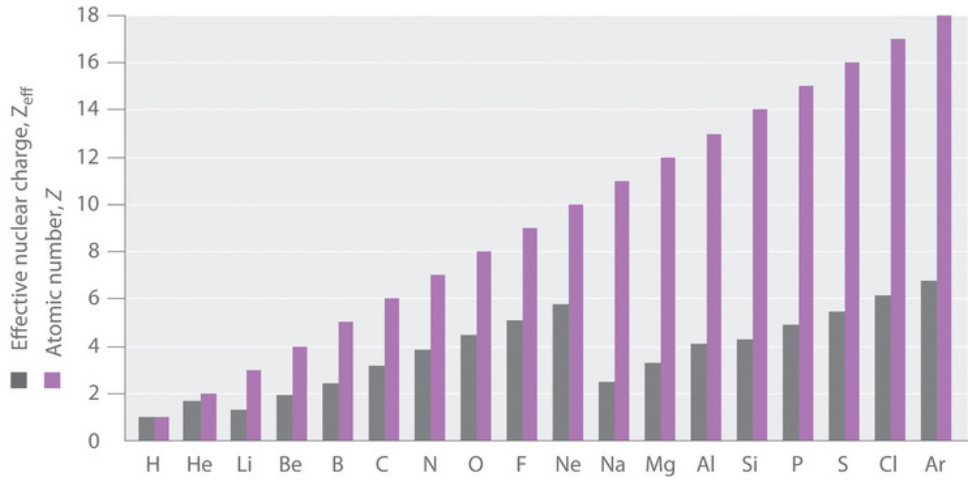


Figure **2.2.2**: Relationship between the Effective Nuclear Charge Z_{eff} and the Atomic Number Z for the Outer Electrons of the Elements of the First Three Rows of the (CC BY-SA-NC 3.0; anonynous)

The shielding constant can be estimated by totaling the screening by **all nonvalence electrons** (n) except the one in question.

$$S = \sum_{i}^{n-1} S_i \tag{2.2.2}$$

where S_i is the shielding of the ith electron.

> *Electrons that are shielded from the full charge of the nucleus experience an effective nuclear charge (Z_{eff}) of the nucleus, which is some degree less than the full nuclear charge an electron would feel in a hydrogen atom or hydrogenlike ion.*

From Equations 2.2.1 and 2.2.2, Z_{eff} for a specific electron can be estimated is the shielding constants for that electron of all other electrons in species is known. A simple approximation is that all other non-valence electrons shield equally and fully:

$$S_i = 1 \tag{2.2.3}$$

This crude approximation is demonstrated in Example **2.2.1**.

✔ EXAMPLE 2.2.1: FLUORINE, NEON, AND SODIUM

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

Solution

Each species has 10 electrons, and the number of nonvalence electrons is 2 (10 total electrons - 8 valence), but the effective nuclear charge varies because each has a different atomic number A. This is an application of Equations 2.2.1 and 2.2.2. We use the simple assumption that all electrons shield equally and fully the valence electrons (Equation 2.2.3).

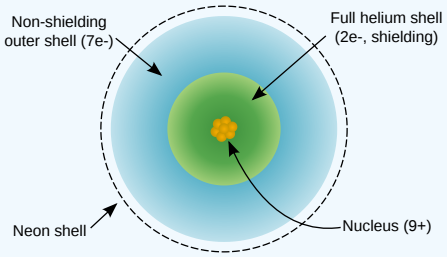


Diagram of a fluorine atom showing the extent of effective nuclear charge. (CC BY-SA 3.0; NikNaks via Wikipedia).

The charge Z of the nucleus of a fluorine atom is 9, but the valence electrons are screened appreciably by the core electrons (four electrons from the 1s and 2s orbitals) and partially by the 7 electrons in the 2p orbitals.

- $Z_{\text{eff}}(\text{F}^-) = 9 - 2 = 7+$
- $Z_{\text{eff}}(\text{Ne}) = 10 - 2 = 8+$
- $Z_{\text{eff}}(\text{Na}^+) = 11 - 2 = 9+$

So the sodium cation has the greatest effective nuclear charge. This also suggests that Na^+ has the smallest radius of these species and that is correct.

? EXERCISE 2.2.1: MAGNESIUM SPECIES

What is the effective attraction Z_{eff} experienced by the valence electrons in the magnesium anion, the neutral magnesium atom, and magnesium cation? Use the simple approximation for shielding constants. Compare your result for the magnesium atom to the more accurate value in Figure 2.2.2 and proposed an origin for the difference.

Answer

- $Z_{\text{eff}}(\text{Mg}^-) = 12 - 10 = 2+$
- $Z_{\text{eff}}(\text{Mg}) = 12 - 10 = 2+$
- $Z_{\text{eff}}(\text{Mg}^+) = 12 - 10 = 2+$

Remember that the simple approximations in Equations 2.2.2 and 2.2.3 suggest that valence electrons **do not shield** other valence electrons. Therefore, each of these species has the same number of non-valence electrons and Equation 2.2.1 suggests the effective charge on each valence electron is identical for each of the three species.

This is not correct and a more complex model is needed to predict the experimental observed Z_{eff} value. The ability of valence electrons to shield other valence electrons or in partial amounts (e.g., $S_i \neq 1$) is in violation of Equations 2.2.2 and 2.2.3. That fact that these approximations are poor is suggested by the experimental Z_{eff} value shown in Figure 2.2.2 for Mg of 3.2+. This is appreciably larger than the +2 estimated above, which means these simple approximations overestimate the total shielding constant S. A more sophisticated model is needed.

2.2.2 ELECTRON PENETRATION

The approximation in Equation 2.2.3 is a good first order description of electron shielding, but the actual Z_{eff} experienced by an electron in a given orbital depends not only on the spatial distribution of the electron in that orbital but also on the distribution of all the other electrons present. This leads to large differences in Z_{eff} for different elements, as shown in Figure 2.2.2 for the elements of the first three rows of the periodic table.

Penetration describes the proximity to which an electron can approach to the nucleus. In a multi-electron system, electron penetration is defined by an electron's relative electron density (probability density) near the nucleus of an atom (Figure 2.2.3). Electrons in different orbitals have different electron densities around the nucleus. In other words, penetration depends on the shell (n) and subshell (l).

For example, a 1s electron (Figure 2.2.3; purple curve) has greater electron density near the nucleus than a 2p electron (Figure 2.2.3; red curve) and has a greater penetration. This related to the shielding constants since the 1s electrons are closer to the nucleus than a 2p electron, hence the 1s screens a 2p electron almost perfectly ($S = 1$. However, the 2s electron has a lower shielding constant ($S < 1$ because it can penetrate close to the nucleus in the small area of electron density within the first spherical node (Figure 2.2.3; green curve). In this way the 2s electron can "avoid" some of the shielding effect of the inner 1s electron.

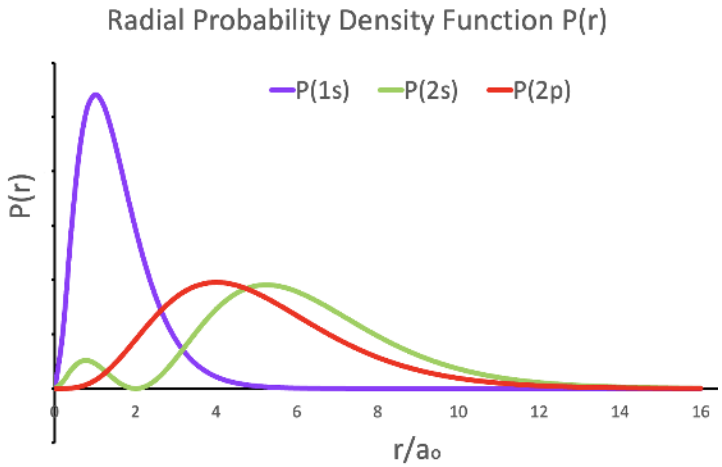


Figure **2.2.3**: Orbital Penetration. A comparison of the radial probability densities of the 2*s* and 2*p* orbitals for various states of the hydrogen atom shows that the 2*s* orbital penetrates inside the 1*s* orbital more than the 2*p* orbital does. Consequently, when an electron is in the small inner lobe of the 2*s* orbital, it experiences a relatively large value of Z_{eff}, which causes the energy of the 2*s* orbital to be lower than the energy of the 2*p* orbital. (Graph; CC BY 4.0 ; Ta-Wei Li)

For the same shell value (n) the penetrating power of an electron follows this trend in subshells (Figure **2.2.3**):

$$s > p > d \approx f. \tag{2.2.4}$$

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

$$1s > 2s > 2p > 3s > 3p > 4s > 3d > 4p > 5s > 4d > 5p > 6s > 4f \ \ldots \tag{2.2.5}$$

DEFINITION: PENETRATION

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

Table **2.2.1**: Effective Nuclear Charges for Selected Atoms

Atom	Sublevel	Z	Z_{eff}
H	1s	1	1
He	1s	2	1.69
Li	1s, 2s	3	2.69, 1.28
Be	1s, 2s	4	3.68, 1.91
B	1s, 2s, 2p	5	4.68, 2.58, 2.42
F	1s, 2s, 2p	9	8.65, 5.13, 5.10
Na	1s, 2s, 2p, 3s	11	10.63, 6.57, 6.80, 2.51

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

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

A BETTER ESTIMATION OF SHIELDING: SLATER RULES

The concepts of electron shielding, orbital penetration and effective nuclear charge were introduced above, but we did so in a qualitative manner (e.g., Equations **2.2.4** and **2.2.5**). A more accurate model for estimating electron shielding and corresponding effective nuclear charge experienced is Slater's Rules. However, the application of these rules is outside the scope of this text.



Z_{eff} and Electron Shielding: Z_{eff} and Electron Shielding(opens in new window) [youtu.be]

2.2.3 SUMMARY

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

2.2.4 IMPORTANT APPLICATIONS: PERIODIC TRENDS DUE TO PENETRATION AND SHIELDING

- **Effective Nuclear Charge (Z_{eff}):** The effective nuclear charge increases from left to right and increases from top to bottom on the periodic table.
- **Atomic Radius:** The atomic radius decreases from left to right, and increases from top to bottom.
- **Ionization Energies:** The ionization energies increase from left to right, and decrease from top to bottom.
- **Electronegativity:** The electronegativity of the elements is highest near flourine. In general, it increases from left to right and decreases from top to bottom.

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2.3: SIZES OF ATOMS AND IONS

LEARNING OBJECTIVES

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

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

2.3.1 ATOMIC RADII

Recall that the probability of finding an electron in the various available orbitals falls off slowly as the distance from the nucleus increases. This point is illustrated in Figure **2.3.1** which shows a plot of total electron density for all occupied orbitals for three noble gases as a function of their distance from the nucleus. Electron density diminishes gradually with increasing distance, which makes it impossible to draw a sharp line marking the boundary of an atom.

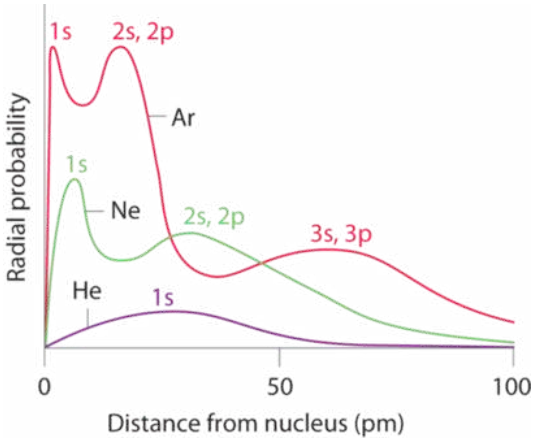


Figure **2.3.1**: Plots of Radial Probability as a Function of Distance from the Nucleus for He, Ne, and Ar. In He, the 1*s* electrons have a maximum radial probability at ≈30 pm from the nucleus. In Ne, the 1*s* electrons have a maximum at ≈8 pm, and the 2*s* and 2*p* electrons combine to form another maximum at ≈35 pm (the $n = 2$ shell). In Ar, the 1*s* electrons have a maximum at ≈2 pm, the 2*s* and 2*p* electrons combine to form a maximum at ≈18 pm, and the 3*s* and 3*p* electrons combine to form a maximum at ≈70 pm.

Figure **2.3.1** also shows that there are distinct peaks in the total electron density at particular distances and that these peaks occur at different distances from the nucleus for each element. Each peak in a given plot corresponds to the electron density in a given principal shell. Because helium has only one filled shell ($n = 1$), it shows only a single peak. In contrast, neon, with filled $n = 1$ and 2 principal shells, has two peaks. Argon, with filled $n = 1$, 2, and 3 principal shells, has three peaks. The peak for the filled $n = 1$ shell occurs at successively shorter distances for neon ($Z = 10$) and argon ($Z = 18$) because, with a greater number of protons, their nuclei are more positively charged than that of helium. Because the $1s^2$ shell is closest to the nucleus, its electrons are very poorly shielded by electrons in filled shells with larger values of n. Consequently, the two electrons in the $n = 1$ shell experience nearly the full nuclear charge, resulting in a strong electrostatic interaction between the electrons and the nucleus. The energy of the $n = 1$ shell also decreases tremendously (the filled 1*s* orbital becomes more stable) as the nuclear charge increases. For similar reasons, the filled $n = 2$ shell in argon is located closer to the nucleus and has a lower energy than the $n = 2$ shell in neon.

Figure **2.3.1** illustrates the difficulty of measuring the dimensions of an individual atom. Because distances between the nuclei in pairs of covalently bonded atoms can be measured quite precisely, however, chemists use these distances as a basis for describing the approximate sizes of atoms. For example, the internuclear distance in the diatomic Cl_2 molecule is known to be 198 pm. We assign half of this distance to each chlorine atom, giving chlorine a **covalent atomic radius** (r_{cov}), which is half the distance between the nuclei of two like atoms joined by a covalent bond in the same molecule, of 99 pm or 0.99 Å (Figure **2.3.2***a*). Atomic radii are often measured in angstroms (Å), a non-SI unit: $1 \text{ Å} = 1 \times 10^{-10} \text{ m} = 100 \text{ pm}$.

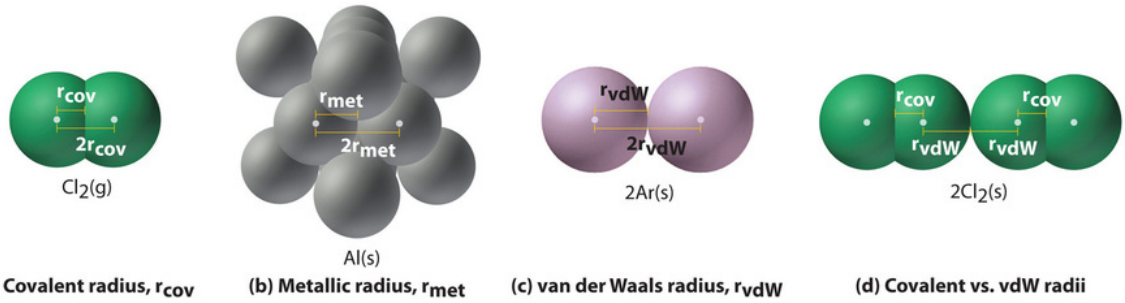


Figure **2.3.2**: Definitions of the Atomic Radius. (a) The covalent atomic radius, r_{cov}, is half the distance between the nuclei of two like atoms joined by a covalent bond in the same molecule, such as Cl_2. (b) The metallic atomic radius, r_{met}, is half the distance between the nuclei of two adjacent atoms in a pure solid metal, such as aluminum. (c) The van der Waals atomic radius, r_{vdW}, is half the distance between the nuclei of two like atoms, such as argon, that are closely packed but not bonded. (d) This is a depiction of covalent versus van der Waals radii of chlorine. The covalent radius of Cl_2 is half the distance between the two chlorine atoms in a single molecule of Cl_2. The van der Waals radius is half the distance between chlorine nuclei in two different but touching Cl_2 molecules. Which do you think is larger? Why?

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

Covalent atomic radii can be determined for most of the nonmetals, but how do chemists obtain atomic radii for elements that do not form covalent bonds? For these elements, a variety of other methods have been developed. With a metal, for example, the **metallic atomic radius** (r_{met}) is defined as half the distance between the nuclei of two adjacent metal atoms in the solid (Figure **2.3.2***b*). For elements such as the noble gases, most of which form no stable compounds, we can use what is called the **van der Waals atomic radius** (r_{vdW}), which is half the internuclear distance between two nonbonded atoms in the solid (Figure **2.3.2***c*). This is somewhat difficult for helium which does not form a solid at any temperature. An atom such as chlorine has both a covalent radius (the distance between the two atoms in a Cl_2 molecule) and a van der Waals radius (the distance between two Cl atoms in different molecules in, for example, $Cl_2(s)$ at low temperatures). These radii are generally not the same (Figure **2.3.2***d*).

2.3.2 PERIODIC TRENDS IN ATOMIC RADII

Because it is impossible to measure the sizes of both metallic and nonmetallic elements using any one method, chemists have developed a self-consistent way of calculating atomic radii using the quantum mechanical functions. Although the radii values obtained by such calculations are not identical to any of the experimentally measured sets of values, they do provide a way to compare the intrinsic sizes of all the elements and clearly show that atomic size varies in a periodic fashion (Figure **2.3.3**).

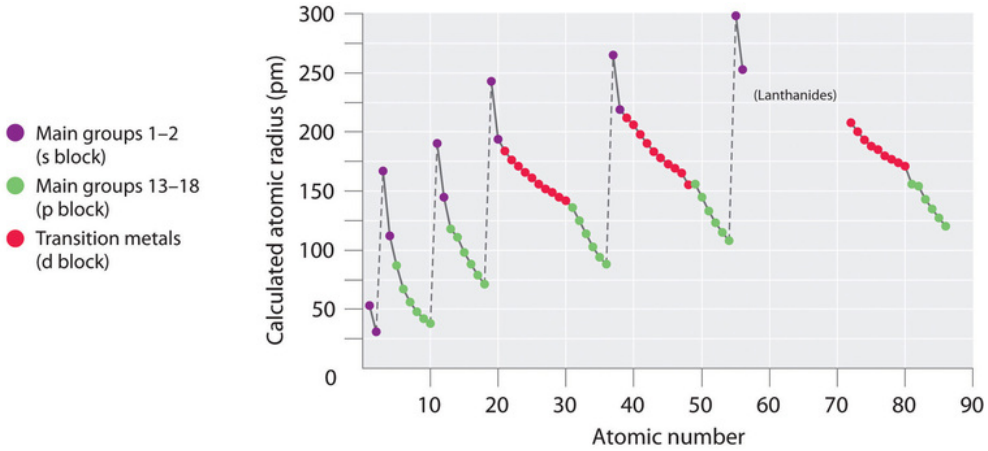


Figure **2.3.3**: A Plot of Periodic Variation of Atomic Radius with Atomic Number for the First Six Rows of the Periodic Table

In the periodic table, atomic radii decrease from left to right across a row and increase from top to bottom down a column. Because of these two trends, the largest atoms are found in the lower left corner of the periodic table, and the smallest are found in the upper right corner (Figure **2.3.4**).

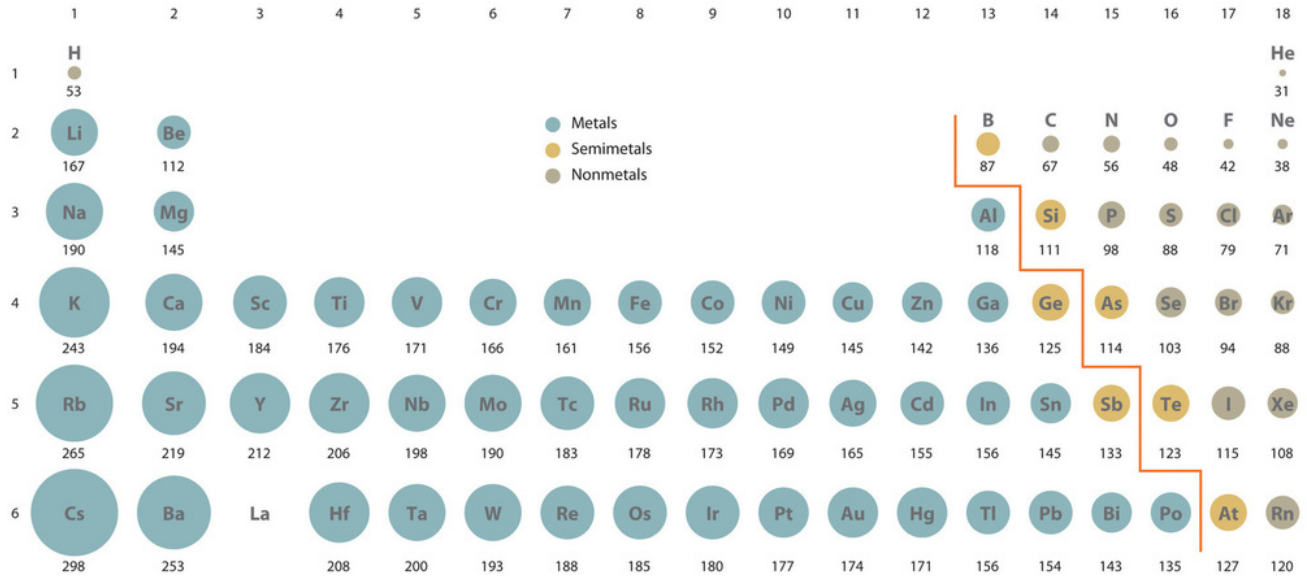


Figure **2.3.4** Calculated Atomic Radii (in Picometers) of the *s*-, *p*-, and *d*-Block Elements. The sizes of the circles illustrate the relative sizes of the atoms. The calculated values are based on quantum mechanical wave functions. Source: Web elements [www.webelements.com]. Web Elements is an excellent online source for looking up atomic properties.

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

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

The atoms in the second row of the periodic table (Li through Ne) illustrate the effect of electron shielding. All have a filled $1s^2$ inner shell, but as we go from left to right across the row, the nuclear charge increases from +3 to +10. Although electrons are being added to the 2*s* and 2*p* orbitals, *electrons in the same principal shell are not very effective at shielding one another from the nuclear charge*. Thus the single 2*s* electron in lithium experiences an effective nuclear charge of approximately +1 because the electrons in the filled $1s^2$ shell effectively neutralize two of the three positive charges in the nucleus. (More detailed calculations give a value of Z_{eff} = +1.26 for Li.) In contrast, the two 2*s* electrons in beryllium do not shield each other very well, although the filled $1s^2$ shell effectively neutralizes two of the four positive charges in the nucleus. This means that the effective nuclear charge experienced by the 2*s* electrons in beryllium is between +1 and +2 (the calculated value is +1.66). Consequently, beryllium is significantly smaller than lithium. Similarly, as we proceed across the row, the increasing nuclear charge is not effectively neutralized by the electrons being added to the 2*s* and 2*p* orbitals. The result is a steady increase in the effective nuclear charge and a steady decrease in atomic size (Figure **2.3.5**).

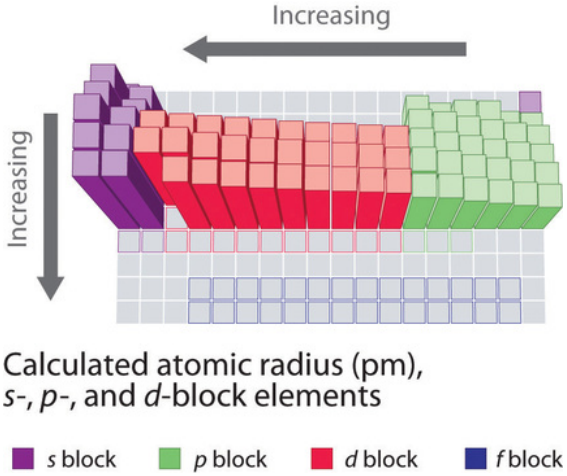


Figure **2.3.5**: The Atomic Radius of the Elements. The atomic radius of the elements increases as we go from right to left across a period and as we go down the periods in a group.

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

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

NOT ALL ELECTRONS SHIELD EQUALLY

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

EXAMPLE 2.3.1

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

Given: three elements

Asked for: arrange in order of increasing atomic radius

Strategy:

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

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

Solution:

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

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

EXERCISE 2.3.1

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

Answer

O < S < P < K



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

2.3.3 IONIC RADII AND ISOELECTRONIC SERIES

An ion is formed when either one or more electrons are removed from a neutral atom to form a positive ion (cation) or when additional electrons attach themselves to neutral atoms to form a negative one (anion). The designations cation or anion come from the early experiments with electricity which found that positively charged particles were attracted to the negative pole of a battery, the cathode, while negatively charged ones were attracted to the positive pole, the anode.

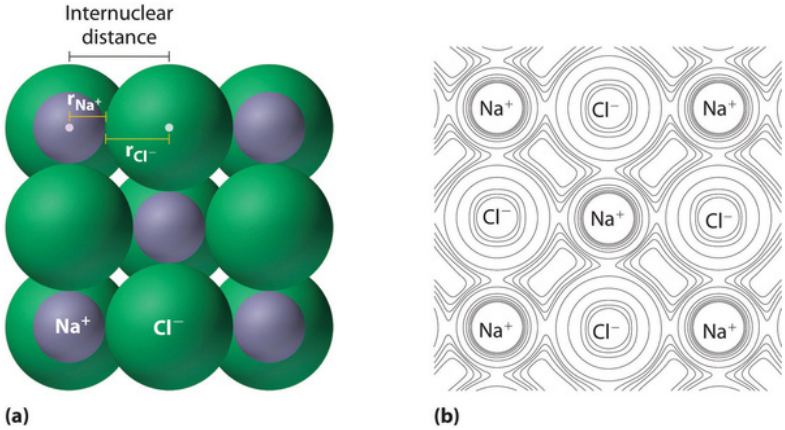


Figure **2.3.6**: Definition of Ionic Radius. (a) The internuclear distance is apportioned between adjacent cations (positively charged ions) and anions (negatively charged ions) in the ionic structure, as shown here for Na^+ and Cl^- in sodium chloride. (b) This depiction of electron density contours for a single plane of atoms in the NaCl structure shows how the lines connect points of equal electron density. Note the relative sizes of the electron density contour lines around Cl^- and Na^+.

Ionic compounds consist of regular repeating arrays of alternating positively charged cations and negatively charges anions. Although it is not possible to measure an ionic radius directly for the same reason it is not possible to directly measure an atom's radius, it *is* possible to measure the distance between the nuclei of a cation and an adjacent anion in an ionic compound to determine the ionic radius (the radius of a cation or anion) of one or both. As illustrated in Figure **2.3.6**, the internuclear distance corresponds to the *sum* of the radii of the cation and anion. A variety of methods have been developed to divide the experimentally measured distance proportionally between the smaller cation and larger anion. These methods produce sets of ionic radii that are internally consistent from one ionic compound to another, although each method gives slightly different values. For example, the radius of the Na^+ ion is essentially the same in NaCl and Na_2S, as long as the same method is used to measure it. Thus despite minor differences due to methodology, certain trends can be observed.

A comparison of ionic radii with atomic radii (Figure **2.3.7**) shows that *a cation, having lost an electron, is always smaller than its parent neutral atom, and an anion, having gained an electron, is always larger than the parent neutral atom*. When one or more electrons is removed from a neutral atom, two things happen: (1) repulsions between electrons in the same principal shell decrease because fewer electrons are present, and (2) the effective nuclear charge felt by the remaining electrons increases because there are fewer electrons to shield one another from the nucleus. Consequently, the size of the region of space occupied by electrons decreases and the ion shrinks (compare Li at 167 pm with Li^+ at 76 pm). If different numbers of electrons can be removed to produce ions with different charges, the ion with the greatest positive charge is the smallest (compare Fe^{2+} at 78 pm with Fe^{3+} at 64.5 pm). Conversely, adding one or more electrons to

a neutral atom causes electron–electron repulsions to increase and the effective nuclear charge to decrease, so the size of the probability region increases and the ion expands (compare F at 42 pm with F^- at 133 pm).

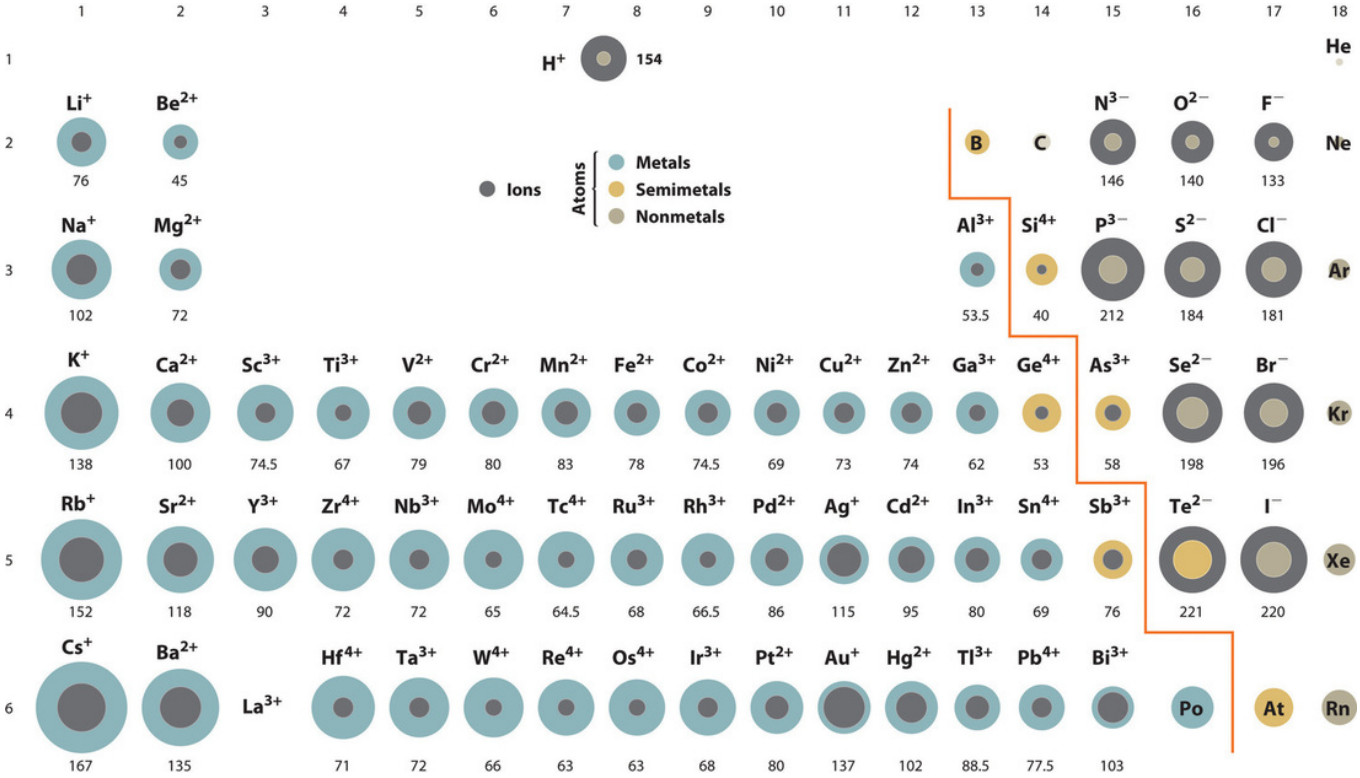


Figure **2.3.7**: Ionic Radii (in Picometers) of the Most Common Ionic States of the *s*-, *p*-, and *d*-Block Elements.Gray circles indicate the sizes of the ions shown; colored circles indicate the sizes of the neutral atoms. Source: Ionic radius data from R. D. Shannon, "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides," *Acta Crystallographica* 32, no. 5 (1976): 751–767.

> *Cations are **always** smaller than the neutral atom and anions are **always** larger.*

Because most elements form either a cation or an anion but not both, there are few opportunities to compare the sizes of a cation and an anion derived from the same neutral atom. A few compounds of sodium, however, contain the Na^- ion, allowing comparison of its size with that of the far more familiar Na^+ ion, which is found in *many* compounds. The radius of sodium in each of its three known oxidation states is given in Table **2.3.1**. All three species have a nuclear charge of +11, but they contain 10 (Na^+), 11 (Na^0), and 12 (Na^-) electrons. The Na^+ ion is significantly smaller than the neutral Na atom because the $3s^1$ electron has been removed to give a closed shell with $n = 2$. The Na^- ion is larger than the parent Na atom because the additional electron produces a $3s^2$ valence electron configuration, while the nuclear charge remains the same.

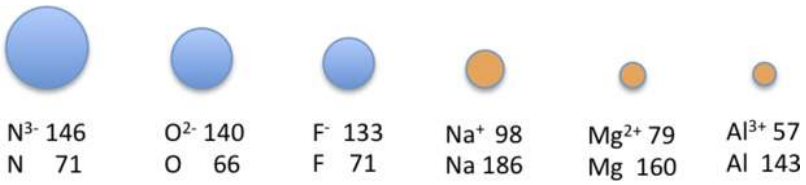
Table **2.3.1**: Experimentally Measured Values for the Radius of Sodium in Its Three Known Oxidation States

	Na^+	Na^0	Na^-
Electron Configuration	$1s^2 2s^2 2p^6$	$1s^2 2s^2 2p^6 3s^1$	$1s^2 2s^2 2p^6 3s^2$
Radius (pm)	102	154*	202†

*The metallic radius measured for Na(s). †Source: M. J. Wagner and J. L. Dye, "Alkalides, Electrides, and Expanded Metals," Annual Review of Materials Science 23 (1993): 225–253.

Ionic radii follow the same vertical trend as atomic radii; that is, for ions with the same charge, the ionic radius increases going down a column. The reason is the same as for atomic radii: shielding by filled inner shells produces little change in the effective nuclear charge felt by the outermost electrons. Again, principal shells with larger values of *n* lie at successively greater distances from the nucleus.

Because elements in different columns tend to form ions with different charges, it is not possible to compare ions of the same charge across a row of the periodic table. Instead, elements that are next to each other tend to form ions with the same number of electrons but with different overall charges because of their different atomic numbers. Such a set of species is known as an **isoelectronic series**. For example, the isoelectronic series of species with the neon closed-shell configuration ($1s^2 2s^2 2p^6$) is shown in Table **2.3.3**.



The sizes of the ions in this series decrease smoothly from N^{3-} to Al^{3+}. All six of the ions contain 10 electrons in the 1*s*, 2*s*, and 2*p* orbitals, but the nuclear charge varies from +7 (N) to +13 (Al). As the positive charge of the nucleus increases while the number of electrons remains the same, there is a greater electrostatic attraction between the electrons and the nucleus, which causes a decrease in radius. Consequently, the ion with the greatest nuclear charge (Al^{3+}) is the smallest, and the ion with the smallest nuclear charge (N^{3-}) is the largest. The neon atom in this isoelectronic series is not listed in Table **2.3.3**, because neon forms no covalent or ionic compounds and hence its radius is difficult to measure.

Table **2.3.3**: Radius of Ions with the Neon Closed-Shell Electron Configuration. Source: R. D. Shannon, "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides," Acta Crystallographica 32, no. 5 (1976): 751–767.

Ion	Radius (pm)	Atomic Number
N^{3-}	146	7
O^{2-}	140	8
F^{-}	133	9
Na^{+}	98	11
Mg^{2+}	79	12
Al^{3+}	57	13

✔ EXAMPLE 2.3.2

Based on their positions in the periodic table, arrange these ions in order of increasing radius: Cl^{-}, K^{+}, S^{2-}, and Se^{2-}.

Given: four ions

Asked for: order by increasing radius

Strategy:

A. Determine which ions form an isoelectronic series. Of those ions, predict their relative sizes based on their nuclear charges. For ions that do not form an isoelectronic series, locate their positions in the periodic table.

B. Determine the relative sizes of the ions based on their principal quantum numbers *n* and their locations within a row.

Solution:

A We see that S and Cl are at the right of the third row, while K and Se are at the far left and right ends of the fourth row, respectively. K^{+}, Cl^{-}, and S^{2-} form an isoelectronic series with the [Ar] closed-shell electron configuration; that is, all three ions contain 18 electrons but have different nuclear charges. Because K^{+} has the greatest nuclear charge ($Z = 19$), its radius is smallest, and S^{2-} with $Z = 16$ has the largest radius. Because selenium is directly below sulfur, we expect the Se^{2-} ion to be even larger than S^{2-}.

B The order must therefore be $K^{+} < Cl^{-} < S^{2-} < Se^{2-}$.

? EXERCISE 2.3.2

Based on their positions in the periodic table, arrange these ions in order of increasing size: Br^{-}, Ca^{2+}, Rb^{+}, and Sr^{2+}.

Answer

$Ca^{2+} < Sr^{2+} < Rb^{+} < Br^{-}$

2.3.4 SUMMARY

Ionic radii share the same vertical trend as atomic radii, but the horizontal trends differ due to differences in ionic charges. A variety of methods have been established to measure the size of a single atom or ion. The **covalent atomic radius (r_{cov})** is half the internuclear distance in a molecule with two identical atoms bonded to each other, whereas the **metallic atomic radius (r_{met})** is defined as half the distance between the nuclei of two adjacent atoms in a metallic element. The **van der Waals radius (r_{vdW})** of an element is half the internuclear distance between two nonbonded atoms in a solid. Atomic radii decrease from left to right across a row because of the increase

in effective nuclear charge due to poor electron screening by other electrons in the same principal shell. Moreover, atomic radii increase from top to bottom down a column because the effective nuclear charge remains relatively constant as the principal quantum number increases. The **ionic radii** of cations and anions are always smaller or larger, respectively, than the parent atom due to changes in electron–electron repulsions, and the trends in ionic radius parallel those in atomic size. A comparison of the dimensions of atoms or ions that have the same number of electrons but different nuclear charges, called an **isoelectronic series**, shows a clear correlation between increasing nuclear charge and decreasing size.

2.3.5 CONTRIBUTORS AND ATTRIBUTIONS

- Modified by Joshua Halpern (Howard University)

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2.4: IONIZATION ENERGY

LEARNING OBJECTIVES

- To correlate ionization energies with the chemistry of the elements

We have seen that when elements react, they often gain or lose enough electrons to achieve the valence electron configuration of the nearest noble gas. Why is this so? In this section, we develop a more quantitative approach to predicting such reactions by examining periodic trends in the energy changes that accompany ion formation.

2.4.1 IONIZATION ENERGIES

Because atoms do not spontaneously lose electrons, energy is required to remove an electron from an atom to form a cation. Chemists define the ionization energy (I) of an element as the amount of energy needed to remove an electron from the gaseous atom E in its ground state. I is therefore the energy required for the reaction

$$E_{(g)} \rightarrow E^+_{(g)} + e^- \qquad \text{energy required=I} \tag{2.4.1}$$

Because an input of energy is required, the ionization energy is always positive ($I > 0$) for the reaction as written in Equation 2.4.1. Larger values of I mean that the electron is more tightly bound to the atom and harder to remove. Typical units for ionization energies are kilojoules/mole (kJ/mol) or electron volts (eV):

$$1\ eV/atom = 96.49\ kJ/mol$$

If an atom possesses more than one electron, the amount of energy needed to remove successive electrons increases steadily. We can define a first ionization energy (I_1), a second ionization energy (I_2), and in general an nth ionization energy (I_n) according to the following reactions:

$$\mathrm{E(g)} \rightarrow \mathrm{E^+(g) + e^-} \qquad I_1 = \text{1st ionization energy} \tag{2.4.2}$$

$$\mathrm{E^+(g)} \rightarrow \mathrm{E^{2+}(g) + e^-} \qquad I_2 = \text{2nd ionization energy} \tag{2.4.3}$$

$$\mathrm{E^{2+}(g)} \rightarrow \mathrm{E^{3+}(g) + e^-} \qquad I_3 = \text{3rd ionization energy} \tag{2.4.4}$$

Values for the ionization energies of Li and Be listed in Table 2.4.1 show that successive ionization energies for an element increase as they go; that is, it takes more energy to remove the second electron from an atom than the first, and so forth. There are two reasons for this trend. First, the second electron is being removed from a positively charged species rather than a neutral one, so in accordance with Coulomb's law, more energy is required. Second, removing the first electron reduces the repulsive forces among the remaining electrons, so the attraction of the remaining electrons to the nucleus is stronger.

> *Successive ionization energies for an element* ***increase****.*

Table 2.4.1: Ionization Energies (in kJ/mol) for Removing Successive Electrons from Li and Be. Source: Data from CRC Handbook of Chemistry and Physics (2004).

Reaction	Electronic Transition	I	Reaction	Electronic Transition	I
$\mathrm{Li\,(g) \rightarrow Li^+(g) + e^-}$	$1s^22s^1 \rightarrow 1s^2$	I_1 = 520.2	$\mathrm{Be(g) \rightarrow Be^+(g) + e^-}$	$1s^22s^2 \rightarrow 1s^22s^1$	I_1 = 899.5
$\mathrm{Li^+(g) \rightarrow Li^{2+}(g) + e^-}$	$1s^2 \rightarrow 1s^1$	I_2 = 7298.2	$\mathrm{Be^+(g) \rightarrow Be^{2+}(g) + e^-}$	$1s^22s^1 \rightarrow 1s^2$	I_2 = 1757.1
$\mathrm{Li^{2+}(g) \rightarrow Li^{3+}(g) + e^-}$	$1s^1 \rightarrow 1s^0$	I_3 = 11,815.0	$\mathrm{Be^{2+}(g) \rightarrow Be^{3+}(g) + e^-}$	$1s^2 \rightarrow 1s^1$	I_3 = 14,848.8
			$\mathrm{Be^{3+}(g) \rightarrow Be^{4+}(g) + e^-}$	$1s^1 \rightarrow 1s^0$	I_4 = 21,006.6

The increase in successive ionization energies, however, is not linear, but increases drastically when removing electrons in lower n orbitals closer to the nucleus. The most important consequence of the values listed in Table 2.4.1 is that the chemistry of Li is dominated by the $\mathrm{Li^+}$ ion, while the chemistry of Be is dominated by the +2 oxidation state. The energy required to remove the *second* electron from Li:

$$\mathrm{Li^+(g) \rightarrow Li^{2+}(g) + e^-} \tag{2.4.5}$$

is more than 10 times greater than the energy needed to remove the first electron. Similarly, the energy required to remove the *third* electron from Be:

$$Be^{2+}(g) \rightarrow Be^{3+}(g) + e^- \quad (2.4.6)$$

is about 15 times greater than the energy needed to remove the first electron and around 8 times greater than the energy required to remove the second electron. Both Li^+ and Be^{2+} have $1s^2$ closed-shell configurations, and much more energy is required to remove an electron from the $1s^2$ core than from the 2*s* valence orbital of the same element. The chemical consequences are enormous: lithium (and all the alkali metals) forms compounds with the 1+ ion but not the 2+ or 3+ ions. Similarly, beryllium (and all the alkaline earth metals) forms compounds with the 2+ ion but not the 3+ or 4+ ions. *The energy required to remove electrons from a filled core is prohibitively large and simply cannot be achieved in normal chemical reactions.*

> *The energy required to remove electrons from a filled core is prohibitively large under normal reaction conditions.*



Ionization Energy: Ionization Energy, YouTube(opens in new window) [youtu.be] (opens in new window)

2.4.2 IONIZATION ENERGIES OF *S*- AND *P*-BLOCK ELEMENTS

Ionization energies of the elements in the third row of the periodic table exhibit the same pattern as those of ***Li*** and ***Be*** (Table **2.4.2**): successive ionization energies increase steadily as electrons are removed from the valence orbitals (3*s* or 3*p*, in this case), followed by an especially large increase in ionization energy when electrons are removed from filled core levels as indicated by the bold diagonal line in Table **2.4.2**. Thus in the third row of the periodic table, the largest increase in ionization energy corresponds to removing the fourth electron from ***Al***, the fifth electron from Si, and so forth—that is, removing an electron from an ion that has the valence electron configuration of the preceding noble gas. This pattern explains why the chemistry of the elements normally involves only valence electrons. Too much energy is required to either remove or share the inner electrons.

Table **2.4.2**: Successive Ionization Energies (in kJ/mol) for the Elements in the Third Row of the Periodic Table.Source: Data from CRC Handbook of Chemistry and Physics (2004).

Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	495.8	**4562.4***	—	—	—	—	—
Mg	737.7	1450.7	**7732.7**	—	—	—	—
Al	577.4.4	1816.7	2744.8	**11,577.4.4**	—	—	—
Si	786.5	1577.1	3231.6	4355.5	**16,090.6**	—	—
P	1011.8	1907.4.4	2914.1	4963.6	6274.0	**21,267.4.3**	—
S	999.6	2251.8	3357	4556.2	7004.3	8495.8	**27,107.4.3**
Cl	1251.2	2297.7	3822	5158.6	6540	9362	11,018.2
Ar	1520.6	2665.9	3931	5771	7238	8781.0	11,995.3

*Inner-shell electron

EXAMPLE 2.4.1: HIGHEST FOURTH IONIZATION ENERGY

From their locations in the periodic table, predict which of these elements has the highest fourth ionization energy: B, C, or N.

Given: three elements

Asked for: element with highest fourth ionization energy

Strategy:

a. List the electron configuration of each element.

b. Determine whether electrons are being removed from a filled or partially filled valence shell. Predict which element has the highest fourth ionization energy, recognizing that the highest energy corresponds to the removal of electrons from a filled electron core.

Solution:

A These elements all lie in the second row of the periodic table and have the following electron configurations:

- B: [He]$2s^2 2p^1$
- C: [He]$2s^2 2p^2$
- N: [He]$2s^2 2p^3$

B The fourth ionization energy of an element (I_4) is defined as the energy required to remove the fourth electron:

$$E^{3+}_{(g)} \rightarrow E^{4+}_{(g)} + e^-$$

Because carbon and nitrogen have four and five valence electrons, respectively, their fourth ionization energies correspond to removing an electron from a partially filled valence shell. The fourth ionization energy for boron, however, corresponds to removing an electron from the filled $1s^2$ subshell. This should require much more energy. The actual values are as follows: B, 25,026 kJ/mol; C, 6223 kJ/mol; and N, 7475 kJ/mol.

EXERCISE 2.4.1: LOWEST SECOND IONIZATION ENERGY

From their locations in the periodic table, predict which of these elements has the lowest second ionization energy: Sr, Rb, or Ar.

Answer

Sr

The first column of data in Table 2.4.2 shows that first ionization energies tend to increase across the third row of the periodic table. This is because the valence electrons do not screen each other very well, allowing the effective nuclear charge to increase steadily across the row. The valence electrons are therefore attracted more strongly to the nucleus, so atomic sizes decrease and ionization energies increase. These effects represent two sides of the same coin: stronger electrostatic interactions between the electrons and the nucleus further increase the energy required to remove the electrons.

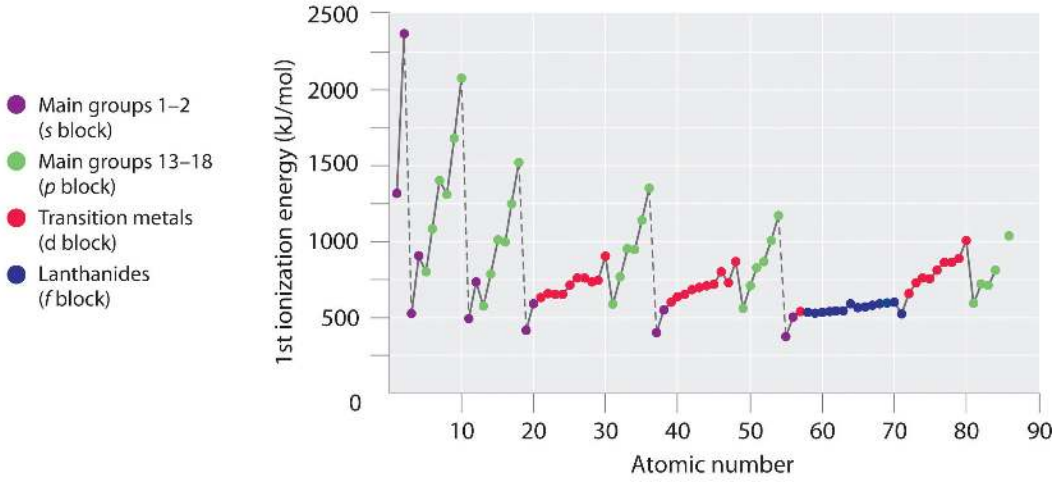


Figure **2.4.1**: A Plot of Periodic Variation of First Ionization Energy with Atomic Number for the First Six Rows of the Periodic Table. There is a decrease in ionization energy within a group (most easily seen here for groups 1 and 18).

the main groups 1 and 2 are purple, the main groups 13 through 18 are green, the transition metals are red, and the lanthanides are blue.

However, the first ionization energy decreases at Al ([Ne]$3s^2 3p^1$) and at S ([Ne]$3s^2 3p^4$). The electron configurations of these "exceptions" provide the answer why. The electrons in aluminum's filled $3s^2$ subshell are better at screening the $3p^1$ electron than they are at screening each other from the nuclear charge, so the *s* electrons penetrate closer to the nucleus than the *p* electron does and the *p* electron is more easily removed. The decrease at S occurs because the two electrons in the same *p* orbital repel each other. This makes the S atom slightly less stable than would otherwise be expected, as is true of all the group 16 elements.

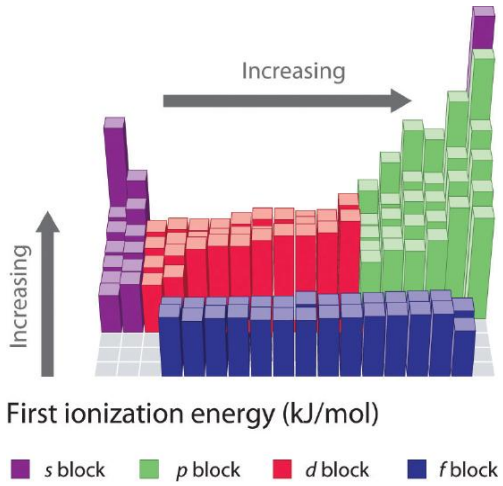


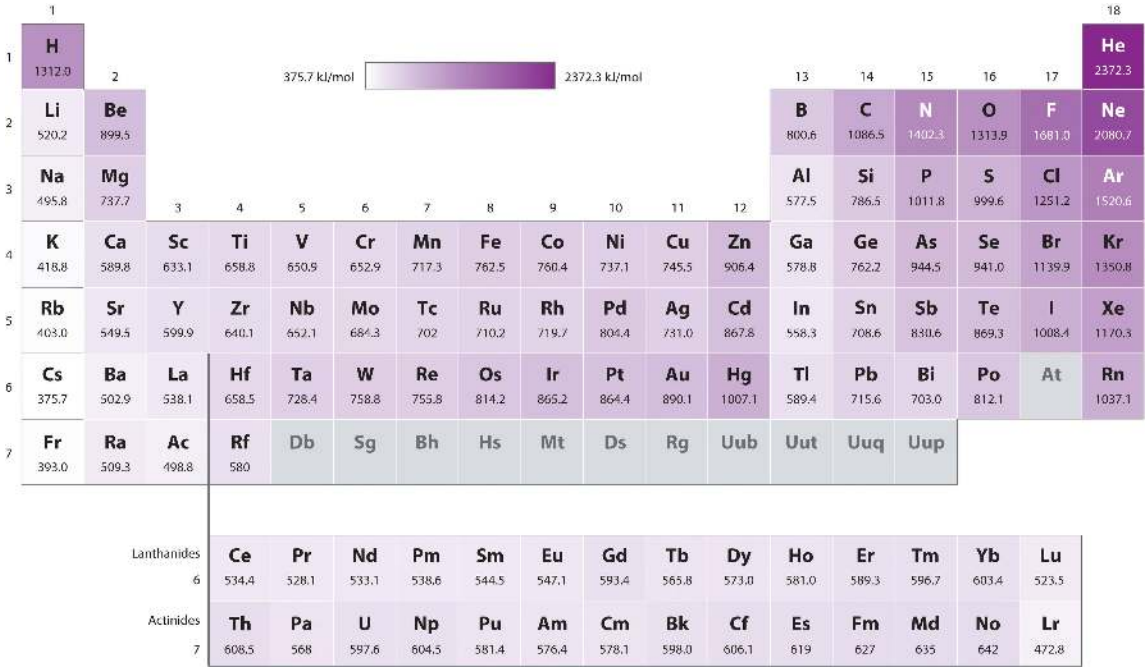
Figure **2.4.2**: First Ionization Energies of the *s*-, *p*-, *d*-, and *f*-Block Elements

The s blocks are purple, the p blocks are green, the d blocks are red, and the f blocks are blue. First ionization energy increase from left to right and from bottom to top.

The first ionization energies of the elements in the first six rows of the periodic table are plotted in Figure **2.4.1** and are presented numerically and graphically in Figure **2.4.2**. These figures illustrate three important trends:

1. The changes seen in the second (Li to Ne), fourth (K to Kr), fifth (Rb to Xe), and sixth (Cs to Rn) rows of the *s* and *p* blocks follow a pattern similar to the pattern described for the third row of the periodic table. The transition metals are included in the fourth, fifth, and sixth rows, however, and the lanthanides are included in the sixth row. The first ionization energies of the transition metals are somewhat similar to one another, as are those of the lanthanides. Ionization energies increase from left to right across each row, with discrepancies occurring at ns^2np^1 (group 13), ns^2np^4 (group 16), and $ns^2(n-1)d^{10}$ (group 12).
2. First ionization energies generally decrease down a column. Although the principal quantum number *n* increases down a column, filled inner shells are effective at screening the valence electrons, so there is a relatively small increase in the effective nuclear charge. Consequently, the atoms become larger as they acquire electrons. Valence electrons that are farther from the nucleus are less tightly bound, making them easier to remove, which causes ionization energies to decrease. *A larger radius typically corresponds to a lower ionization energy*.

3. Because of the first two trends, the elements that form positive ions most easily (have the lowest ionization energies) lie in the lower left corner of the periodic table, whereas those that are hardest to ionize lie in the upper right corner of the periodic table. Consequently, ionization energies generally increase diagonally from lower left (Cs) to upper right (He).



The darkness of the shading inside the cells of the table indicates the relative magnitudes of the ionization energies. Elements in gray have undetermined first ionization energies. Source: Data from *CRC Handbook of Chemistry and Physics* (2004).

> *Generally, I_1 increases diagonally from the lower left of the periodic table to the upper right.*

Gallium (Ga), which is the first element following the first row of transition metals, has the following electron configuration: [Ar]$4s^2 3d^{10} 4p^1$. Its first ionization energy is significantly lower than that of the immediately preceding element, zinc, because the filled $3d^{10}$ subshell of gallium lies inside the 4*p* subshell, shielding the single 4*p* electron from the nucleus. Experiments have revealed something of even greater interest: the second and third electrons that are removed when gallium is ionized come from the $4s^2$ orbital, *not* the $3d^{10}$ subshell. The chemistry of gallium is dominated by the resulting Ga^{3+} ion, with its [Ar]$3d^{10}$ electron configuration. This and similar electron configurations are particularly stable and are often encountered in the heavier *p*-block elements. They are sometimes referred to as *pseudo noble gas configurations*. In fact, for elements that exhibit these configurations, *no chemical compounds are known in which electrons are removed from the $(n - 1)d^{10}$ filled subshell*.

2.4.3 IONIZATION ENERGIES OF TRANSITION METALS & LANTHANIDES

As we noted, the first ionization energies of the transition metals and the lanthanides change very little across each row. Differences in their second and third ionization energies are also rather small, in sharp contrast to the pattern seen with the *s*- and *p*-block elements. The reason for these similarities is that the transition metals and the lanthanides form cations by losing the *ns* electrons before the $(n - 1)d$ or $(n - 2)f$ electrons, respectively. This means that transition metal cations have $(n - 1)d^n$ valence electron configurations, and lanthanide cations have $(n - 2)f^n$ valence electron configurations. Because the $(n - 1)d$ and $(n - 2)f$ shells are closer to the nucleus than the *ns* shell, the $(n - 1)d$ and $(n - 2)f$ electrons screen the *ns* electrons quite effectively, reducing the effective nuclear charge felt by the *ns* electrons. As *Z* increases, the increasing positive charge is largely canceled by the electrons added to the $(n - 1)d$ or $(n - 2)f$ orbitals.

That the *ns* electrons are removed before the $(n - 1)d$ or $(n - 2)f$ electrons may surprise you because the orbitals were filled in the reverse order. In fact, the *ns*, the $(n - 1)d$, and the $(n - 2)f$ orbitals are so close to one another in energy, and interpenetrate one another so extensively, that very small changes in the effective nuclear charge can change the order of their energy levels. As the *d* orbitals are filled, the effective nuclear charge causes the 3*d* orbitals to be slightly lower in energy than the 4*s* orbitals. The [Ar]$3d^2$ electron configuration of Ti^{2+} tells us that the 4*s* electrons of titanium are lost before the 3*d* electrons; this is confirmed by experiment. A similar pattern is seen with the lanthanides, producing cations with an $(n - 2)f^n$ valence electron configuration.

Because their first, second, and third ionization energies change so little across a row, these elements have important *horizontal* similarities in chemical properties in addition to the expected vertical similarities. For example, all the first-row transition metals except scandium form

stable compounds as M^{2+} ions, whereas the lanthanides primarily form compounds in which they exist as M^{3+} ions.

EXAMPLE 2.4.2: LOWEST FIRST IONIZATION ENERGY

Use their locations in the periodic table to predict which element has the lowest first ionization energy: Ca, K, Mg, Na, Rb, or Sr.

Given: six elements

Asked for: element with lowest first ionization energy

Strategy:

Locate the elements in the periodic table. Based on trends in ionization energies across a row and down a column, identify the element with the lowest first ionization energy.

Solution:

These six elements form a rectangle in the two far-left columns of the periodic table. Because we know that ionization energies increase from left to right in a row and from bottom to top of a column, we can predict that the element at the bottom left of the rectangle will have the lowest first ionization energy: Rb.

EXERCISE 2.4.2: HIGHEST FIRST IONIZATION ENERGY

Use their locations in the periodic table to predict which element has the highest first ionization energy: As, Bi, Ge, Pb, Sb, or Sn.

Answer

As

2.4.4 SUMMARY

The tendency of an element to lose electrons is one of the most important factors in determining the kind of compounds it forms. Periodic behavior is most evident for **ionization energy (*I*)**, the energy required to remove an electron from a gaseous atom. The energy required to remove successive electrons from an atom increases steadily, with a substantial increase occurring with the removal of an electron from a filled inner shell. Consequently, only valence electrons can be removed in chemical reactions, leaving the filled inner shell intact. Ionization energies explain the common oxidation states observed for the elements. Ionization energies increase diagonally from the lower left of the periodic table to the upper right. Minor deviations from this trend can be explained in terms of particularly stable electronic configurations, called **pseudo noble gas configurations**, in either the parent atom or the resulting ion.

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2.5: ELECTRON AFFINITIES

LEARNING OBJECTIVES

- To master the concept of electron affinity as a measure of the energy released by adding an electron to an atom or ion.
- To recognize the inverse relationship of ionization energies and electron affinities

The electron affinity (***EA***) of an element ***X*** is defined as the energy released that occurs when an electron is added to a gaseous atom or ion:

$$X(g) + e^- \rightarrow X^-(g) \qquad EA = E(X) - E(X^-) \tag{2.5.1}$$

where $E(X)$ is the energy of the gaseous atom ***X*** and $E(X^-)$ is the energy of the gaseous anion X^-. The positive electron affinities (EA>0) imply that the energy is released when an electron is added, which is an exothermic process. The negative EA imply that the energy must be added to the system to produce an anion. A more positive EA indicates a stronger attraction for an additional electron. (Figure **2.5.1**).

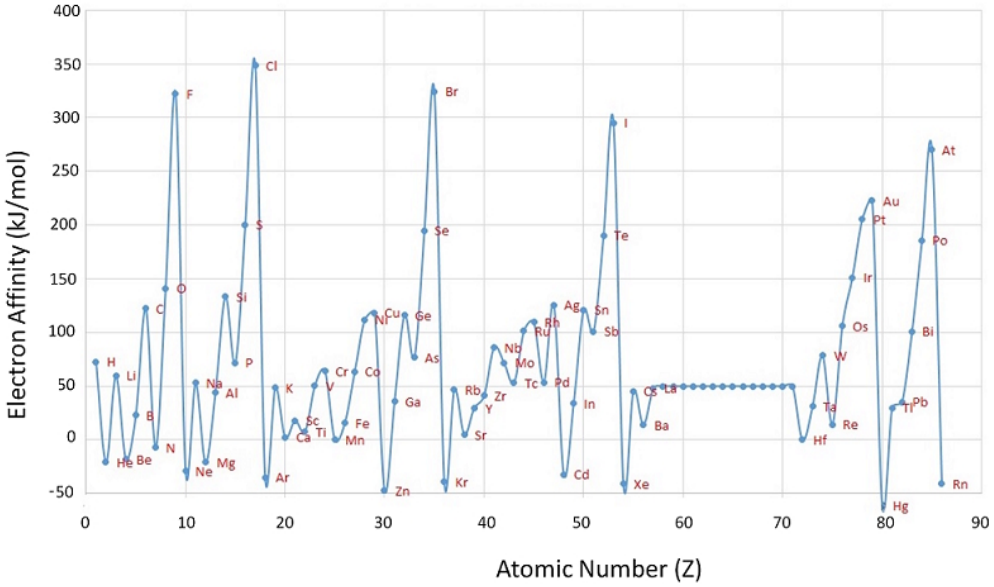


Figure **2.5.1**: A Plot of Periodic Variation of Electron Affinity with Atomic Number for the First Six Rows of the Periodic Table. Notice that electron affinities can be both positive and negative. from Robert J. Lancashire (University of the West Indies).

The chlorine atom has the most positive electron affinity of any element, which means that more energy is released when an electron is added to a gaseous chlorine atom than to an atom of any other element:

$$\mathrm{Cl(g) + e^- \rightarrow Cl^-(g)} \qquad EA = +348.6\ kJ/mol \tag{2.5.2}$$

In contrast, beryllium does not form a stable anion, so its effective electron affinity is

$$\mathrm{Be(g) + e^- \rightarrow Be^-(g)} \qquad EA \leq 0 \tag{2.5.3}$$

Nitrogen is unique in that it has an electron affinity of approximately zero. Adding an electron neither releases nor requires a significant amount of energy:

$$\mathrm{N(g) + e^- \rightarrow N^-(g)} \qquad EA \approx 0 \tag{2.5.4}$$

> *Generally, electron affinities become more positive across a row of the periodic table.*

In general, electron affinities of the main-group elements become less positive as we proceed down a column. This is because as *n* increases, the extra electrons enter orbitals that are increasingly far from the nucleus.

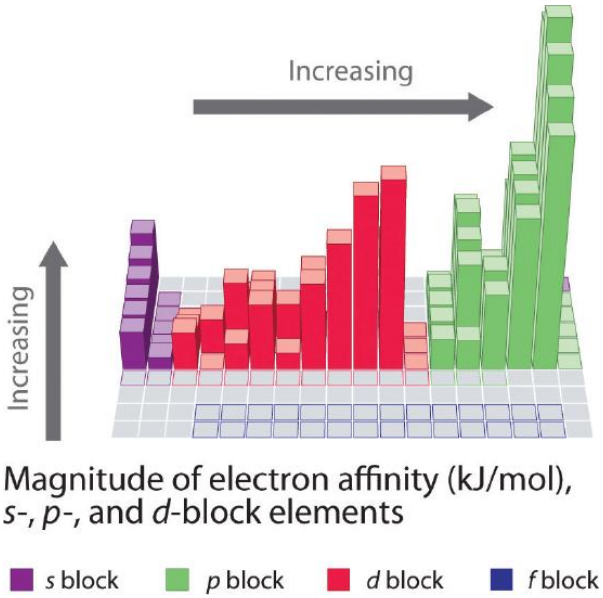


Figure 2.5.2: Electron Affinities (in kJ/mol) of the *s*-, *p*-, and *d*-Block Elements.

The s blocks are purple, the p blocks are green, the d blocks are red, and the f blocks are blue. Electron affinity increases from left to right and bottom to top.

Atoms with the largest radii, which have the lowest ionization energies (affinity for their own valence electrons), also have the lowest affinity for an added electron. There are, however, two major exceptions to this trend:

1. The electron affinities of elements B through F in the second row of the periodic table are *less* positive than those of the elements immediately below them in the third row. Apparently, the increased electron–electron repulsions experienced by electrons confined to the relatively small 2*p* orbitals overcome the increased electron–nucleus attraction at short nuclear distances. Fluorine, therefore, has a lower affinity for an added electron than does chlorine. Consequently, the elements of the *third* row (n = 3) have the most positive electron affinities. Farther down a column, the attraction for an added electron decreases because the electron is entering an orbital more distant from the nucleus. Electron–electron repulsions also decrease because the valence electrons occupy a greater volume of space. These effects tend to cancel one another, so the changes in electron affinity within a family are much smaller than the changes in ionization energy.
2. The electron affinities of the alkaline earth metals become more positive from Be to Ba. The energy separation between the filled ns^2 and the empty *np* subshells decreases with increasing n, so that formation of an anion from the heavier elements becomes energetically more favorable.

≤ 0 kJ/mol → +348.6 kJ/mol

1 H +72.8																2 He < 0
3 Li +59.6	4 Be ≤ 0											5 B +27.0	6 C +121.8	7 N -6.8	8 O +141.0	9 F +328.2	10 Ne < 0
11 Na +52.9	12 Mg ≤ 0											13 Al +41.8	14 Si +134.1	15 P +72.0	16 S +200.4	17 Cl +348.6	18 Ar < 0
19 K +48.4	20 Ca +2.4	21 Sc +17.3	22 Ti +7.3	23 V +50.9	24 Cr +65.2	25 Mn ≤ 0	26 Fe +14.8	27 Co +63.9	28 Ni +111.7	29 Cu +119.2	30 Zn ≤ 0	31 Ga +29.1	32 Ge +118.9	33 As +77.7	34 Se +195.0	35 Br +324.5	36 Kr < 0
37 Rb +46.9	38 Sr +5.0	39 Y +30.0	40 Zr +41.8	41 Nb +88.5	42 Mo +72.1	43 Tc +53.0	44 Ru +101.0	45 Rh +110.3	46 Pd +54.2	47 Ag +125.9	48 Cd ≤ 0	49 In +37.0	50 Sn +107.3	51 Sb +101.1	52 Te +190.2	53 I +295.2	54 Xe < 0
55 Cs +45.5	56 Ba +14.0	57 La +53.8	72 Hf ≤ 0	73 Ta +31.7	74 W +78.8	75 Re +5.8	76 Os +104.0	77 Ir +150.9	78 Pt +205.0	79 Au +222.7	80 Hg ≤ 0	81 Tl +30.9	82 Pb +34.4	83 Bi +90.9	84 Po +190.0	85 At +295.0	86 Rn < 0

Figure 2.5.3: There are many more exceptions to the trends across rows and down columns than with first ionization energies. Elements that do not form stable ions, such as the noble gases, are assigned an effective electron affinity that is greater than or equal to zero. Elements for which no data are available are shown in gray. Source: Data from *Journal of Physical and Chemical Reference Data* 28, no. 6 (1999).

The equations for second and higher electron affinities are analogous to those for second and higher ionization energies:

$$X(g) + e^- \rightarrow X^-(g) \qquad EA_1 = E(X) - E(X^-) \tag{2.5.5}$$

$$X^-(g) + e^- \rightarrow X^{2-}(g) \qquad EA_2 = E(X^-) - E(X^{2-}) \tag{2.5.6}$$

As we have seen, the first electron affinity can be greater than or equal to zero or negative, depending on the electron configuration of the atom. In contrast, the second electron affinity is *always* positive because the increased electron–electron repulsions in a dianion are far greater than the attraction of the nucleus for the extra electrons. For example, the first electron affinity of oxygen is +141 kJ/mol, but the second electron affinity is −744 kJ/mol:

$$O(g) + e^- \rightarrow O^-(g) \qquad EA_1 = +141\ kJ/mol \tag{2.5.7}$$

$$O^-(g) + e^- \rightarrow O^{2-}(g) \qquad EA_2 = -744\ kJ/mol \tag{2.5.8}$$

Thus the formation of a gaseous oxide (O^{2-}) ion is energetically quite *unfavorable* (estimated by adding both steps):

$$O(g) + 2e^- \rightarrow O^{2-}(g) \qquad EA = -603\ kJ/mol \tag{2.5.9}$$

Similarly, the formation of all common dianions (such as S^{2-}) or trianions (such as P^{3-}) is energetically unfavorable in the gas phase.

> *While first electron affinities can be positive, negative, or zero, second electron affinities are always negative.*

If energy is required to form both positively charged cations and monatomic polyanions, why do ionic compounds such as MgO, Na_2S, and Na_3P form at all? The key factor in the formation of stable ionic compounds is the favorable electrostatic interactions between the cations and the anions *in the crystalline salt*.

✔ EXAMPLE 2.5.1: CONTRASTING ELECTRON AFFINITIES OF SB, SE, AND TE

Based on their positions in the periodic table, which of Sb, Se, or Te would you predict to have the most positive electron affinity?

Given: three elements

Asked for: element with most positive electron affinity

Strategy:

A. Locate the elements in the periodic table. Use the trends in electron affinities going down a column for elements in the same group. Similarly, use the trends in electron affinities from left to right for elements in the same row.

B. Place the elements in order, listing the element with the most positive electron affinity first.

Solution:

A We know that electron affinities become less positive going down a column (except for the anomalously low electron affinities of the elements of the second row), so we can predict that the electron affinity of Se is more positive than that of Te. We also know that electron affinities become more positive from left to right across a row, and that the group 15 elements tend to have values that are less positive than expected. Because Sb is located to the left of Te and belongs to group 15, we predict that the electron affinity of Te is more positive than that of Sb. The overall order is Se > Te > Sb, so Se has the most positive electron affinity among the three elements.

? EXERCISE 2.5.1: CONTRASTING ELECTRON AFFINITIES OF RB, SR, AND XE

Based on their positions in the periodic table, which of Rb, Sr, or Xe would you predict to most likely form a gaseous anion?

Answer

Rb

2.5.1 SUMMARY

The **electron affinity** (*EA*) of an element is the energy released that occurs when an electron is added to a gaseous atom to give an anion. In general, elements with the most positive electron affinities (the highest affinity for an added electron) are those with the smallest size and highest ionization energies and are located in the upper right corner of the periodic table.

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2.E: PERIODIC PROPERTIES OF THE ELEMENTS (EXERCISES)

2.E.1 DEVELOPMENT OF THE PERIODIC TABLE

2.E.1.1 CONCEPTUAL PROBLEMS

1. Johannes Dobereiner is credited with developing the concept of chemical triads. Which of the group 15 elements would you expect to compose a triad? Would you expect B, Al, and Ga to act as a triad? Justify your answers.
2. Despite the fact that Dobereiner, Newlands, Meyer, and Mendeleev all contributed to the development of the modern periodic table, Mendeleev is credited with its origin. Why was Mendeleev's periodic table accepted so rapidly?
3. How did Moseley's contribution to the development of the periodic table explain the location of the noble gases?
4. The *eka*- naming scheme devised by Mendeleev was used to describe undiscovered elements.
    1. Use this naming method to predict the atomic number of *eka*-mercury, *eka*-astatine, *eka*-thallium, and *eka*-hafnium.
    2. Using the *eka*-prefix, identify the elements with these atomic numbers: 79, 40, 51, 117, and 121.

2.E.1.2 NUMERICAL PROBLEM

5. Based on the data given, complete the table.

Species	Molar Mass (g/mol)	Density (g/cm3)	Molar Volume (cm3/mol)
A	40.078		25.85
B	39.09	0.856	
C	32.065		16.35
D		1.823	16.98
E	26.98		9.992
F	22.98	0.968	

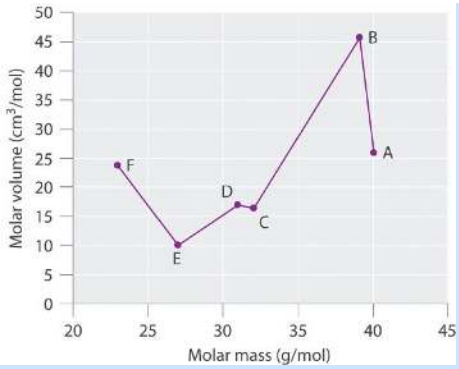
Plot molar volume versus molar mass for these substances. According to Meyer, which would be considered metals and which would be considered nonmetals?

2.E.1.3 NUMERICAL ANSWER

5.

Meyer found that the alkali metals had the highest molar volumes, and that molar volumes decreased steadily with increasing atomic mass, then leveled off, and finally rose again. The elements located on the rising portion of a plot of molar volume versus molar mass were typically nonmetals. If we look at the plot of the data in the table, we can immediately identify those elements with the largest molar volumes (A, B, F) as metals located on the left side of the periodic table. The element with the smallest molar volume (E) is aluminum. The plot shows that the subsequent elements (C, D) have molar volumes that are larger than that of E, but smaller than those of A and B. Thus, C and D are most likely to be nonmetals (which is the case: C = sulfur, D = phosphorus).

Species	Molar Mass (g/mol)	Density (g/cm^3)	Molar Volume (cm^3/mol)
A	**40.078**	1.550	**25.85**
B	**39.09**	**0.856**	45.67
C	**32.065**	1.961	**16.35**
D	30.95	**1.823**	**16.98**
E	**26.98**	2.700	**9.992**
F	**22.98**	**0.968**	23.7



2.E.2 EFFECTIVE NUCLEAR CHARGE

2.E.2.1 CONCEPTUAL PROBLEMS

6. Which orbital is more effective in shielding? 1s or 2p?
7. True/False: The greater the penetration of an orbital, the greater the shielding capability of that orbital.
8. Using the classical Bohr model and ignoring penetration effects, estimate the effective nuclear charge Z_{eff} of experienced by the outermost electron of the following elements:
   a. Mg
   b. C
   c. F
   d. Ca
9. Which of these have the smallest electron affinity? B, C, N, O, or F.
10. Which atom has a stronger effective nuclear charge and why? (assuming S is the same in both cases) Li, or N
11. Why does the Hydrogen electron experiences the full charge of the nucleus without any shielding?
12. Which atom has a smaller radii? Be or F?
13. Which electron has higher energy level? 2s or 2p? and why?
14. Why do the orbitals of a hydrogen atom increase energy as follows: 1s<2s=2p<3s=3p=3d<4s=4p=4d<....
15. Which electrons shields better in an atom? 2s or 2p? 3p or 3d?
16. Why can we relate classical physics to quantum mechanics when it comes to subatomic activity?
17. What is penetration?
18. What happens to the energy of a given orbital as the nuclear charge Z of a species increases? In a multielectron atom and for a given nuclear charge, the Z_{eff} experienced by an electron depends on its value of l. Why?
19. The electron density of a particular atom is divided into two general regions. Name these two regions and describe what each represents.
20. As the principal quantum number increases, the energy difference between successive energy levels decreases. Why? What would happen to the electron configurations of the transition metals if this decrease did not occur?
21. Describe the relationship between electron shielding and Z_{eff} on the outermost electrons of an atom. Predict how chemical reactivity is affected by a decreased effective nuclear charge.
22. If a given atom or ion has a single electron in each of the following subshells, which electron is easier to remove?
    - 2*s*, 3*s*
    - 3*p*, 4*d*
    - 2*p*, 1*s*
    - 3*d*, 4*s*

2.E.2.2 CONCEPTUAL ANSWERS

6. 1s
7. T
8. a. 12-10 =2
   b. 6-2=4
   c. 9-2=7
   d. 20-18=2

9. -
10. nitrogen atom has a stronger effective nuclear charge than lithium due to its greater number of protons in the nucleus holding the electrons tighter.
11. Hydrogen atom has only one electron total, therefore there are no other, lower energy (more penetrating), electrons available to help shield this electron from the nucleus.
12. Fluorine has a smaller radii than Beryllium due to its greater number of protons providing a greater effective nuclear charge on the outer electrons and therefore pulling them in tighter and providing a smaller atomic radii.
13. 2p has higher energy level because the negatively charged electron experiences less of an effective nuclear charge than the 2s electron.
14. because a Hydrogen atom has only one electron, that experiences no shielding from other electrons and therefore its energy level only depends on its distance away from the nucleus, which is dependent on it value of (n).
15. 2s shields the atom better than 2p because the s orbitals is much closer and surrounds the nucleus more than the p orbitals, which extend farther out. 3p shields better than 3d, because p orbitals are closer to the nucleus than the 3d orbitals.
16. Classical physics and quantum mechanics both can deal with subatomic activity such as electron interactions, orbital location, size, and shape, and distances to find forces of attractions.
17. Penetration is how well the outer electrons are shielded from the nucleus by the core electrons. The outer electrons therefore experience less of an attraction to the nucleus.

2.E.3 SIZES OF ATOMS AND IONS

2.E.3.1 CONCEPTUAL PROBLEMS

23. The electrons of the 1*s* shell have a stronger electrostatic attraction to the nucleus than electrons in the 2*s* shell. Give two reasons for this.
24. Predict whether Na or Cl has the more stable $1s^2$ shell and explain your rationale.
25. Arrange K, F, Ba, Pb, B, and I in order of decreasing atomic radius.
26. Arrange Ag, Pt, Mg, C, Cu, and Si in order of increasing atomic radius.
27. Using the periodic table, arrange Li, Ga, Ba, Cl, and Ni in order of increasing atomic radius.
28. Element M is a metal that forms compounds of the type MX_2, MX_3, and MX_4, where X is a halogen. What is the expected trend in the ionic radius of M in these compounds? Arrange these compounds in order of decreasing ionic radius of M.
29. The atomic radii of Na and Cl are 190 and 79 pm, respectively, but the distance between sodium and chlorine in NaCl is 282 pm. Explain this discrepancy.
30. Are shielding effects on the atomic radius more pronounced across a row or down a group? Why?
31. What two factors influence the size of an ion relative to the size of its parent atom? Would you expect the ionic radius of S^{2-} to be the same in both MgS and Na_2S? Why or why not?
32. Arrange Br^-, Al^{3+}, Sr^{2+}, F^-, O^{2-}, and I^- in order of increasing ionic radius.
33. Arrange P^{3-}, N^{3-}, Cl^-, In^{3+}, and S^{2-} in order of decreasing ionic radius.
34. How is an isoelectronic series different from a series of ions with the same charge? Do the cations in magnesium, strontium, and potassium sulfate form an isoelectronic series? Why or why not?
35. What isoelectronic series arises from fluorine, nitrogen, magnesium, and carbon? Arrange the ions in this series by
    1. increasing nuclear charge.
    2. increasing size.
36. What would be the charge and electron configuration of an ion formed from calcium that is isoelectronic with
    1. a chloride ion?
    2. Ar^+?

2.E.3.2 CONCEPTUAL ANSWERS

23. The 1*s* shell is closer to the nucleus and therefore experiences a greater electrostatic attraction. In addition, the electrons in the 2*s* subshell are shielded by the filled $1s^2$ shell, which further decreases the electrostatic attraction to the nucleus.
24.
25. Ba > K > Pb > I > B > F
26.

27.
28.
29. The sum of the calculated atomic radii of sodium and chlorine *atoms* is 253 pm. The sodium cation is significantly smaller than a neutral sodium atom (102 versus 154 pm), due to the loss of the single electron in the 3*s* orbital. Conversely, the chloride ion is much larger than a neutral chlorine atom (181 versus 99 pm), because the added electron results in greatly increased electron–electron repulsions within the filled $n = 3$ principal shell. Thus, transferring an electron from sodium to chlorine decreases the radius of sodium by about 50%, but causes the radius of chlorine to almost double. The net effect is that the distance between a sodium ion and a chloride ion in NaCl is *greater* than the sum of the atomic radii of the neutral atoms.

2.E.3.3 NUMERICAL PROBLEMS

37. Plot the ionic charge versus ionic radius using the following data for Mo: Mo^{3+}, 69 pm; Mo^{4+}, 65 pm; and Mo^{5+}, 61 pm. Then use this plot to predict the ionic radius of Mo^{6+}. Is the observed trend consistent with the general trends discussed in the chapter? Why or why not?
38. Internuclear distances for selected ionic compounds are given in the following table.
    - If the ionic radius of Li^+ is 76 pm, what is the ionic radius of each of the anions?

	LiF	LiCl	LiBr	LiI
Distance (pm)	209	257	272	296

    - What is the ionic radius of Na^+?

	NaF	NaCl	NaBr	NaI
Distance (pm)	235	282	298	322

    - Arrange the gaseous species Mg^{2+}, P^{3-}, Br^-, S^{2-}, F^-, and N^{3-} in order of increasing radius and justify your decisions.

2.E.4 IONIZATION ENERGY

2.E.4.1 CONCEPTUAL PROBLEMS

39. Identify each statement as either true or false and explain your reasoning.
    a. Ionization energies increase with atomic radius.
    b. Ionization energies decrease down a group.
    c. Ionization energies increase with an increase in the magnitude of the electron affinity.
    d. Ionization energies decrease diagonally across the periodic table from He to Cs.
    e. Ionization energies depend on electron configuration.
    f. Ionization energies decrease across a row.
40. Based on electronic configurations, explain why the first ionization energies of the group 16 elements are lower than those of the group 15 elements, which is contrary to the general trend.
41. The first through third ionization energies do not vary greatly across the lanthanides. Why? How does the effective nuclear charge experienced by the ns electron change when going from left to right (with increasing atomic number) in this series?
42. Most of the first row transition metals can form at least two stable cations, for example iron(II) and iron(III). In contrast, scandium and zinc each form only a single cation, the Sc^{3+} and Zn^{2+} ions, respectively. Use the electron configuration of these elements to provide an explanation.
43. Of the elements Nd, Al, and Ar, which will readily form(s) +3 ions? Why?
44. Orbital energies can reverse when an element is ionized. Of the ions B^{3+}, Ga^{3+}, Pr^{3+}, Cr^{3+}, and As^{3+}, in which would you expect this reversal to occur? Explain your reasoning.
45. The periodic trends in electron affinities are not as regular as periodic trends in ionization energies, even though the processes are essentially the converse of one another. Why are there so many more exceptions to the trends in electron affinities compared to ionization energies?
46. Elements lying on a lower right to upper left diagonal line cannot be arranged in order of increasing electronegativity according to where they occur in the periodic table. Why?
47. Why do ionic compounds form if energy is required to form gaseous cations?

48. Why is Pauling's definition of electronegativity considered to be somewhat limited?

49. Based on their positions in the periodic table, arrange Sb, O, P, Mo, K, and H in order of increasing electronegativity.

50. Based on their positions in the periodic table, arrange V, F, B, In, Na, and S in order of decreasing electronegativity.

2.E.4.2 CONCEPTUAL ANSWERS

43. Both Al and Nd will form a cation with a +3 charge. Aluminum is in Group 13, and loss of all three valence electrons will produce the Al^{3+} ion with a noble gas configuration. Neodymium is a lanthanide, and all of the lanthanides tend to form +3 ions because the ionization potentials do not vary greatly across the row, and a +3 charge can be achieved with many oxidants. Argon (Ar) does not form +3 ions because it is a noble gas with a full valence shell.

49. K < Mo ≈ Sb < P ≈ H < O

2.E.4.3 NUMERICAL PROBLEMS

51. The following table gives values of the first and third ionization energies for selected elements:

Number of Electrons	Element	I_1 ($E \rightarrow E^+ + e^-$, kJ/mol)	Element	I_3 ($E^{2+} \rightarrow E^{3+} + e^-$, kJ/mol)
11	Na	495.9	Al	2744.8
12	Mg	737.8	Si	3231.6
13	Al	577.6	P	2914.1
14	Si	786.6	S	3357
15	P	1011.9	Cl	3822
16	S	999.6	Ar	3931
17	Cl	1251.2	K	4419.6
18	Ar	1520.6	Ca	4912.4

Plot the ionization energies versus the number of electrons. Explain why the slopes of the I_1 and I_3 plots are different, even though the species in each row of the table have the same electron configurations.

52. Would you expect the third ionization energy of iron, corresponding to the removal of an electron from a gaseous Fe^{2+} ion, to be larger or smaller than the fourth ionization energy, corresponding to the removal of an electron from a gaseous Fe^{3+} ion? Why? How would these ionization energies compare to the first ionization energy of Ca?

53. Which would you expect to have the highest first ionization energy: Mg, Al, or Si? Which would you expect to have the highest third ionization energy. Why?

54. Use the values of the first ionization energies given in Figure 7.11 to construct plots of first ionization energy versus atomic number for (a) boron through oxygen in the second period; and (b) oxygen through tellurium in group 16. Which plot shows more variation?

Explain the reason for the variation in first ionization energies for this group of elements.

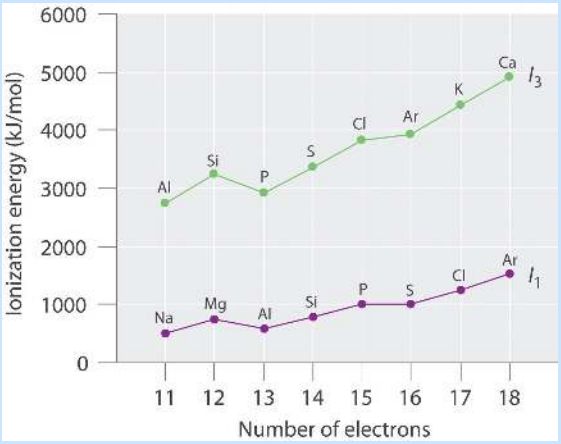
55. Arrange Ga, In, and Zn in order of increasing first ionization energies. Would the order be the same for second and third ionization energies? Explain your reasoning.
56. Arrange each set of elements in order of increasing magnitude of electron affinity.
    1. Pb, Bi, and Te
    2. Na, K, and Rb
    3. P, C, and Ge
57. Arrange each set of elements in order of decreasing magnitude of electron affinity.
    1. As, Bi, and N
    2. O, F, and Ar
    3. Cs, Ba, and Rb
58. Of the species F, O^-, Al^{3+}, and Li^+, which has the highest electron affinity? Explain your reasoning.
59. Of the species O^-, N^{2-}, Hg^{2+}, and H^+, which has the highest electron affinity? Which has the lowest electron affinity? Justify your answers.
60. The Mulliken electronegativity of element A is 542 kJ/mol. If the electron affinity of A is −72 kJ/mol, what is the first ionization energy of element A? Use the data in the following table as a guideline to decide if A is a metal, a nonmetal, or a semimetal. If 1 g of A contains 4.85×10^{21} molecules, what is the identity of element A?

	Na	Al	Si	S	Cl
EA (kJ/mol)	−59.6	−41.8	−134.1	−200.4	−348.6
I (kJ/mol)	495.8	577.5	786.5	999.6	1251.2

61. Based on their valence electron configurations, classify the following elements as either electrical insulators, electrical conductors, or substances with intermediate conductivity: S, Ba, Fe, Al, Te, Be, O, C, P, Sc, W, Na, B, and Rb.
62. Using the data in Problem 10, what conclusions can you draw with regard to the relationship between electronegativity and electrical properties? Estimate the approximate electronegativity of a pure element that is very dense, lustrous, and malleable.
63. Of the elements Al, Mg, O_2, Ti, I_2, and H_2, which, if any, would you expect to be a good reductant? Explain your reasoning.
64. Of the elements Zn, B, Li, Se, Co, and Br_2, which if any, would you expect to be a good oxidant? Explain your reasoning.
65. Determine whether each species is a good oxidant, a good reductant, or neither.
    1. Ba
    2. Mo
    3. Al
    4. Ni
    5. O_2
    6. Xe
66. Determine whether each species is a good oxidant, a good reductant, or neither.
    1. Ir
    2. Cs
    3. Be
    4. B
    5. N
    6. Po
    7. Ne
67. Of the species I_2, O^-, Zn, Sn^{2+}, and K^+, choose which you would expect to be a good oxidant. Then justify your answer.
68. Based on the valence electron configuration of the noble gases, would you expect them to have positive or negative electron affinities? What does this imply about their most likely oxidation states? their reactivity?

2.E.4.4 NUMERICAL ANSWERS

51.



The general features of both plots are roughly the same, with a small peak at 12 electrons and an essentially level region from 15–16 electrons. The slope of the I_3 plot is about twice as large as the slope of the I_1 plot, however, because the I_3 values correspond to removing an electron from an ion with a +2 charge rather than a neutral atom. The greater charge increases the effect of the steady rise in effective nuclear charge across the row.

52.

53. Electron configurations: Mg, $1s^2 2s^2 2p^6 3s^2$; Al, $1s^2 2s^2 2p^6 3s^2 3p^1$; Si, $1s^2 2s^2 2p^6 3s^2 3p^2$; First ionization energies increase across the row due to a steady increase in effective nuclear charge; thus, Si has the highest first ionization energy. The third ionization energy corresponds to removal of a 3*s* electron for Al and Si, but for Mg it involves removing a 2*p* electron from a filled inner shell; consequently, the third ionization energy of Mg is the highest.

54.

55.

56.

57. 1. Bi > As > N
    2. F > O >> Ar
    3. Rb > Cs > Ba

58.

59. $Hg^{2+} > H^+ > O^- > N^{2-}$; Hg^{2+} has the highest positive charge plus a relatively low energy vacant set of orbitals (the 6*p* subshell) to accommodate an added electron, giving it the greatest electron affinity; N^{2-} has a greater negative charge than O^-, so electron–electron repulsions will cause its electron affinity to be even lower (more negative) than that of O^-.

60.

61. insulators: S, O, C (diamond), P; conductors: Ba, Fe, Al, C (graphite), Be, Sc, W, Na, Rb; Te and B are semimetals and semiconductors.

62.

63. Mg, Al, Ti, and H_2

64.

65. 1. reductant
    2. neither
    3. reductant
    4. reductant
    5. oxidant
    6. neither

66.

67. I_2 is the best oxidant, with a moderately strong tendency to accept an electron to form the I^- ion, with a closed shell electron configuration. O^- would probably also be an oxidant, with a tendency to add an electron to form salts containing the oxide ion, O^{2-}. Zn and Sn^{2+} are all reductants, while K^+ has no tendency to act as an oxidant or a reductant.

2.E.5 ELECTRON AFFINITIES

see above question to tease out

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2.S: PERIODIC PROPERTIES OF THE ELEMENTS (SUMMARY)

2.S.1 7.1: DEVELOPMENT OF THE PERIODIC TABLE

- 1869: Dmitri Mendeleev (Russia) and Lothar Meyer (Germany) publish nearly identical schemes for classifying the elements
- Both had arranged the elements in order of increasing atomic weights
- Mendeleev predicted the existence and properties of Germanium (Ge) and Gallium (Ga). When they were discovered, their properties were found to closely match those predicted by Mendeleev
- 1913: Henry Moseley discovers concept of atomic numbers. Observed that frequencies of Xrays were different for each element. Was able to arrange these frequencies in order by assigning each element a unique whole number, which he called the *atomic number*

2.S.2 7.2: EFFECTIVE NUCLEAR CHARGE

- Orbitals with the same value of *n* are referred to as a *shell*
- When looking at a radial electrondensity graph, the maxima (peaks) designate the areas with the higher probabilities of finding electrons
- The 1s shell in Argon is closer to the nucleus than that of Helium. This is because both 1s shells are the only ones not shielded from the nucleus by other electrons. However, since Argon has a stronger nuclear charge, it can attract its electrons more easily
- radial electron density – probability of finding the electron at a particular distance from the nucleus
- as nuclear charge increases, 1s shells pulled closer to nucleus

2.S.3 7.3: SIZES OF ATOMS AND IONS

Atomic radius: radius of an atom of a given element

1. Within each group, the atomic radius tends to increase going from top to bottom
2. Within each period, the atomic radius tends to decrease moving left to right

Two factors determine the size of the outermost orbital

1. Its principal quantum number (as it increases, the size of the orbital increases)
2. The effective nuclear charge (reduces the size of the orbital by pulling electrons closer)

Atomic Sizes

- atomic radius – estimation of radius of atoms
- estimate by assuming that atoms are spheres that touch each other
- atomic radius increases down a group, decrease down row
- atomic radius affected by principal quantum number and effective nuclear charge
- increase principal quantum number, increases size of orbital
- increase effective nuclear charge, reduces size or orbital

2.S.4 7.4: IONIZATION ENERGY

Ionization energy: energy required to remove an electron from a gaseous atom when the atom is in its ground state.

- first ionization energy – energy needed to remove the first electron
- second ionization energy – energy needed to remove second electron
- the greater ionization energy, harder it is to remove electrons
- The *first* ionization energy, I_1, is the energy needed to remove the first electron. The *second* ionization energy, I_2, removes the second electron, and so on. The HIGHER the ionization energy, the MORE DIFFICULT it is to remove an electron. Every element exhibits a large increase in ionization energy when electrons are removed from its noblegas core. The inner electrons are too tightly bound to the nucleus to be lost from the atom or even shared with another atom

$$I_1 < I_2 < I_3$$

- Positive nuclear charge remains same, number electrons decreases -> effective nuclear charge increases
- Greater effective nuclear charge, greater energy required to remove electron
- Sharp increase in ionization energy when inner-shell electron removed
- Only outer most electrons involved in sharing and transfer of electrons in bonding and reactions

Periodic Trends in Ionization Energies

1. Within each period, I_1 generally increases with increasing atomic number. The alkali metals show the lowest ionization energy in each row, and the noble gases the highest
2. Within each group, ionization energy generally decreases with increasing atomic number.

- Energy needed to remove electrons from outer shell depends on nuclear charge and average distance between of the electron from the nucleus
- As we move across a period, there is both an increase in effective nuclear charge and a decrease in atomic radius, causing the ionization energy to increase
- As we move down a column, the atomic radius increases, while the effective charge remains essentially constant. Thus, the attraction between the nucleus and the electron decreases in this direction, causing the ionization energy to decrease.

2.S.5 7.5: ELECTRON AFFINITIES

- **Electron affinity**: energy change that occurs when an electron is added to a gaseous atom or ion
- For most neutral atoms and for all positively charged ions, energy is released when an electron is added
- The greater the attraction between the species and the added electron, the more exothermic the process
- On the other hand, adding an electron to anions and to some atoms makes them unstable.
- The general trend for electron affinity is to become increasingly negative (stronger binding of electrons) as we move across each period toward the halogens. The halogens have the most negative electron affinities since they are one electron short of noblegas configuration
- Electron affinities do not change greatly as we go down a group

2.S.6 7.6: METALS, NONMETALS, AND METALLOIDS

Metallic Elements and Nonmetallic Elements

Metallic elements	Nonmetallic elements
Distinguishing luster	Nonlustrous; various colors
Malleable and ductile as solids	Solids are usually brittle; may be hard or soft
Good thermal and electrical conductivity	Poor conductors of heat and electricity
Most metallic oxides are basic, ionic solids	Most nonmetallic oxides are molecular, acidic compounds
Exist in aqueous solution mainly as cations	Exist in aqueous solution mainly as anions or oxyanions

Metals

- See properties above. All are solids at room temperature except mercury, which is a liquid.
- Metals tend to have low ionization energies and are consequently oxidized (lose electrons) when they undergo chemical reaction.
- Compounds of metals with nonmetals tend to be ionic substances
- Most metals are **basic oxides** (oxide that either reacts with water to form a base or reacts with an acid to form a salt and water)

Nonmetals

- Generally have lower melting points than those of metals.
- Seven nonmetals exist as diatomic molecules under ordinary conditions (H_2, N_2, O_2, F_2, Cl_2, Br_2, I_2). Bromine is liquid; Iodine is a volatile solid, the rest are gases. The remaining nonmetals are solids.
- Nonmetals, in reacting with metals, tend to gain electrons and become anions
- Compound composed entirely of nonmetals are molecular substances
- Most nonmetals are **acidic oxides** (oxide that forms acid when added to water; soluble nonmetal oxides are acidic oxides)

Metalloids

- Have properties intermediate between those of metals and nonmetals. May have some metallic properties but lack others.
- Several metalloids are electrical semiconductors

Trends in Metallic and Nonmetallic Character

Metallic character: the extent to which an element exhibits the physical and chemical properties characteristic of metals, for example, luster, malleability, ductility, and good thermal and electrical conductivity.

1. Metallic character is strongest for the elements in the leftmost part of the periodic table and tends to decrease as we move to the right in any period
2. Within any group of representative elements, the metallic character increases progressively from top to bottom

2.S.7 7.7: GROUP TRENDS FOR THE ACTIVE METALS

Group 1: The Alkali Metals

- Metallic properties; silvery, metallic luster, high thermal and electrical conductivity
- Low densities and melting points; increasing atomic radius and decreasing ionization energy as we move down the family
- Lowest I_1 values of the elements, which reflects the ease with which their outer electrons can be removed. This makes the alkali metals very reactive, readily losing one electron.
- In the hydrides of the alkali metals (LiH, NaH, and so forth), hydrogen is present as H, called the **hydride ion**.
- The alkali metals react vigorously with water, producing hydrogen gas and solutions of alkali metal hydroxides (very exothermic).

Group 2: The Alkaline Earth Metals

- Solids, typical metallic properties, denser and harder than alkali metals (also melt at higher temperatures)
- Less reactive than alkali metals (have slightly higher ionization energy)
- Ease with which the elements lose their electrons increases as we move down the family

2.S.8 7.8: GROUP TRENDS FOR SELECTED NONMETALS

Hydrogen

- Hydrogen is a nonmetal, which occurs as a diatomic gas under normal conditions
- Its ionization energy is considerably higher (due to lack of shielding, and thus higher Z_{eff}) thatn the metals and is more like the nonmetals
- Hydrogen generally reacts with other nonmetals to form molecular compounds (typically highly exothermic)
- Hydrogen reacts with active metals to form metal hydrides that contain the H hydride ion
- Hydrogen can also lose an electron to yield the aqueous H^+ ion

Group 16: The Oxygen Family

- As we proceed down group 6A, the increase in metallic character is clearly evident
- **Allotropes**: different forms of the same element in the same state (ie: O_2 and O_3)
- Oxygen has a great tendency to attract electrons from other elements ("oxidize" them)
- Oxygen in combination with metals is almost always present as the oxide, O^2 ion, which has noblegas configuration and is particularly stable
- Sulfur is the second most important element in the 6A group. It also exists in several allotropic, the most common and stable being S_8.
- Sulfur also has a great tendency to gain electrons from other elements to form sulfides
- Because Sulfur is below Oxygen, its tendency to form sulfide anions is not is not as great as that of Oxygen to form oxide ions

Group 17: The Halogens

- All halogens are typical nonmetals. Their melting and boiling points increase with increasing atomic numbers
- Fluorine and Chlorine are gases at room temperature, Bromine is a liquid, and Iodine is a solid
- The halogens have among the most negative electron affinities; they have a great tendency to gain electrons.
- Fluorine and Chlorine are the most reactive. Fluorine removes electrons from almost any substance, even water, and usually very exothermically.
- Halogens react with most metals to form ionic halides and with Hydrogen to form gaseous hydrogen halides.

Group 18: The Noble Gases

- All noble gases are monoatomic (single atom)
- All have large first ionization energies, with a decrease as we go down the group
- Until the early 1960's, they were called *inert gases* because they were thought to be incapable of forming chemical compounds.
- Only noblegas compounds known today are: XeF_2, XeF_4, XeF_6, and KrF_2

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CHAPTER OVERVIEW

3: BASIC CONCEPTS OF CHEMICAL BONDING

A general chemistry Libretexts Textmap organized around the textbook

Chemistry: The Central Science

by Brown, LeMay, Bursten, Murphy, and Woodward

Template:HideTOC

We described the relationship between the chemical properties and reactivity of an element and its position in the periodic table. In this chapter and the following chapter, we describe the interactions that hold atoms together in chemical substances, and we examine the factors that determine how the atoms of a substance are arranged in space. Our goal is to understand how the properties of the component atoms in a chemical compound determine the structure and reactivity of the compound. The properties described previously were properties of isolated atoms, yet most of the substances in our world consist of atoms held together in molecules, ionic compounds, or metallic solids. The properties of these substances depend on not only the characteristics of the component atoms but also how those atoms are bonded to one another.

What you learn in this chapter about chemical bonding and molecular structure will help you understand how different substances with the same atoms can have vastly different physical and chemical properties. For example, oxygen gas (O_2) is essential for life, yet ozone (O_3) is toxic to cells, although as you learned previously, ozone in the upper atmosphere shields us from harmful ultraviolet light. Moreover, you saw that diamond is a hard, transparent solid that is a gemstone; graphite is a soft, black solid that is a lubricant; and fullerenes are molecular species with carbon cage structures—yet all of these are composed of carbon. As you learn about bonding, you will also discover why, although carbon and silicon both have ns^2np^2 valence electron configurations and form dioxides, CO_2 is normally a gas that condenses into the volatile molecular solid known as dry ice, whereas SiO_2 is a nonvolatile solid with a network structure that can take several forms, including beach sand and quartz crystals.

3.1: Chemical Bonds, Lewis Symbols, and the Octet Rule

3.2: Ionic Bonding

3.3: Covalent Bonding

3.4: Bond Polarity and Electronegativity

3.5: Drawing Lewis Structures

3.6: Resonance Structures

3.7: Exceptions to the Octet Rule

3.8: Strength of Covalent Bonds

3.E: Basic Concepts of Chemical Bonding (Exercises)

3.S: Basic Concepts of Chemical Bonding (Summary)

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3.1: CHEMICAL BONDS, LEWIS SYMBOLS, AND THE OCTET RULE

LEARNING OBJECTIVES

- To use Lewis electron dot symbols to predict the number of bonds an element will form.

Why are some substances chemically bonded molecules and others are an association of ions? The answer to this question depends upon the electronic structures of the atoms and nature of the chemical forces within the compounds. Although there are no sharply defined boundaries, chemical bonds are typically classified into three main types: ionic bonds, covalent bonds, and metallic bonds. In this chapter, each type of bond wil be discussed and the general properties found in typical substances in which the bond type occurs

1. Ionic bonds results from ***electrostatic forces that exist between ions of opposite charge***. These bonds typically involves a metal with a nonmetal
2. Covalent bonds ***result from the sharing of electrons between two atoms***. The bonds typically involves one nonmetallic element with another
3. Metallic bonds These bonds are found in solid metals (copper, iron, aluminum) with each metal bonded to several neighboring groups and bonding electrons free to move throughout the 3-dimensional structure.

Each bond classification is discussed in detail in subsequent sections of the chapter. Let's look at the preferred arrangements of electrons in atoms when they form chemical compounds.

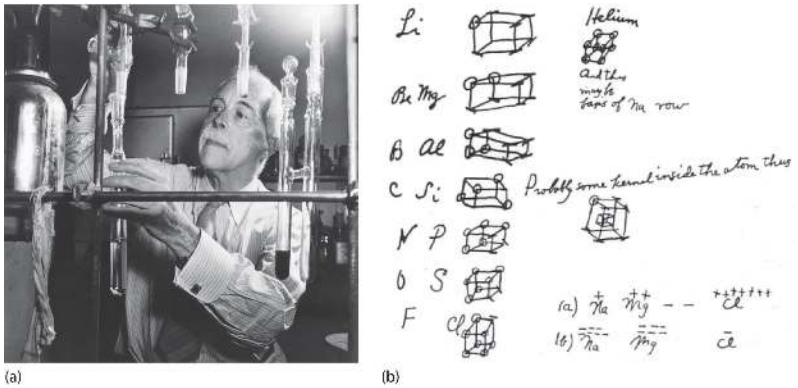


Figure **3.1.1**: G. N. Lewis and the Octet Rule. (a) Lewis is working in the laboratory. (b) In Lewis's original sketch for the octet rule, he initially placed the electrons at the corners of a cube rather than placing them as we do now.

3.1.1 LEWIS SYMBOLS

At the beginning of the 20th century, the American chemist G. N. Lewis (1875–1946) devised a system of symbols—now called *Lewis electron dot symbols* (often shortened to *Lewis dot symbols*) that can be used for predicting the number of bonds formed by most elements in their compounds. Each Lewis dot symbol consists of the chemical symbol for an element surrounded by dots that represent its valence electrons.

LEWIS DOT SYMBOLS:

- convenient representation of valence electrons
- allows you to keep track of valence electrons during bond formation
- consists of the chemical symbol for the element plus a dot for each valence electron

To write an element's Lewis dot symbol, we place dots representing its valence electrons, one at a time, around the element's chemical symbol. Up to four dots are placed above, below, to the left, and to the right of the symbol (in any order, as long as elements with four or fewer valence electrons have no more than one dot in each position). The next dots, for elements with more than four valence electrons, are again distributed one at a time, each paired with one of the first four. For example, the electron configuration for atomic sulfur is [Ne]$3s^2 3p^4$, thus there are ***six*** valence electrons. Its Lewis symbol would therefore be:



Fluorine, for example, with the electron configuration [He]$2s^2 2p^5$, has seven valence electrons, so its Lewis dot symbol is constructed as follows:

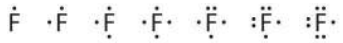


Figure 8.1.2.

Lewis used the unpaired dots to predict the number of bonds that an element will form in a compound. Consider the symbol for nitrogen in Figure 8.1.2. The Lewis dot symbol explains why nitrogen, with three unpaired valence electrons, tends to form compounds in which it shares the unpaired electrons to form three bonds. Boron, which also has three unpaired valence electrons in its Lewis dot symbol, also tends to form compounds with three bonds, whereas carbon, with four unpaired valence electrons in its Lewis dot symbol, tends to share all of its unpaired valence electrons by forming compounds in which it has four bonds.

Element	Electron config.	Electron dot symbol
Li	[He]$2s^1$	Li•
Be	[He]$2s^2$	•Be•
B	[He]$2s^2 2p^1$	•B•
C	[He]$2s^2 2p^2$	•C•
N	[He]$2s^2 2p^3$	•N:
O	[He]$2s^2 2p^4$	:O:
F	[He]$2s^2 2p^5$	:F:
Ne	[He]$2s^2 2p^6$	:Ne:

Figure **3.1.2**: Lewis Dot Symbols for the Elements in Period 2

L i has one dot on the right, B e has one dot on the left and right, B has one dot on the left, right, and above. C has one dot above, below, on the left and on the right. N has one dot above, below, on the left and two dots on the right. O has two dots on the left and right and one dot above and below. F has two dots above, on the left, on the right and on dot below. N e has two dots above, below, on the right, and on the left.



3.1.2 THE OCTET RULE

In 1904, Richard Abegg formulated what is now known as *Abegg's rule*, which states that the difference between the maximum positive and negative valences of an element is frequently eight. This rule was used later in 1916 when Gilbert N. Lewis formulated the "octet rule" in his cubical atom theory. The **octet rule** refers to the tendency of atoms to prefer to have eight electrons in the *valence shell*. When atoms have fewer than eight electrons, they tend to react and form more stable compounds. Atoms will react to get in the most stable state possible. A complete octet is very stable because all orbitals will be full. Atoms with greater stability have less energy, so a reaction that increases the stability of the atoms will release energy in the form of heat or light ;reactions that decrease stability must absorb energy, getting colder.

When discussing the octet rule, we do not consider *d* or *f* electrons. Only the s and p electrons are involved in the octet rule, making it a useful rule for the *main group elements* (elements not in the transition metal or inner-transition metal blocks); an octet in these atoms corresponds to an electron configurations ending with s^2p^6.

DEFINITION: OCTET RULE

A stable arrangement is attended when the atom is surrounded by eight electrons. This octet can be made up by own electrons and some electrons which are shared. Thus, an atom continues to form bonds until an octet of electrons is made. This is known as octet rule by Lewis.

1. Normally two electrons pairs up and forms a bond, e.g., $\mathbf{H_2}$
2. For most atoms there will be a maximum of eight electrons in the valence shell (octet structure), e.g., $\mathbf{CH_4}$

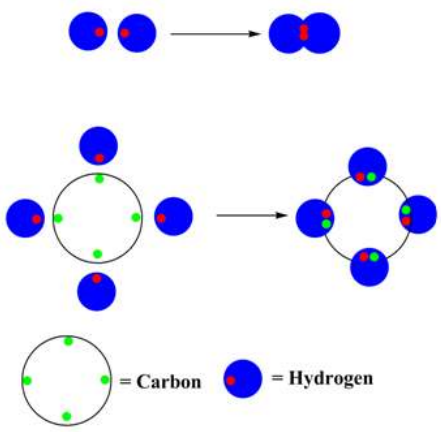


Figure 1: Bonding in $\boldsymbol{H_2}$ and methane ($\boldsymbol{CH_4}$)

A hydrogen bonds with each of the four valence electrons of a carbon meaning that four hydrogens can bond with one carbon.

The other tendency of atoms is to maintain a neutral charge. Only the noble gases (the elements on the right-most column of the periodic table) have zero charge with filled valence octets. All of the other elements have a charge when they have eight electrons all to themselves. The result of these two guiding principles is the explanation for much of the reactivity and bonding that is observed within atoms: atoms seek to share electrons in a way that minimizes charge while fulfilling an octet in the valence shell.

The noble gases rarely form compounds. They have the most stable configuration (full octet, no charge), so they have no reason to react and change their configuration. All other elements attempt to gain, lose, or share electrons to achieve a noble gas configuration.

EXAMPLE 3.1.1: SALT

The formula for table salt is NaCl. It is the result of Na^+ ions and Cl^- ions bonding together. If sodium metal and chlorine gas mix under the right conditions, they will form salt. The sodium loses an electron, and the chlorine gains that electron. In the process, a great amount of light and heat is released. The resulting salt is mostly unreactive — it is stable. It will not undergo any explosive reactions, unlike the sodium and chlorine that it is made of. Why?

Solution

Referring to the octet rule, atoms attempt to get a noble gas electron configuration, which is eight valence electrons. Sodium has one valence electron, so giving it up would result in the same electron configuration as neon. Chlorine has seven valence electrons, so if it takes one it will have eight (an octet). Chlorine has the electron configuration of argon when it gains an electron.

The octet rule could have been satisfied if chlorine gave up all seven of its valence electrons and sodium took them. In that case, both would have the electron configurations of noble gasses, with a full valence shell. However, their charges would be much higher. It would be Na^{7-} and Cl^{7+}, which is much less stable than Na^+ and Cl^-. Atoms are more stable when they have no charge, or a small charge.

Lewis dot symbols can also be used to represent the ions in ionic compounds. The reaction of cesium with fluorine, for example, to produce the ionic compound CsF can be written as follows:



No dots are shown on Cs^+ in the product because cesium has lost its single valence electron to fluorine. The transfer of this electron produces the Cs^+ ion, which has the valence electron configuration of Xe, and the F^- ion, which has a total of eight valence electrons (an octet) and the Ne electron configuration. This description is consistent with the statement that among the main group elements, ions in simple binary ionic compounds generally have the electron configurations of the nearest noble gas. The charge of each ion is written in the product, and the anion and its electrons are enclosed in brackets. This notation emphasizes that the ions are associated electrostatically; no electrons are shared between the two elements.

> *Atoms often gain, lose, or share electrons to achieve the same number of electrons as the noble gas closest to them in the periodic table.*

As you might expect for such a qualitative approach to bonding, there are exceptions to the octet rule, which we describe elsewhere. These include molecules in which one or more atoms contain fewer or more than eight electrons.

3.1.3 SUMMARY

Lewis dot symbols can be used to predict the number of bonds formed by most elements in their compounds. One convenient way to predict the number and basic arrangement of bonds in compounds is by using **Lewis electron dot symbols**, which consist of the chemical symbol for an element surrounded by dots that represent its valence electrons, grouped into pairs often placed above, below, and to the left and right of the symbol. The structures reflect the fact that the elements in period 2 and beyond tend to gain, lose, or share electrons to reach a total of eight valence electrons in their compounds, the so-called **octet rule**. Hydrogen, with only two valence electrons, does not obey the octet rule.

3.1.4 CONTRIBUTORS AND ATTRIBUTIONS

- Mike Blaber (Florida State University)
- Wikipedia
- National Programme on Technology Enhanced Learning (India)

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3.2: IONIC BONDING

LEARNING OBJECTIVES

- To describe the characteristics of ionic bonding.
- To quantitatively describe the energetic factors involved in the formation of an ionic bond.

Ions are atoms or molecules which are electrically charged. **Cations** are positively charged and **anions** carry a negative charge. Ions form when atoms gain or lose electrons. Since electrons are negatively charged, an atom that loses one or more electrons will become positively charged; an atom that gains one or more electrons becomes negatively charged. **Ionic bonding** is the attraction between positively- and negatively-charged ions. These oppositely charged ions attract each other to form ionic networks (or **lattices**). Electrostatics explains why this happens: opposite charges attract and like charges repel. When many ions attract each other, they form large, ordered, crystal lattices in which each ion is surrounded by ions of the opposite charge. Generally, when metals react with non-metals, electrons are transferred from the metals to the non-metals. The metals form positively-charged ions and the non-metals form negatively-charged ions.

3.2.1 GENERATING IONIC BONDS

Ionic bonds form when metals and non-metals chemically react. By definition, a metal is relatively stable if it loses electrons to form a complete valence shell and becomes positively charged. Likewise, a non-metal becomes stable by gaining electrons to complete its valence shell and become negatively charged. When metals and non-metals react, the metals lose electrons by transferring them to the non-metals, which gain them. Consequently, ions are formed, which instantly attract each other—ionic bonding.

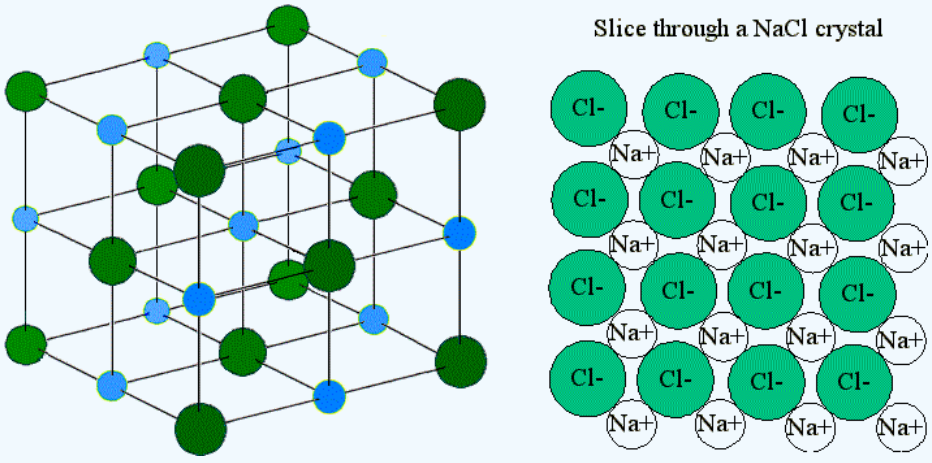
In the overall ionic compound, positive and negative charges must be balanced, because electrons cannot be created or destroyed, only transferred. Thus, the total number of electrons lost by the cationic species must equal the total number of electrons gained by the anionic species.

EXAMPLE 3.2.1: SODIUM CHLORIDE

For example, in the reaction of Na (sodium) and Cl (chlorine), each Cl atom takes one electron from a Na atom. Therefore each Na becomes a Na^+ cation and each Cl atom becomes a Cl^- anion. Due to their opposite charges, they attract each other to form an ionic lattice. The formula (ratio of positive to negative ions) in the lattice is **NaCl**.

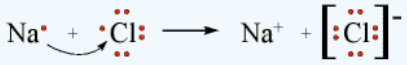
$$2\,Na\,(s) + Cl\,2\,(g) \rightarrow 2\,NaCl\,(s)$$

These ions are arranged in solid NaCl in a regular three-dimensional arrangement (or lattice):



NaCl lattice. (left) 3-D structure and (right) simple 2D slice through lattes. Images used with permission from Wikipedia and Mike Blaber.

The chlorine has a high affinity for electrons, and the sodium has a low ionization energy. Thus the chlorine gains an electron from the sodium atom. This can be represented using ewis dot symbols (here we will consider one chlorine atom, rather than Cl_2):



Chlorine becomes more negative when it takes the one valence electron from sodium when it makes an octet.

The arrow indicates the transfer of the electron from sodium to chlorine to form the Na^+ metal ion and the Cl^- chloride ion. Each ion now has an **octet** of electrons in its valence shell:

- Na^+: $2s^2 2p^6$
- Cl^-: $3s^2 3p^6$

3.2.2 ENERGETICS OF IONIC BOND FORMATION

Ionic bonds are formed when positively and negatively charged ions are held together by electrostatic forces. Consider a single pair of ions, one cation and one anion. How strong will the force of their attraction be? According to **Coulomb's Law**, the energy of the electrostatic attraction (***E***) between two charged particles is proportional to the magnitude of the charges and inversely proportional to the internuclear distance between the particles (***r***):

$$E \propto \frac{Q_1 Q_2}{r} \tag{3.2.1}$$

$$E = k\frac{Q_1 Q_2}{r} \tag{3.2.2}$$

where each ion's charge is represented by the symbol Q. The proportionality constant k is equal to 2.31×10^{-28} J·m. This value of k includes the charge of a single electron (1.6022×10^{-19} C) for each ion. The equation can also be written using the charge of each ion, expressed in coulombs (C), incorporated in the constant. In this case, the proportionality constant, k, equals 8.999×109 J·m/C^2. In the example given, Q_1 = +1(1.6022×10^{-19} C) and Q_2 = −1(1.6022×10^{-19} C). If Q_1 and Q_2 have opposite signs (as in NaCl, for example, where Q_1 is +1 for Na^+ and Q_2 is −1 for Cl^-), then E is negative, which means that energy is *released* when oppositely charged ions are brought together from an infinite distance to form an isolated ion pair.

> *Energy is always released when a bond is formed and correspondingly, it always requires energy to break a bond.*

As shown by the green curve in the lower half of Figure **3.2.1**, the maximum energy would be released when the ions are infinitely close to each other, at $r = 0$. Because ions occupy space and have a structure with the positive nucleus being surrounded by electrons, however, they cannot be infinitely close together. At very short distances, repulsive electron–electron interactions between electrons on adjacent ions become stronger than the attractive interactions between ions with opposite charges, as shown by the red curve in the upper half of Figure **3.2.1**. The total energy of the system is a balance between the attractive and repulsive interactions. The purple curve in Figure **3.2.1** shows that the total energy of the system reaches a minimum at r_0, the point where the electrostatic repulsions and attractions are exactly balanced. This distance is the same as the experimentally measured **bond distance**.

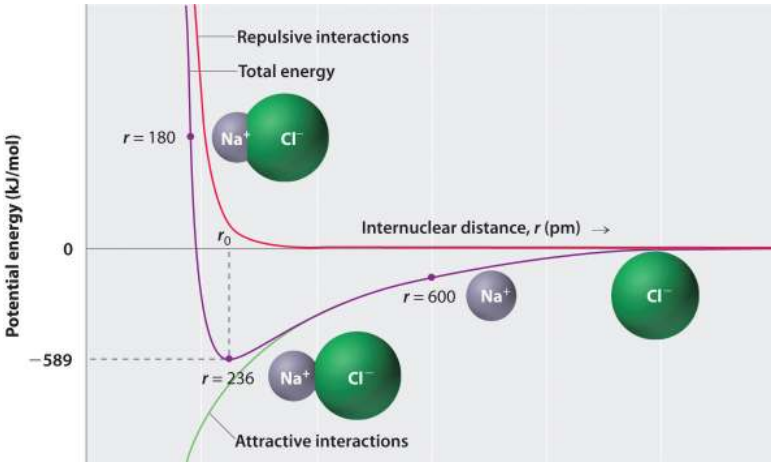


Figure **3.2.1**: A Plot of Potential Energy versus Internuclear Distance for the Interaction between a Gaseous Na^+ Ion and a Gaseous Cl^- Ion. The energy of the system reaches a minimum at a particular distance (r_0) when the attractive and repulsive interactions are balanced.

Consider the energy released when a gaseous Na^+ ion and a gaseous Cl^- ion are brought together from $r = \infty$ to $r = r_0$. Given that the observed gas-phase internuclear distance is 236 pm, the energy change associated with the formation of an ion pair from an $Na^+_{(g)}$ ion and a $Cl^-_{(g)}$ ion is as follows:

$$\begin{aligned} E &= k\frac{Q_1Q_2}{r_0} \\ &= (2.31 \times 10^{-28}\,\text{J} \cdot \cancel{\text{m}}) \left(\frac{(+1)(-1)}{236\ \cancel{\text{pm}} \times 10^{-12}\ \cancel{\text{m/pm}}} \right) \\ &= -9.79 \times 10^{-19}\ J/ion\ pair \end{aligned}$$

The negative value indicates that energy is released. Our convention is that if a chemical process provides energy to the outside world, the energy change is negative. If it requires energy, the energy change is positive. To calculate the energy change in the formation of a mole of NaCl pairs, we need to multiply the energy per ion pair by Avogadro's number:

$$E = \left(-9.79 \times 10^{-19}\ J/\cancel{ionpair}\right)\left(6.022 \times 10^{23}\ \cancel{ion\ pair}/mol\right) = -589\ kJ/mol \tag{3.2.3}$$

This is the energy released when 1 mol of gaseous ion pairs is formed, *not* when 1 mol of positive and negative ions condenses to form a crystalline lattice. Because of long-range interactions in the lattice structure, this energy does not correspond directly to the **lattice energy** of the crystalline solid. However, the large negative value indicates that bringing positive and negative ions together is energetically very favorable, whether an ion pair or a crystalline lattice is formed.

We summarize the important points about ionic bonding:

- At r_0, the ions are more stable (have a lower potential energy) than they are at an infinite internuclear distance. When oppositely charged ions are brought together from $r = \infty$ to $r = r_0$, the energy of the system is lowered (energy is released).
- Because of the low potential energy at r_0, energy must be added to the system to separate the ions. The amount of energy needed is the bond energy.
- The energy of the system reaches a minimum at a particular internuclear distance (the bond distance).

EXAMPLE 3.2.2: LIF

Calculate the amount of energy released when 1 mol of gaseous Li^+F^- ion pairs is formed from the separated ions. The observed internuclear distance in the gas phase is 156 pm.

Given: cation and anion, amount, and internuclear distance

Asked for: energy released from formation of gaseous ion pairs

Strategy:

Substitute the appropriate values into Equation 3.2.2 to obtain the energy released in the formation of a single ion pair and then multiply this value by Avogadro's number to obtain the energy released per mole.

Solution:

Inserting the values for Li^+F^- into Equation 3.2.2 (where $Q_1 = +1$, $Q_2 = -1$, and $r = 156$ pm), we find that the energy associated with the formation of a single pair of Li^+F^- ions is

$$\begin{aligned} E &= k\frac{Q_1Q_2}{r_0} \\ &= \left(2.31 \times 10^{-28} J \cdot \cancel{m}\right)\left(\frac{(+1)(-1)}{156\ pm \times 10^{-12}\ \cancel{m/pm}}\right) \\ &= -1.48 \times 10^{-18} \end{aligned}$$

Then the energy released per mole of Li^+F^- ion pairs is

$$E = \left(-1.48 \times 10^{-18} J/\cancel{\text{ion pair}}\right)\left(6.022 \times 10^{23}\ \cancel{\text{ion pair}}/mol\right)$$
$$-891\ kJ/mol$$

Because Li^+ and F^- are smaller than Na^+ and Cl^- (see Section 7.3), the internuclear distance in LiF is shorter than in NaCl. Consequently, in accordance with Equation 3.2.2, much more energy is released when 1 mol of gaseous Li^+F^- ion pairs is formed (−891 kJ/mol) than when 1 mol of gaseous Na^+Cl^- ion pairs is formed (−589 kJ/mol).

? EXERCISE 3.2.2: MAGNESIUM OXIDE

Calculate the amount of energy released when 1 mol of gaseous **MgO** ion pairs is formed from the separated ions. The internuclear distance in the gas phase is 175 pm.

Answer

-3180 kJ/mol = -3.18×10^3 kJ/mol

3.2.3 ELECTRON CONFIGURATION OF IONS

How does the energy released in lattice formation compare to the energy required to strip away a second electron from the Na^+ ion? Since the Na^+ ion has a noble gas electron configuration, stripping away the next electron from this stable arrangement would require more energy than what is released during lattice formation (Sodium I_2 = 4,560 kJ/mol). Thus, sodium is present in ionic compounds as Na^+ and not Na^{2+}. Likewise, adding an electron to fill a valence shell (and achieve noble gas electron configuration) is exothermic or only slightly endothermic. To add an additional electron into a ***new*** subshell requires tremendous energy - more than the lattice energy. Thus, we find Cl^- in ionic compounds, but not Cl^{2-}.

Table **3.2.1**: Lattice energies range from around 700 kJ/mol to 4000 kJ/mol:

Compound	Lattice Energy (kJ/mol)
LiF	1024
LiI	744
NaF	911
NaCl	788
NaI	693
KF	815
KBr	682
KI	641
MgF_2	2910
$SrCl_2$	2130
MgO	3938

This amount of energy can compensate for values as large as I_3 for valence electrons (i.e. can strip away up to 3 valence electrons). Because most transition metals would require the removal of more than 3 electrons to attain a noble gas core, they are not found in ionic compounds with a noble gas core. A transition metal always loses electrons first from the higher 's' subshell, before losing from the underlying 'd' subshell. (The remaining electrons in the unfilled d subshell are the reason for the bright colors observed in many transition metal compounds!) For example, iron ions will **not** form a noble gas core:

- Fe: $[Ar]4s^2 3d^6$
- Fe^{2+}: $[Ar]\ 3d^6$
- Fe^{3+}: $[Ar]\ 3d^5$

Some metal ions can form a pseudo noble gas core (and be colorless), for example:

- Ag: $[Kr]5s^1 4d^{10}$ Ag^+ $[Kr]4d^{10}$ Compound: AgCl
- Cd: $[Kr]5s^2 4d^{10}$ Cd^{2+} $[Kr]4d^{10}$ Compound: CdS

The valence electrons do not adhere to the "octet rule" in this case (a limitation of the usefulness of this rule). Note: The silver and cadmium atoms lost the 5s electrons in achieving the ionic state.

> *When a positive ion is formed from an atom, electrons are **always** lost first from the subshell with the largest principle quantum number*

3.2.4 POLYATOMIC IONS

Not all ionic compounds are formed from only two elements. Many **polyatomic ions** exist, in which two or more atoms are bound together by covalent bonds. They form a stable grouping which carries a charge (positive or negative). The group of atoms as a whole acts as a charged species in forming an ionic compound with an oppositely charged ion. Polyatomic ions may be either positive or negative, for example:

- NH_4^+ (ammonium) = cation
- SO_4^{2-} (sulfate) = anion

The principles of ionic bonding with polyatomic ions are the same as those with monatomic ions. Oppositely charged ions come together to form a crystalline lattice, releasing a lattice energy. Based on the shapes and charges of the polyatomic ions, these compounds may form crystalline lattices with interesting and complex structures.

3.2.5 SUMMARY

The amount of energy needed to separate a gaseous ion pair is its bond energy. The formation of ionic compounds are usually ***extremely exothermic***. The strength of the electrostatic attraction between ions with opposite charges is directly proportional to the magnitude of the charges on the ions and inversely proportional to the internuclear distance. The total energy of the system is a balance between the repulsive interactions between electrons on adjacent ions and the attractive interactions between ions with opposite charges.

3.2.6 CONTRIBUTORS AND ATTRIBUTIONS

- Wikibooks [en.wikibooks.org]
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3.3: COVALENT BONDING

LEARNING OBJECTIVES

- To understand the relationship between bond order, bond length, and bond energy.

In proposing his theory that octets can be completed by two atoms sharing electron pairs, Lewis provided scientists with the first description of covalent bonding. In this section, we expand on this and describe some of the properties of covalent bonds. The general properties of Ionic substances are:

- usually brittle
- high melting point
- organized into an ordered lattice of atoms, which can be cleaved along a smooth line

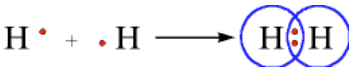
However, the vast majority of chemical substances are ***not ionic*** in nature. G.N. Lewis reasoned that an atom might attain a noble gas electron configuration by ***sharing*** electrons.

> *A chemical bond formed by sharing a pair of electrons is called a covalent bond*

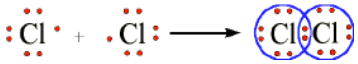
3.3.1 LEWIS STRUCTURES

Lewis structures (also known as Lewis dot diagrams, electron dot diagrams, Lewis dot formulas, Lewis dot structures, and electron dot structures) are diagrams that show the bonding between atoms of a molecule and the lone pairs of electrons that may exist in the molecule. Lewis structures show each atom and its position in the structure of the molecule using its chemical symbol. Lines are drawn between atoms that are bonded to one another (pairs of dots can be used instead of lines). Excess electrons that form lone pairs are represented as pairs of dots, and are placed next to the atoms.

The diatomic hydrogen molecule (H_2) is the simplest model of a covalent bond, and is represented in Lewis structures as:



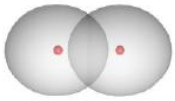
The ***shared pair*** of electrons provides ***each*** hydrogen atom with two electrons in its valence shell (the 1*s*) orbital. In a sense, each hydrogen atoms has the electron configuration of the noble gas helium When two chlorine atoms covalently bond to form Cl_2, the following sharing of electrons occurs:



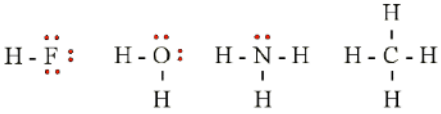
Each chlorine atom shared the bonding pair of electrons and achieves the electron configuration of the noble gas argon. In Lewis structures the bonding pair of electrons is usually displayed as a line, and the unshared electrons as dots:



The shared electrons are not located in a fixed position between the nuclei. In the case of the H_2 compound, the electron density is concentrated between the two nuclei:



The two atoms are bound into the H_2 molecule mainly due to the attraction of the positively charged nuclei for the negatively charged electron cloud located between them. Examples of hydride compounds of the above elements (covalent bonds with hydrogen:



3.3.2 MULTIPLE BONDS

The sharing of a pair of electrons represents a single covalent bond, usually just referred to as a ***single bond***. However, in many molecules atoms attain complete octets by sharing more than one pair of electrons between them:

- Two electron pairs shared a ***double bond***
- Three electron pairs shared a ***triple bond***



If two electron pairs are shared then two lines are drawn. If three electron pairs are shared then three lines are drawn

Because each nitrogen contains 5 valence electrons, they need to share 3 pairs to each achieve a valence octet. N_2 is fairly inert, due to the strong triple bond between the two nitrogen atoms and the N - N bond distance in N_2 is 1.10 Å (fairly short). From a study of various Nitrogen containing compounds bond distance as a function of bond type can be summarized as follows:

- **N–N**: 1.47Å
- **N=N**: 1.24Å
- **N : =N**:1.10Å

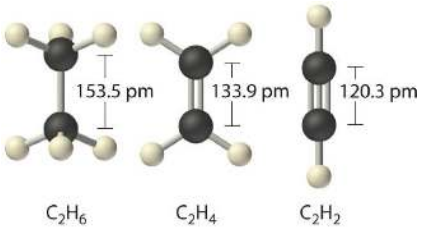
For the nonmetals (and the 's' block metals) the number of valence electrons is equal to the group number:

nonmetals (and the 's' block metals) the number of valence electrons is equal to the group number

Element	Group	Valence electrons	Bonds needed to form valence octet
aF	17	7	1
O	16	6	2
N	15	5	3
C	14	4	4



Thus, the Lewis bonds successfully describe the covalent interactions between various nonmetal elements. When we draw Lewis structures, we place one, two, or three pairs of electrons between adjacent atoms. In the Lewis bonding model, the number of electron pairs that hold two atoms together is called the bond order. For a single bond, such as the C–C bond in $H_3C–CH_3$, the bond order is one. For a double bond (such as $H_2C=CH_2$), the bond order is two. For a triple bond, such as HC≡CH, the bond order is three.



When analogous bonds in similar compounds are compared, bond length decreases as bond order increases. The bond length data in Table **3.3.1**, for example, show that the C–C distance in $H_3C–CH_3$ (153.5 pm) is longer than the distance in $H_2C=CH_2$ (133.9 pm), which in turn is longer than that in HC≡CH (120.3 pm). Additionally, as noted in Section 8.5, molecules or ions whose bonding must be described using resonance structures usually have bond distances that are intermediate between those of single and double bonds, as we demonstrated with

the C–C distances in benzene. The relationship between bond length and bond order is not linear, however. A double bond is not half as long as a single bond, and the length of a C=C bond is not the average of the lengths of C≡C and C–C bonds. Nevertheless, as bond orders increase, bond lengths generally decrease.

Table **3.3.1**: Bond Lengths and Bond Dissociation Energies for Bonds with Different Bond Orders in Selected Gas-Phase Molecules at 298 K

Compound	Bond Order	Bond Length (pm)	Bond Dissociation Energy (kJ/mol)	Compound	Bond Order	Bond Length (pm)	Bond Dissociation Energy (kJ/mol)
$H_3C–CH_3$	1	153.5	376	$H_3C–NH_2$	1	147.1	331
$H_2C=CH_2$	2	133.9	728	$H_2C=NH$	2	127.3	644
HC≡CH	3	120.3	965	HC≡N	3	115.3	937
$H_2N–NH_2$	1	144.9	275.3	$H_3C–OH$	1	142.5	377
HN=NH	2	125.2	456	$H_2C=O$	2	120.8	732
N≡N	3	109.8	945.3	O=C=O	2	116.0	799
HO–OH	1	147.5	213	C≡O	3	112.8	1076.5
O=O	2	120.7	498.4				

Sources: Data from *CRC Handbook of Chemistry and Physics* (2004); *Lange's Handbook of Chemistry* (2005); CCCBDB [cccbdb.nist.gov].

As a general rule, the distance between bonded atoms decreases as the number of shared electron pairs increases



3.3.3 THE RELATIONSHIP BETWEEN BOND ORDER & BOND ENERGY

As shown in Table **3.3.1**, triple bonds between like atoms are shorter than double bonds, and because more energy is required to completely break all three bonds than to completely break two, a triple bond is also stronger than a double bond. Similarly, double bonds between like atoms are stronger and shorter than single bonds. Bonds of the same order between *different* atoms show a wide range of bond energies, however.

Table **3.3.1**: Average Bond Energies (kJ/mol) for Commonly Encountered Bonds at 273 K

Single Bonds										Multiple Bonds	
H–H	432	C–C	346	N–N	≈167	O–O	≈142	F–F	155	C=C	602
H–C	411	C–Si	318	N–O	201	O–F	190	F–Cl	249	C≡C	835
H–Si	318	C–N	305	N–F	283	O–Cl	218	F–Br	249	C=N	615
H–N	386	C–O	358	N–Cl	313	O–Br	201	F–I	278	C≡N	887
H–P	≈322	C–S	272	N–Br	243	O–I	201	Cl–Cl	240	C=O	749
H–O	459	C–F	485	P–P	201	S–S	226	Cl–Br	216	C≡O	1072
H–S	363	C–Cl	327			S–F	284	Cl–I	208	N=N	418
H–F	565	C–Br	285			S–Cl	255	Br–Br	190	N≡N	942
H–Cl	428	C–I	213			S–Br	218	Br–I	175	N=O	607
H–Br	362	Si–Si	222					I–I	149	O=O	494
H–I	295	Si–O	452							S=O	532

Source: Data from J. E. Huheey, E. A. Keiter, and R. L. Keiter, *Inorganic Chemistry*, 4th ed. (1993).

Table **3.3.2** lists the average values for some commonly encountered bonds. Although the values shown vary widely, we can observe four trends:

1. Bonds between hydrogen and atoms in the same column of the periodic table decrease in strength as we go down the column. Thus an H–F bond is stronger than an H–I bond, H–C is stronger than H–Si, H–N is stronger than H–P, H–O is stronger than H–S, and so forth. The reason for this is that the region of space in which electrons are shared between two atoms becomes proportionally smaller as one of the atoms becomes larger (part (a) in Figure 8.3.1).
2. Bonds between like atoms usually become *weaker* as we go down a column (important exceptions are noted later). For example, the C–C single bond is stronger than the Si–Si single bond, which is stronger than the Ge–Ge bond, and so forth. As two bonded atoms become larger, the region between them occupied by bonding electrons becomes *proportionally* smaller, as illustrated in part (b) in Figure 8.3.1. Noteworthy exceptions are single bonds between the period 2 atoms of groups 15, 16, and 17 (i.e., N, O, F), which are unusually weak compared with single bonds between their larger congeners. It is likely that the N–N, O–O, and F–F single bonds are weaker than might be expected due to strong repulsive interactions between lone pairs of electrons on *adjacent* atoms. The trend in bond energies for the halogens is therefore\[\ce{Cl\bond{-}Cl > Br\bond{-}Br > F\bond{-}F > I–I} \nonumber \] Similar effects are also seen for the O–O versus S–S and for N–N versus P–P single bonds.

> *Bonds between hydrogen and atoms in a given column in the periodic table are weaker down the column; bonds between like atoms usually become weaker down a column.*

3. Because elements in periods 3 and 4 rarely form multiple bonds with themselves, their multiple bond energies are not accurately known. Nonetheless, they are presumed to be significantly weaker than multiple bonds between lighter atoms of the same families. Compounds containing an Si=Si double bond, for example, have only recently been prepared, whereas compounds containing C=C double bonds are one of the best-studied and most important classes of organic compounds.
4. Multiple bonds between carbon, oxygen, or nitrogen and a period 3 element such as phosphorus or sulfur tend to be unusually strong. In fact, multiple bonds of this type dominate the chemistry of the period 3 elements of groups 15 and 16. Multiple bonds to phosphorus or sulfur occur as a result of *d*-orbital interactions, e..g, for the SO_4^{2-} ion. In contrast, silicon in group 14 has little tendency to form discrete silicon–oxygen double bonds. Consequently, SiO_2 has a three-dimensional network structure in which each silicon atom forms four Si–O single bonds, which makes the physical and chemical properties of SiO_2 very different from those of CO_2.

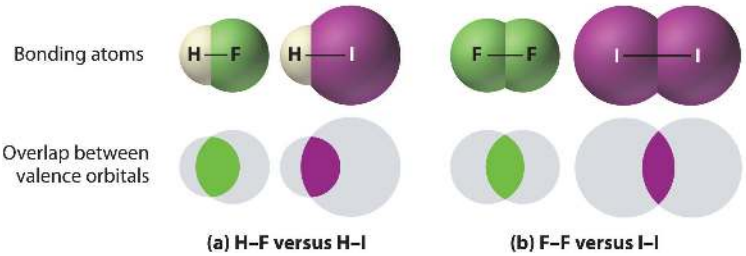


Figure **3.3.1**: The Strength of Covalent Bonds Depends on the Overlap between the Valence Orbitals of the Bonded Atoms. The relative sizes of the region of space in which electrons are shared between (a) a hydrogen atom and lighter (smaller) vs. heavier (larger) atoms in the same periodic group; and (b) two lighter versus two heavier atoms in the same group. Although the absolute amount of shared space increases in both cases on going from a light to a heavy atom, the amount of space *relative to the size of the bonded atom* decreases; that is, the *percentage* of total orbital volume decreases with increasing size. Hence the strength of the bond decreases.

Bond strengths increase as bond order **increases**, while bond distances **decrease**.

3.3.4 THE RELATIONSHIP BETWEEN MOLECULAR STRUCTURE AND BOND ENERGY

Bond energy is defined as the energy required to break a particular bond in a molecule in the gas phase. Its value depends on not only the identity of the bonded atoms but also their environment. Thus the bond energy of a C–H single bond is *not* the same in all organic compounds. For example, the energy required to break a C–H bond in methane varies by as much as 25% depending on how many other bonds in the molecule have already been broken (Table **3.3.2**); that is, the C–H bond energy depends on its molecular environment. Except for diatomic molecules, the bond energies listed in Table **3.3.2** are *average* values for all bonds of a given type in a range of molecules. Even so, they are not likely to differ from the actual value of a given bond by more than about 10%.

Table **3.3.3**: Energies for the Dissociation of Successive C–H Bonds in Methane

Reaction	D (kJ/mol)
$CH_4(g) \rightarrow CH_3(g) + H(g)$	439
$CH_3(g) \rightarrow CH_2(g) + H(g)$	462
$CH_2(g) \rightarrow CH(g) + H(g)$	424
$CH(g) \rightarrow C(g) + H(g)$	338

Source: Data from *CRC Handbook of Chemistry and Physics* (2004).

We can estimate the enthalpy change for a chemical reaction by adding together the average energies of the bonds broken in the reactants and the average energies of the bonds formed in the products and then calculating the difference between the two. If the bonds formed in the products are stronger than those broken in the reactants, then energy will be released in the reaction ($\Delta H_{rxn} < 0$):

$$\Delta H_{rxn} \approx \sum(\text{bond energies of bonds broken}) - \sum(\text{bond energies of bonds formed}) \tag{3.3.1}$$

The ≈ sign is used because we are adding together *average* bond energies; hence this approach does not give exact values for ΔH_{rxn}.

Let's consider the reaction of 1 mol of *n*-heptane (C_7H_{16}) with oxygen gas to give carbon dioxide and water. This is one reaction that occurs during the combustion of gasoline:

$$CH_3(CH_2)_5CH_{3(l)} + 11O_{2(g)} \rightarrow 7CO_{2(g)} + 8H_2O_{(g)} \tag{3.3.2}$$

In this reaction, 6 C–C bonds, 16 C–H bonds, and 11 O=O bonds are broken per mole of *n*-heptane, while 14 C=O bonds (two for each CO_2) and 16 O–H bonds (two for each H_2O) are formed. The energy changes can be tabulated as follows:

Bonds Broken (kJ/mol) and Bonds Formed (kJ/mol)

Bonds Broken (kJ/mol)		Bonds Formed (kJ/mol)	
6 C–C	346 × 6 = 2076	14 C=O	799 × 14 = 11,186
16 C–H	411 × 16 = 6576	16 O–H	459 × 16 = 7344
11 O=O	494 × 11 = 5434		**Total** = 18,530
	Total = 14,086		

The bonds in the products are stronger than the bonds in the reactants by about 4444 kJ/mol. This means that ΔH_{rxn} is approximately −4444 kJ/mol, and the reaction is highly exothermic (which is not too surprising for a combustion reaction).

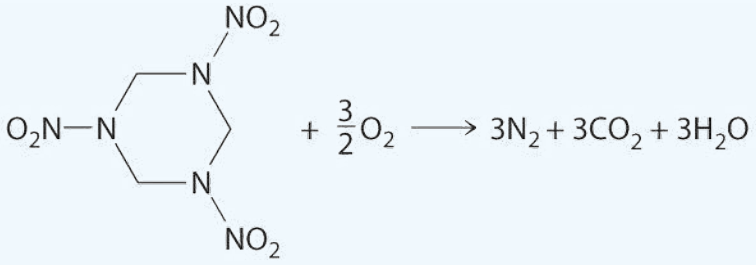
If we compare this approximation with the value obtained from measured ΔH_f^o values ($\Delta H_{rxn} = -481\ 7kJ/mol$), we find a discrepancy of only about 8%, less than the 10% typically encountered. Chemists find this method useful for calculating approximate enthalpies of reaction for molecules whose actual ΔH_f^o values are unknown. These approximations can be important for predicting whether a reaction is **exothermic** or **endothermic**—and to what degree.



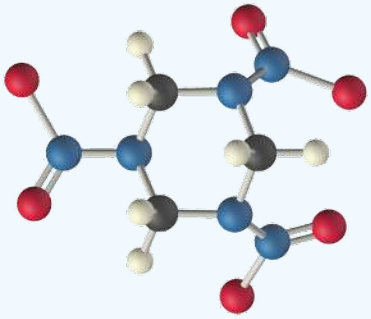
EXAMPLE 3.3.1

The compound RDX (Research Development Explosive) is a more powerful explosive than dynamite and is used by the military. When detonated, it produces gaseous products and heat according to the following reaction. Use the approximate bond energies in Table 8.3.2

to estimate the ΔH_{rxn} per mole of RDX.



RDX



RDX

Given: chemical reaction, structure of reactant, and Table 8.3.2.

Asked for: ΔH_{rxn} per mole

Strategy:

A. List the types of bonds broken in RDX, along with the bond energy required to break each type. Multiply the number of each type by the energy required to break one bond of that type and then add together the energies. Repeat this procedure for the bonds formed in the reaction.

B. Use Equation 8.3.1 to calculate the amount of energy consumed or released in the reaction (ΔH_{rxn}).

Solution:

We must add together the energies of the bonds in the reactants and compare that quantity with the sum of the energies of the bonds in the products. A nitro group ($–NO_2$) can be viewed as having one N–O single bond and one N=O double bond, as follows:



In fact, however, both N–O distances are usually the same because of the presence of two equivalent resonance structures.

A We can organize our data by constructing a table:

Bonds Broken (kJ/mol)

Bonds Broken (kJ/mol)		Bonds Broken (kJ/mol)	
6 C–H	411 × 6 = 2466	6 C=O	799 × 6 = 4794
3 N–N	167 × 3 = 501	6 O–H	459 × 6 = 2754
3 N–O	201 × 3 = 603		**Total** = 10,374
3 N=O	607 × 3 = 1821		
1.5 O=O	494 × 1.5 = 741		
	Total = 7962		

B From Equation 8.3.1, we have

$$\Delta H_{rxn} \approx \sum(\text{bond energies of bonds broken}) - \sum(\text{bond energies of bonds formed})$$

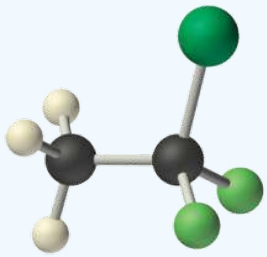
$$= 7962\ kJ/mol - 10,374\ kJ/mol$$

\[=−2412 \;kJ/mol]

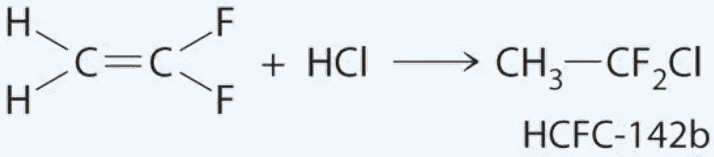
Thus this reaction is also highly exothermic.

? EXERCISE 3.3.1

The molecule HCFC-142b, a hydrochlorofluorocarbon used in place of chlorofluorocarbons (CFCs) such as the Freons, can be prepared by adding HCl to 1,1-difluoroethylene:



HCFC-142b



Use tabulated bond energies to calculate ΔH_{rxn}.

Answer

−54 kJ/mol

3.3.5 SUMMARY

The strength of a covalent bond depends on the overlap between the valence orbitals of the bonded atoms. **Bond order** is the number of electron pairs that hold two atoms together. Single bonds have a bond order of one, and multiple bonds with bond orders of two (a double bond) and three (a triple bond) are quite common. In closely related compounds with bonds between the same kinds of atoms, the bond with the highest bond order is both the shortest and the strongest. In bonds with the same bond order between different atoms, trends are observed that, with few exceptions, result in the strongest single bonds being formed between the smallest atoms. Tabulated values of average bond energies can be used to calculate the enthalpy change of many chemical reactions. If the bonds in the products are stronger than those in the reactants, the reaction is exothermic and vice versa.

3.3.6 CONTRIBUTORS AND ATTRIBUTIONS

- Mike Blaber (Florida State University)
- Wikipedia

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3.4: BOND POLARITY AND ELECTRONEGATIVITY

LEARNING OBJECTIVES

- To define electronegativity and bond polarity
- To calculate the percent ionic character of a covalent polar bond

The electron pairs shared between two atoms ***are not necessarily shared equally.*** For example, while the bonding electron pair is shared equally in the covalent bond in Cl_2, in $NaCl$ the 3s electron is stripped from the Na atom and is incorporated into the electronic structure of the Cl atom - and the compound is most accurately described as consisting of individual Na^+ and Cl^- ions (ionic bonding). For most covalent substances, their bond character falls **between** these two extremes. As demonstrated below, the **bond polarity** is a useful concept for describing the sharing of electrons between atoms within a covalent bond:

- A ***nonpolar covalent bond*** is one in which the electrons are shared *equally* between two atoms.
- A ***polar covalent bond*** is one in which ***one atom has a greater attraction for the electrons than the other atom***. If this relative attraction is great enough, then the bond is an ***ionic bond.***

3.4.1 ELECTRONEGATIVITY

The elements with the highest ionization energies are generally those with the most negative electron affinities, which are located toward the upper right corner of the periodic table. Conversely, the elements with the lowest ionization energies are generally those with the least negative electron affinities and are located in the lower left corner of the periodic table.

Because the tendency of an element to gain or lose electrons is so important in determining its chemistry, various methods have been developed to quantitatively describe this tendency. The most important method uses a measurement called **electronegativity** (represented by the Greek letter *chi*, χ, pronounced “ky” as in “sky”), defined as the *relative* ability of an atom to attract electrons to itself *in a chemical compound*. Elements with high electronegativities tend to acquire electrons in chemical reactions and are found in the upper right corner of the periodic table. Elements with low electronegativities tend to lose electrons in chemical reactions and are found in the lower left corner of the periodic table.

Unlike ionization energy or electron affinity, the electronegativity of an atom is not a simple, fixed property that can be directly measured in a single experiment. In fact, an atom’s electronegativity should depend to some extent on its chemical environment because the properties of an atom are influenced by its neighbors in a chemical compound. Nevertheless, when different methods for measuring the electronegativity of an atom are compared, they all tend to assign similar relative values to a given element. For example, all scales predict that fluorine has the highest electronegativity and cesium the lowest of the stable elements, which suggests that all the methods are measuring the same fundamental property.

> *Electronegativity is defined as the ability of an atom in a particular molecule to attract electrons to itself. The greater the value, the greater the attractiveness for electrons.*

Electronegativity is a function of:

1. the atom's ***ionization energy*** (how strongly the atom holds on to its own electrons) and
2. the atom's ***electron affinity*** (how strongly the atom attracts other electrons).

Both of these are properties of the *isolated* atom. An element will be *highly electronegative* if it has a large (negative) electron affinity and a high ionization energy (always endothermic, or positive for neutral atoms). Thus, it will attract electrons from other atoms and resist having its own electrons attracted away.

3.4.1.1 THE PAULING ELECTRONEGATIVITY SCALE

The original electronegativity scale, developed in the 1930s by Linus Pauling (1901– 1994) was based on measurements of the strengths of covalent bonds between different elements. Pauling arbitrarily set the electronegativity of fluorine at 4.0 (although today it has been refined to 3.98), thereby creating a scale in which all elements have values between 0 and 4.0.

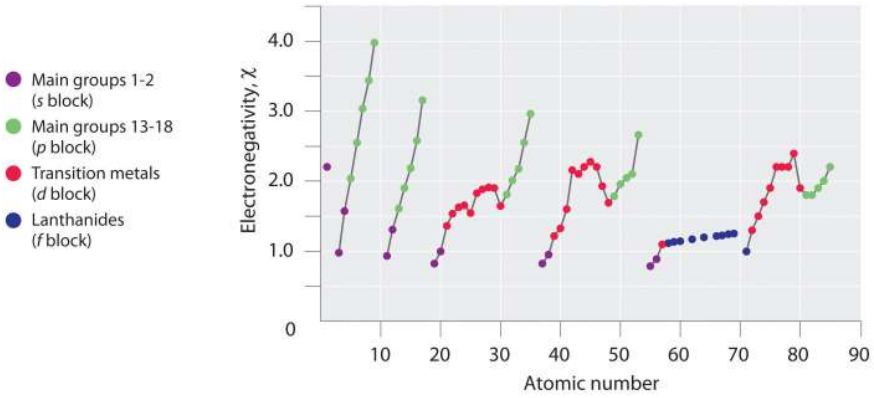
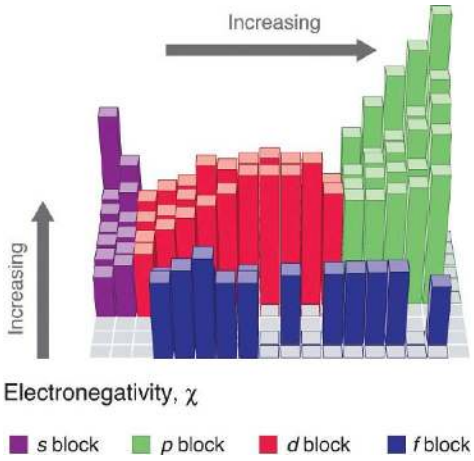


Figure 3.4.1: A Plot of Periodic Variation of Electronegativity with Atomic Number for the First Six Rows of the Periodic Table

The main groups 1 and 2 are purple, the main groups 13 through 18 are green, the transition metals are red, and the lanthanides are blue.

Periodic variations in Pauling's electronegativity values are illustrated in Figures 3.4.1 and 3.4.2. If we ignore the inert gases and elements for which no stable isotopes are known, we see that fluorine ($\chi = 3.98$) is the most electronegative element and cesium is the least electronegative nonradioactive element ($\chi = 0.79$). Because electronegativities generally increase diagonally from the lower left to the upper right of the periodic table, elements lying on diagonal lines running from upper left to lower right tend to have comparable values (e.g., O and Cl and N, S, and Br).

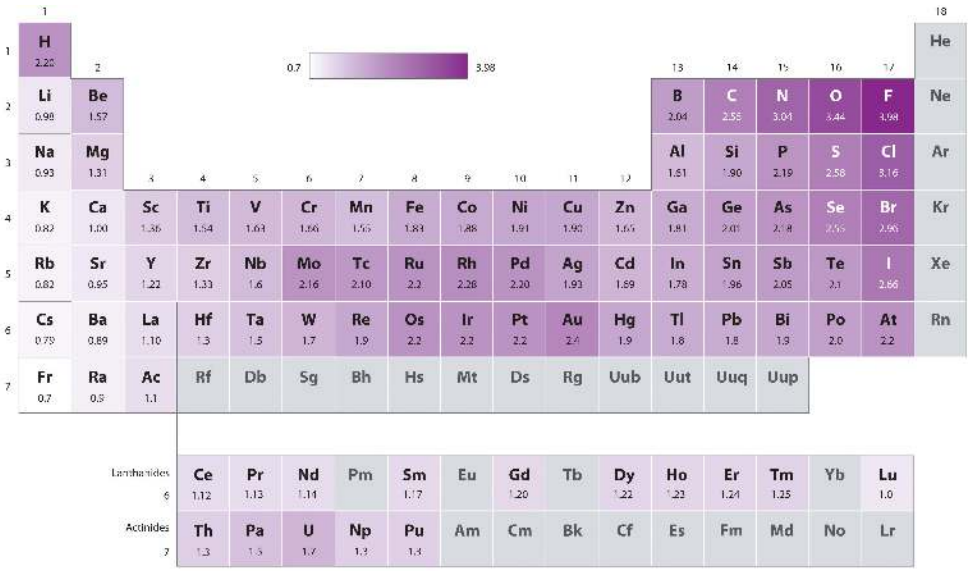


The s blocks are purple, the p blocks are green, the d blocks are red, and the f blocks are blue. Electronegativity increase from bottom to top and left to right.

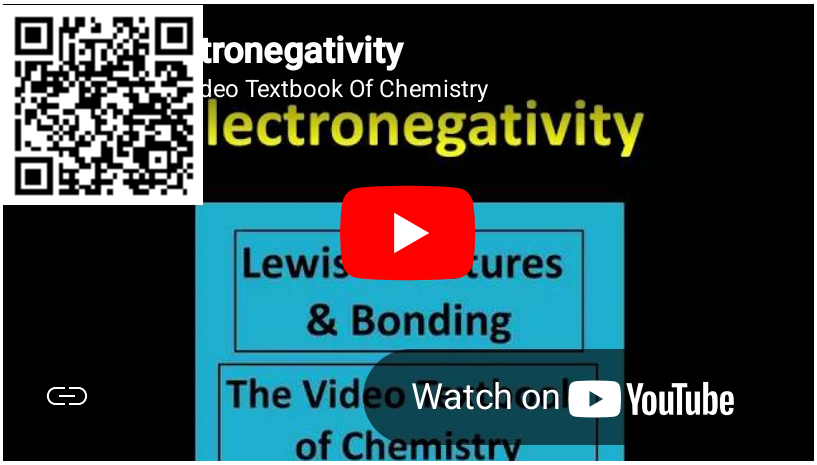
Figure 3.4.2: *Pauling Electronegativity Values of the s-, p-, d-, and f-Block Elements. Values for most of the actinides are approximate. Elements for which no data are available are shown in gray. Source: Data from L. Pauling, The Nature of the Chemical Bond, 3rd ed. (1960).*

LINUS PAULING (1901-1994)

When he was nine, Pauling's father died, and his mother tried to convince him to quit school to support the family. He did not quit school, but was later denied a high school degree, and had to work several jobs to put himself through college. Pauling would go on to become one of the most influential chemists of the century if not all time. He won two Nobel Prizes, one for chemistry in 1954 and one for peace in 1962.



Pauling's method is limited by the fact that many elements do not form stable covalent compounds with other elements; hence their electronegativities cannot be measured by his method. Other definitions have since been developed that address this problem, e.g., the Mulliken, Allred-Rochow, and Allen electronegativity scales. The Mulliken electronegativity of an element is the average of its first ionization energy and the absolute value of its electron affinity, showing the relationship between electronegativity and these other periodic properties.



3.4.2 ELECTRONEGATIVITY DIFFERENCES BETWEEN METALS AND NONMETALS

An element's electronegativity provides us with a single value that we can use to characterize the chemistry of an element. Elements with a high electronegativity ($\chi \geq 2.2$ in Figure **3.4.2**) have very negative affinities and large ionization potentials, so they are generally nonmetals and electrical insulators that tend to gain electrons in chemical reactions (i.e., they are *oxidants*). In contrast, elements with a low electronegativity ($\chi \leq 1.8$) have electron affinities that have either positive or small negative values and small ionization potentials, so they are generally metals and good electrical conductors that tend to lose their valence electrons in chemical reactions (i.e., they are *reductants*). In between the metals and nonmetals, along the heavy diagonal line running from B to At is a group of elements with intermediate electronegativities ($\chi \sim 2.0$). These are the **metalloids** (or semimetals), elements that have some of the chemical properties of both nonmetals and metals. The distinction between metals and nonmetals is one of the most fundamental we can make in categorizing the elements and predicting their chemical behavior. Figure **3.4.3** shows the strong correlation between electronegativity values, metallic versus nonmetallic character, and location in the periodic table.

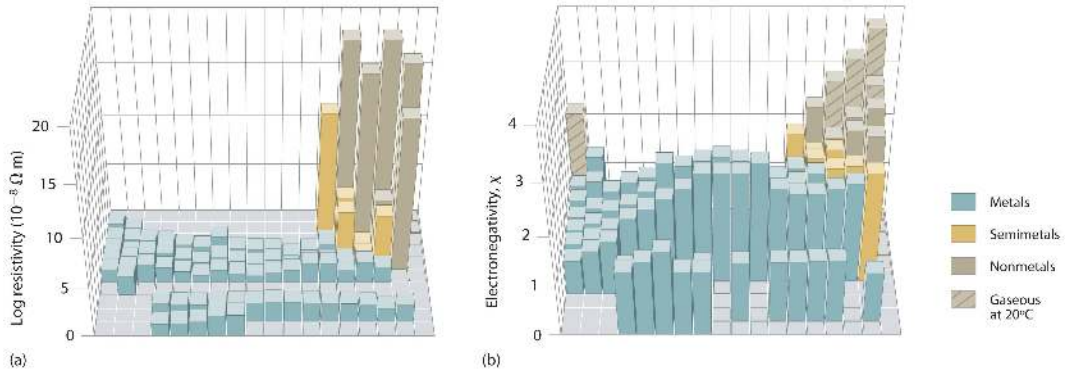


Figure **3.4.3**: Three-Dimensional Plots Demonstrating the Relationship between Electronegativity and the Metallic/Nonmetallic Character of the Elements. (a) A plot of electrical resistivity (measured resistivity to electron flow) at or near room temperature shows that substances with high resistivity (little to no measured electron flow) are electrical insulators, whereas substances with low resistivity (high measured electron flow) are metals. (b) A plot of Pauling electronegativities for a like set of elements shows that high electronegativity values (≥ about 2.2) correlate with high electrical resistivities (insulators). Low electronegativity values (≤ about 2.2) correlate with low resistivities (metals). Because electrical resistivity is typically measured only for solids and liquids, the gaseous elements do not appear in part (a).

Metals are blue, semimetals are yellow, nonmetals are gray, gaseous at 20 degrees C are gray with dashed lines.

Electronegativity values *increase* from lower left to upper right in the periodic table.

The rules for assigning oxidation states(opens in new window) are based on the relative electronegativities of the elements; the more electronegative element in a binary compound is assigned a negative oxidation state. As we shall see, electronegativity values are also used to predict bond energies, bond polarities, and the kinds of reactions that compounds undergo.

✔ EXAMPLE 3.4.1: INCREASING ELECTRONEGATIVITY

On the basis of their positions in the periodic table, arrange Cl, Se, Si, and Sr in order of increasing electronegativity and classify each as a metal, a nonmetal, or a metalloid.

Given: four elements

Asked for: order by increasing electronegativity and classification

Strategy:

A. Locate the elements in the periodic table. From their diagonal positions from lower left to upper right, predict their relative electronegativities.

B. Arrange the elements in order of increasing electronegativity.

C. Classify each element as a metal, a nonmetal, or a metalloid according to its location about the diagonal belt of metalloids running from B to At.

Solution:

A Electronegativity increases from lower left to upper right in the periodic table (Figure 8.4.2). Because Sr lies far to the left of the other elements given, we can predict that it will have the lowest electronegativity. Because Cl lies above and to the right of Se, we can predict that $\chi_{Cl} > \chi_{Se}$. Because Si is located farther from the upper right corner than Se or Cl, its electronegativity should be lower than those of Se and Cl but greater than that of Sr. **B** The overall order is therefore $\chi_{Sr} < \chi_{Si} < \chi_{Se} < \chi_{Cl}$.

C To classify the elements, we note that Sr lies well to the left of the diagonal belt of metalloids running from B to At; while Se and Cl lie to the right and Si lies in the middle. We can predict that Sr is a metal, Si is a metalloid, and Se and Cl are nonmetals.

? EXERCISE 3.4.1

On the basis of their positions in the periodic table, arrange Ge, N, O, Rb, and Zr in order of increasing electronegativity and classify each as a metal, a nonmetal, or a metalloid.

Answer

Rb < Zr < Ge < N < O; metals (Rb, Zr); metalloid (Ge); nonmetal (N, O)

3.4.3 PERCENT IONIC CHARACTER OF A COVALENT POLAR BOND

The two idealized extremes of chemical bonding: (1) ionic bonding—in which one or more electrons are transferred completely from one atom to another, and the resulting ions are held together by purely electrostatic forces—and (2) covalent bonding, in which electrons are shared equally between two atoms. Most compounds, however, have polar covalent bonds, which means that electrons are shared unequally between the bonded atoms. Figure **3.4.4** compares the electron distribution in a polar covalent bond with those in an ideally covalent and an ideally ionic bond. Recall that a lowercase Greek delta (δ) is used to indicate that a bonded atom possesses a partial positive charge, indicated by δ^+, or a partial negative charge, indicated by δ^-, and a bond between two atoms that possess partial charges is a polar bond.

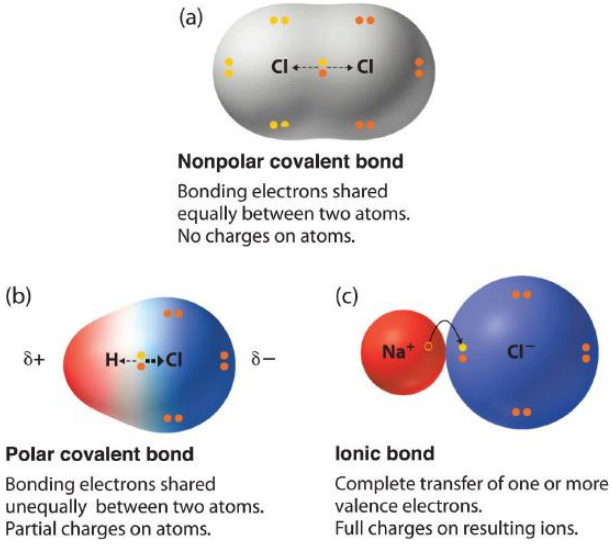


Figure **3.4.4**: The Electron Distribution in a Nonpolar Covalent Bond, a Polar Covalent Bond, and an Ionic Bond Using Lewis Electron Structures. In a purely covalent bond (a), the bonding electrons are shared equally between the atoms. In a purely ionic bond (c), an electron has been transferred completely from one atom to the other. A polar covalent bond (b) is intermediate between the two extremes: the bonding electrons are shared unequally between the two atoms, and the electron distribution is asymmetrical with the electron density being greater around the more electronegative atom. Electron-rich (negatively charged) regions are shown in blue; electron-poor (positively charged) regions are shown in red.

3.4.4 BOND POLARITY

The polarity of a bond—the extent to which it is polar—is determined largely by the relative electronegativities of the bonded atoms. Electronegativity (χ) was defined as the ability of an atom in a molecule or an ion to attract electrons to itself. Thus there is a direct correlation between electronegativity and bond polarity. A bond is *nonpolar* if the bonded atoms have equal electronegativities. If the electronegativities of the bonded atoms are not equal, however, the bond is *polarized* toward the more electronegative atom. A bond in which the electronegativity of B (χ_B) is greater than the electronegativity of A (χ_A), for example, is indicated with the partial negative charge on the more electronegative atom:

$$\underset{\delta^+}{\overset{\text{less electronegative}}{A}} - \underset{\delta^-}{\overset{\text{more electronegative}}{B}} \tag{3.4.1}$$

One way of estimating the ionic character of a bond—that is, the magnitude of the charge separation in a polar covalent bond—is to calculate the difference in electronegativity between the two atoms: $\Delta\chi = \chi_B - \chi_A$.

To predict the polarity of the bonds in Cl_2, HCl, and NaCl, for example, we look at the electronegativities of the relevant atoms: $\chi_{Cl} = 3.16$, $\chi_H = 2.20$, and $\chi_{Na} = 0.93$. Cl_2 must be nonpolar because the electronegativity difference ($\Delta\chi$) is zero; hence the two chlorine atoms share the bonding electrons equally. In NaCl, $\Delta\chi$ is 2.23. This high value is typical of an ionic compound ($\Delta\chi \geq \approx 1.5$) and means that the valence electron of sodium has been completely transferred to chlorine to form Na^+ and Cl^- ions. In HCl, however, $\Delta\chi$ is only 0.96. The bonding electrons are more strongly attracted to the more electronegative chlorine atom, and so the charge distribution is

$$\overset{\delta^+}{H} - \overset{\delta^-}{Cl}$$

Remember that electronegativities are difficult to measure precisely and different definitions produce slightly different numbers. In practice, the polarity of a bond is usually estimated rather than calculated.

Bond polarity and ionic character **increase** with an increasing difference in electronegativity.

As with bond energies, the electronegativity of an atom depends to some extent on its chemical environment. It is therefore unlikely that the reported electronegativities of a chlorine atom in NaCl, Cl_2, ClF_5, and $HClO_4$ would be exactly the same.

3.4.5 DIPOLE MOMENTS

The asymmetrical charge distribution in a polar substance such as HCl produces a **dipole moment** where Qr in meters (m). is abbreviated by the Greek letter mu (μ). The dipole moment is defined as the product of the partial charge Q on the bonded atoms and the distance r between the partial charges:

$$\mu = Qr \tag{3.4.2}$$

where Q is measured in coulombs (C) and r in meters. The unit for dipole moments is the debye (D):

$$1\ D = 3.3356 \times 10^{-30}\ C \cdot m \tag{3.4.3}$$

When a molecule with a dipole moment is placed in an electric field, it tends to orient itself with the electric field because of its asymmetrical charge distribution (Figure **3.4.4**).

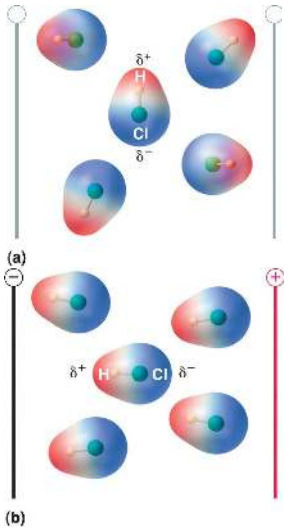


Figure **3.4.5**: Molecules That Possess a Dipole Moment Partially Align Themselves with an Applied Electric Field. In the absence of a field (a), the HCl molecules are randomly oriented. When an electric field is applied (b), the molecules tend to align themselves with the field, such that the positive end of the molecular dipole points toward the negative terminal and vice versa.

We can measure the partial charges on the atoms in a molecule such as HCl using Equation **3.4.2**. If the bonding in HCl were purely ionic, an electron would be transferred from H to Cl, so there would be a full +1 charge on the H atom and a full −1 charge on the Cl atom. The dipole moment of HCl is 1.109 D, as determined by measuring the extent of its alignment in an electric field, and the reported gas-phase H–Cl distance is 127.5 pm. Hence the charge on each atom is

$$Q = \frac{\mu}{r} = 1.109\ \cancel{D}\left(\frac{3.3356 \times 10^{-30}\ C \cdot \cancel{m}}{1\ \cancel{D}}\right)\left(\frac{1}{127.8\ \cancel{pm}}\right)\left(\frac{1\ \cancel{pm}}{10^{-12}\ \cancel{m}}\right) = 2.901 \times 10^{-20}\ C \tag{3.4.4}$$

By dividing this calculated value by the charge on a single electron (1.6022×10^{-19} C), we find that the electron distribution in HCl is asymmetric and that effectively it appears that there is a net negative charge on the Cl of about −0.18, effectively corresponding to about 0.18 e^-. This certainly does not mean that there is a fraction of an electron on the Cl atom, but that the distribution of electron probability favors the Cl atom side of the molecule by about this amount.

$$\frac{2.901 \times 10^{-20}\ \cancel{C}}{1.6022 \times 10^{-19}\ \cancel{C}} = 0.1811\ e^- \tag{3.4.5}$$

To form a neutral compound, the charge on the H atom must be equal but opposite. Thus the measured dipole moment of HCl indicates that the H–Cl bond has approximately 18% ionic character (0.1811 × 100), or 82% covalent character. Instead of writing HCl as

$$\overset{\delta+}{H} - \overset{\delta-}{Cl}$$

we can therefore indicate the charge separation quantitatively as

$$\overset{0.18\delta+}{H} - \overset{0.18\delta-}{Cl}$$

Our calculated results are in agreement with the electronegativity difference between hydrogen and chlorine $\chi_H = 2.20$; $\chi_{Cl} = 3.16$, $\chi_{Cl} - \chi_H = 0.96$), a value well within the range for polar covalent bonds. We indicate the dipole moment by writing an arrow above the molecule. Mathematically, dipole moments are vectors, and they possess both a magnitude and a direction. The dipole moment of a molecule is the vector sum of the dipoles of the individual bonds. In HCl, for example, the dipole moment is indicated as follows:



The arrow shows the direction of electron flow by pointing toward the more electronegative atom.

The charge on the atoms of many substances in the gas phase can be calculated using measured dipole moments and bond distances. Figure **3.4.6** shows a plot of the percent ionic character versus the difference in electronegativity of the bonded atoms for several substances. According to the graph, the bonding in species such as NaCl(g) and CsF(g) is substantially less than 100% ionic in character. As the gas condenses into a solid, however, dipole–dipole interactions between polarized species increase the charge separations. In the crystal, therefore, an electron is transferred from the metal to the nonmetal, and these substances behave like classic ionic compounds. The data in Figure **3.4.6** show that diatomic species with an electronegativity difference of less than 1.5 are less than 50% ionic in character, which is consistent with our earlier description of these species as containing polar covalent bonds. The use of dipole moments to determine the ionic character of a polar bond is illustrated in Example **3.4.2**.

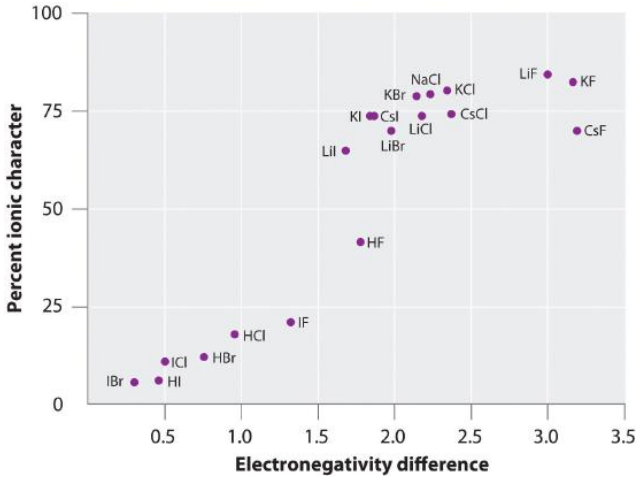


Figure **3.4.6**: A Plot of the Percent Ionic Character of a Bond as Determined from Measured Dipole Moments versus the Difference in Electronegativity of the Bonded Atoms.In the gas phase, even CsF, which has the largest possible difference in electronegativity between atoms, is not 100% ionic. Solid CsF, however, is best viewed as 100% ionic because of the additional electrostatic interactions in the lattice.

EXAMPLE 3.4.2

In the gas phase, NaCl has a dipole moment of 9.001 D and an Na–Cl distance of 236.1 pm. Calculate the percent ionic character in NaCl.

Given: chemical species, dipole moment, and internuclear distance

Asked for: percent ionic character

Strategy:

A Compute the charge on each atom using the information given and Equation 3.4.2.

B Find the percent ionic character from the ratio of the actual charge to the charge of a single electron.

Solution:

A The charge on each atom is given by

$$Q = \frac{\mu}{r}$$

$$= 9.001 \cancel{D} \left(\frac{3.3356 \times 10^{-30} \, C \cdot \cancel{m}}{1 \cancel{D}} \right) \left(\frac{1}{236.1 \cancel{pm}} \right) \left(\frac{1 \cancel{pm}}{10^{-12} \cancel{m}} \right) = 1.272 \times 10^{-19} \, C$$

Thus NaCl behaves as if it had charges of 1.272×10^{-19} C on each atom separated by 236.1 pm.

B The percent ionic character is given by the ratio of the actual charge to the charge of a single electron (the charge expected for the complete transfer of one electron):

$$\% \, ionic \, character = \left(\frac{1.272 \times 10^{-19} \cancel{C}}{1.6022 \times 10^{-19} \cancel{C}} \right) (100) = 79.39\% \simeq 79\%$$

? EXERCISE 3.4.2

In the gas phase, silver chloride (AgCl) has a dipole moment of 6.08 D and an Ag–Cl distance of 228.1 pm. What is the percent ionic character in silver chloride?

Answer

55.5%

3.4.6 SUMMARY

Bond polarity and ionic character increase with an increasing difference in electronegativity. The **electronegativity (χ)** of an element is the relative ability of an atom to attract electrons to itself in a chemical compound and increases diagonally from the lower left of the periodic table to the upper right. The Pauling electronegativity scale is based on measurements of the strengths of covalent bonds between different atoms, whereas the Mulliken electronegativity of an element is the average of its first ionization energy and the absolute value of its electron affinity. Elements with a high electronegativity are generally nonmetals and electrical insulators and tend to behave as oxidants in chemical reactions. Conversely, elements with a low electronegativity are generally metals and good electrical conductors and tend to behave as reductants in chemical reactions.

Compounds with **polar covalent bonds** have electrons that are shared unequally between the bonded atoms. The polarity of such a bond is determined largely by the relative electronegativites of the bonded atoms. The asymmetrical charge distribution in a polar substance produces a **dipole moment**, which is the product of the partial charges on the bonded atoms and the distance between them.

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3.5: DRAWING LEWIS STRUCTURES

LEARNING OBJECTIVES

- To use Lewis dot symbols to explain the stoichiometry of a compound

We begin our discussion of the relationship between structure and bonding in covalent compounds by describing the interaction between two identical neutral atoms—for example, the H_2 molecule, which contains a purely covalent bond. Each hydrogen atom in H_2 contains one electron and one proton, with the electron attracted to the proton by electrostatic forces. As the two hydrogen atoms are brought together, additional interactions must be considered (Figure **3.5.1**):

- The electrons in the two atoms repel each other because they have the same charge (
- *The electrons in the two atoms repel each other because they have the same charge (E > 0).*
- *Similarly, the protons in adjacent atoms repel each other (E > 0).*
- *The electron in one atom is attracted to the oppositely charged proton in the other atom and vice versa (E < 0). Recall that it is impossible to specify precisely the position of the electron in either hydrogen atom. Hence the quantum mechanical probability distributions must be used.*

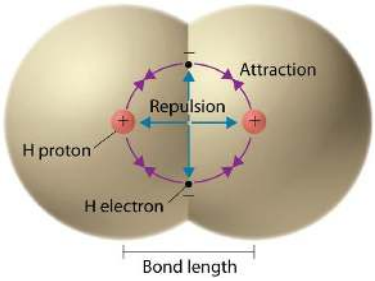


Figure **3.5.1**: Attractive and Repulsive Interactions between Electrons and Nuclei in the Hydrogen Molecule. Electron–electron and proton–proton interactions are repulsive; electron–proton interactions are attractive. At the observed bond distance, the repulsive and attractive interactions are balanced.

A plot of the potential energy of the system as a function of the internuclear distance (Figure **3.5.2**) shows that the system becomes more stable (the energy of the system decreases) as two hydrogen atoms move toward each other from $r = \infty$, until the energy reaches a minimum at $r = r_0$ (the observed internuclear distance in H_2 is 74 pm). Thus at intermediate distances, proton–electron attractive interactions dominate, but as the distance becomes very short, electron–electron and proton–proton repulsive interactions cause the energy of the system to increase rapidly. Notice the similarity between Figures **3.5.1** and **3.5.2**, which described a system containing two oppositely charged *ions*. The shapes of the energy versus distance curves in the two figures are similar because they both result from attractive and repulsive forces between charged entities.

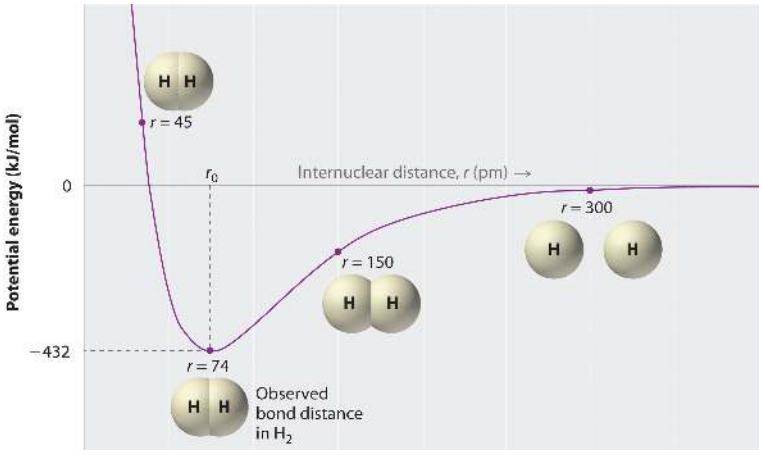


Figure **3.5.2**: A Plot of Potential Energy versus Internuclear Distance for the Interaction between Two Gaseous Hydrogen Atoms.

At long distances, both attractive and repulsive interactions are small. As the distance between the atoms decreases, the attractive electron–proton interactions dominate, and the energy of the system decreases. At the observed bond distance, the repulsive electron–electron and

proton–proton interactions just balance the attractive interactions, preventing a further decrease in the internuclear distance. At very short internuclear distances, the repulsive interactions dominate, making the system less stable than the isolated atoms.

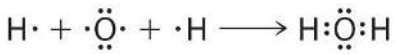
3.5.1 USING LEWIS DOT SYMBOLS TO DESCRIBE COVALENT BONDING

The valence electron configurations of the constituent atoms of a covalent compound are important factors in determining its structure, stoichiometry, and properties. For example, chlorine, with seven valence electrons, is one electron short of an octet. If two chlorine atoms share their unpaired electrons by making a covalent bond and forming Cl_2, they can each complete their valence shell:



Each chlorine atom now has an octet. The electron pair being shared by the atoms is called a bonding pair; the other three pairs of electrons on each chlorine atom are called lone pairs. Lone pairs are not involved in covalent bonding. If both electrons in a covalent bond come from the same atom, the bond is called a coordinate covalent bond. Examples of this type of bonding are presented in Section 8.6 when we discuss atoms with less than an octet of electrons.

We can illustrate the formation of a water molecule from two hydrogen atoms and an oxygen atom using Lewis dot symbols:



The structure on the right is the *Lewis electron structure*, or *Lewis structure*, for H_2O. With two bonding pairs and two lone pairs, the oxygen atom has now completed its octet. Moreover, by sharing a bonding pair with oxygen, each hydrogen atom now has a full valence shell of two electrons. Chemists usually indicate a bonding pair by a single line, as shown here for our two examples:



The following procedure can be used to construct Lewis electron structures for more complex molecules and ions:

1. **Arrange the atoms to show specific connections.** When there is a central atom, it is usually the least electronegative element in the compound. Chemists usually list this central atom first in the chemical formula (as in CCl_4 and CO_3^{2-}, which both have C as the central atom), which is another clue to the compound's structure. Hydrogen and the halogens are almost always connected to only one other atom, so they are usually *terminal* rather than central.
2. **Determine the total number of valence electrons in the molecule or ion.** Add together the valence electrons from each atom. (Recall that the number of valence electrons is indicated by the position of the element in the periodic table.) If the species is a polyatomic ion, remember to add or subtract the number of electrons necessary to give the total charge on the ion. For CO_3^{2-}, for example, we add two electrons to the total because of the −2 charge.
3. **Place a bonding pair of electrons between each pair of adjacent atoms to give a single bond.** In H_2O, for example, there is a bonding pair of electrons between oxygen and each hydrogen.
4. **Beginning with the terminal atoms, add enough electrons to each atom to give each atom an octet (two for hydrogen).** These electrons will usually be lone pairs.
5. **If any electrons are left over, place them on the central atom.** We will explain later that some atoms are able to accommodate more than eight electrons.
6. **If the central atom has fewer electrons than an octet, use lone pairs from terminal atoms to form multiple (double or triple) bonds to the central atom to achieve an octet.** This will not change the number of electrons on the terminal atoms.

Now let's apply this procedure to some particular compounds, beginning with one we have already discussed.

> The central atom is usually the least electronegative element in the molecule or ion; hydrogen and the halogens are usually terminal.

3.5.1.1 THE H_2O MOLECULE

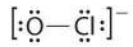
1. Because H atoms are almost always terminal, the arrangement within the molecule must be HOH.
2. Each H atom (group 1) has 1 valence electron, and the O atom (group 16) has 6 valence electrons, for a total of 8 valence electrons.
3. Placing one bonding pair of electrons between the O atom and each H atom gives H:O:H, with 4 electrons left over.
4. Each H atom has a full valence shell of 2 electrons.
5. Adding the remaining 4 electrons to the oxygen (as two lone pairs) gives the following structure:



This is the Lewis structure we drew earlier. Because it gives oxygen an octet and each hydrogen two electrons, we do not need to use step 6.

3.5.1.2 THE OCl^- ION

1. With only two atoms in the molecule, there is no central atom.
2. Oxygen (group 16) has 6 valence electrons, and chlorine (group 17) has 7 valence electrons; we must add one more for the negative charge on the ion, giving a total of 14 valence electrons.
3. Placing a bonding pair of electrons between O and Cl gives O:Cl, with 12 electrons left over.
4. If we place six electrons (as three lone pairs) on each atom, we obtain the following structure:



Both the oxygen and chlorine have 3 electron pairs drawn around them with a bond drawn between them. The molecule has square brackets placed around it and has a negative charge.

Each atom now has an octet of electrons, so steps 5 and 6 are not needed. The Lewis electron structure is drawn within brackets as is customary for an ion, with the overall charge indicated outside the brackets, and the bonding pair of electrons is indicated by a solid line. OCl^- is the hypochlorite ion, the active ingredient in chlorine laundry bleach and swimming pool disinfectant.

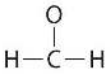
3.5.1.3 THE CH_2O MOLECULE

1. Because carbon is less electronegative than oxygen and hydrogen is normally terminal, C must be the central atom. One possible arrangement is as follows:



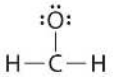
2. Each hydrogen atom (group 1) has one valence electron, carbon (group 14) has 4 valence electrons, and oxygen (group 16) has 6 valence electrons, for a total of [(2)(1) + 4 + 6] = 12 valence electrons.

3. Placing a bonding pair of electrons between each pair of bonded atoms gives the following:



Six electrons are used, and 6 are left over.

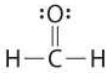
4. Adding all 6 remaining electrons to oxygen (as three lone pairs) gives the following:



Although oxygen now has an octet and each hydrogen has 2 electrons, carbon has only 6 electrons.

5. There are no electrons left to place on the central atom.

6. To give carbon an octet of electrons, we use one of the lone pairs of electrons on oxygen to form a carbon–oxygen double bond:



The bond between the oxygen and carbon is replaced with a double bond. The oxygen also has two lone pairs drawn.

Both the oxygen and the carbon now have an octet of electrons, so this is an acceptable Lewis electron structure. The O has two bonding pairs and two lone pairs, and C has four bonding pairs. This is the structure of formaldehyde, which is used in embalming fluid.

An alternative structure can be drawn with one H bonded to O. *Formal charges*, discussed later in this section, suggest that such a structure is less stable than that shown previously.

EXAMPLE 3.5.1

Write the Lewis electron structure for each species.

a. NCl_3
b. S_2^{2-}
c. NOCl

Given: chemical species

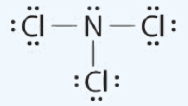
Asked for: Lewis electron structures

Strategy:

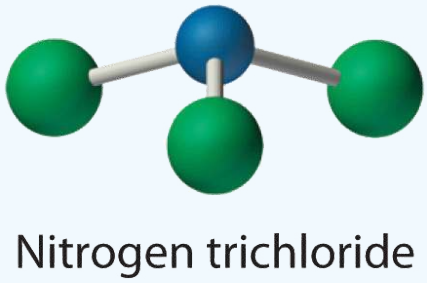
Use the six-step procedure to write the Lewis electron structure for each species.

Solution:

a. Nitrogen is less electronegative than chlorine, and halogen atoms are usually terminal, so nitrogen is the central atom. The nitrogen atom (group 15) has 5 valence electrons and each chlorine atom (group 17) has 7 valence electrons, for a total of 26 valence electrons. Using 2 electrons for each N–Cl bond and adding three lone pairs to each Cl account for (3 × 2) + (3 × 2 × 3) = 24 electrons. Rule 5 leads us to place the remaining 2 electrons on the central N:



Nitrogen trichloride is an unstable oily liquid once used to bleach flour; this use is now prohibited in the United States.



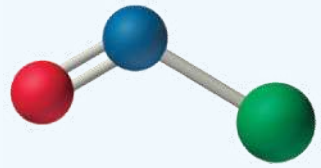
b. In a diatomic molecule or ion, we do not need to worry about a central atom. Each sulfur atom (group 16) contains 6 valence electrons, and we need to add 2 electrons for the −2 charge, giving a total of 14 valence electrons. Using 2 electrons for the S–S bond, we arrange the remaining 12 electrons as three lone pairs on each sulfur, giving each S atom an octet of electrons:

c. Because nitrogen is less electronegative than oxygen or chlorine, it is the central atom. The N atom (group 15) has 5 valence electrons, the O atom (group 16) has 6 valence electrons, and the Cl atom (group 17) has 7 valence electrons, giving a total of 18 valence electrons. Placing one bonding pair of electrons between each pair of bonded atoms uses 4 electrons and gives the following:

Adding three lone pairs each to oxygen and to chlorine uses 12 more electrons, leaving 2 electrons to place as a lone pair on nitrogen:

Because this Lewis structure has only 6 electrons around the central nitrogen, a lone pair of electrons on a terminal atom must be used to form a bonding pair. We could use a lone pair on either O or Cl. Because we have seen many structures in which O forms a double bond but none with a double bond to Cl, it is reasonable to select a lone pair from O to give the following:

All atoms now have octet configurations. This is the Lewis electron structure of nitrosyl chloride, a highly corrosive, reddish-orange gas.



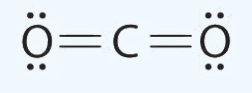
Nitrosyl chloride

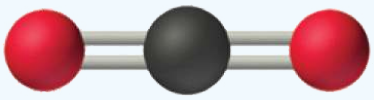
? EXERCISE 3.5.1

Write Lewis electron structures for CO_2 and SCl_2, a vile-smelling, unstable red liquid that is used in the manufacture of rubber.

Answer

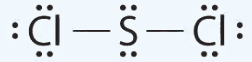
1.



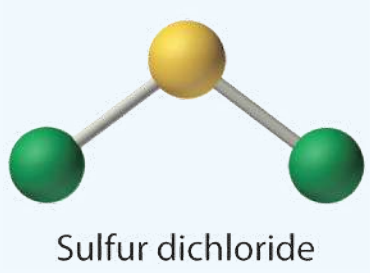


Carbon dioxide

2.



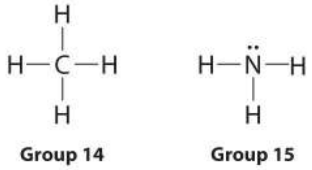
Two chlorines are bonded to a sulfur. The sulfur has 2 lone pairs while the chlorines have 3 lone pairs each.



Sulfur dichloride

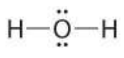
3.5.2 USING LEWIS ELECTRON STRUCTURES TO EXPLAIN STOICHIOMETRY

Lewis dot symbols provide a simple rationalization of why elements form compounds with the observed stoichiometries. In the Lewis model, the number of bonds formed by an element in a neutral compound is the same as the number of unpaired electrons it must share with other atoms to complete its octet of electrons. For the elements of Group 17 (the halogens), this number is one; for the elements of Group 16 (the chalcogens), it is two; for Group 15 elements, three; and for Group 14 elements four. These requirements are illustrated by the following Lewis structures for the hydrides of the lightest members of each group:



Group 14

Group 15



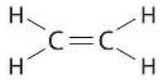
Group 16



Group 17

Elements may form multiple bonds to complete an octet. In ethylene, for example, each carbon contributes two electrons to the double bond, giving each carbon an octet (two electrons/bond × four bonds = eight electrons). Neutral structures with fewer or more bonds exist,

but they are unusual and violate the octet rule.



Ethylene

Allotropes of an element can have very different physical and chemical properties because of different three-dimensional arrangements of the atoms; the number of bonds formed by the component atoms, however, is always the same. As noted at the beginning of the chapter, diamond is a hard, transparent solid; graphite is a soft, black solid; and the fullerenes have open cage structures. Despite these differences, the carbon atoms in all three allotropes form four bonds, in accordance with the octet rule.

> Lewis structures explain why the elements of groups 14–17 form neutral compounds with four, three, two, and one bonded atom(s), respectively.

Elemental phosphorus also exists in three forms: white phosphorus, a toxic, waxy substance that initially glows and then spontaneously ignites on contact with air; red phosphorus, an amorphous substance that is used commercially in safety matches, fireworks, and smoke bombs; and black phosphorus, an unreactive crystalline solid with a texture similar to graphite (Figure **3.5.3**). Nonetheless, the phosphorus atoms in all three forms obey the octet rule and form three bonds per phosphorus atom.

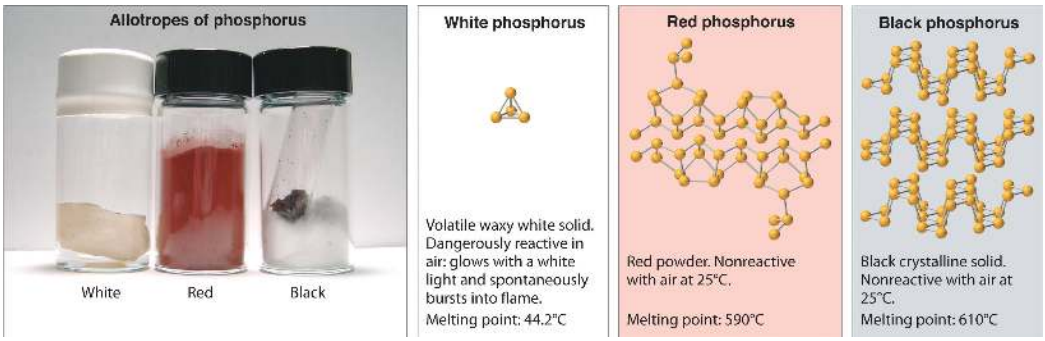


Figure **3.5.3**: The Three Allotropes of Phosphorus: White, Red, and Black. ll three forms contain only phosphorus atoms, but they differ in the arrangement and connectivity of their atoms. White phosphorus contains P_4 tetrahedra, red phosphorus is a network of linked P_8 and P_9 units, and black phosphorus forms sheets of six-membered rings. As a result, their physical and chemical properties differ dramatically.

3.5.3 FORMAL CHARGES

It is sometimes possible to write more than one Lewis structure for a substance that does not violate the octet rule, as we saw for CH_2O, but not every Lewis structure may be equally reasonable. In these situations, we can choose the most stable Lewis structure by considering the formal charge on the atoms, which is the difference between the number of valence electrons in the free atom and the number assigned to it in the Lewis electron structure. The formal charge is a way of computing the charge distribution within a Lewis structure; the sum of the formal charges on the atoms within a molecule or an ion must equal the overall charge on the molecule or ion. A formal charge does *not* represent a true charge on an atom in a covalent bond but is simply used to predict the most likely structure when a compound has more than one valid Lewis structure.

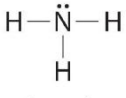
To calculate formal charges, we assign electrons in the molecule to individual atoms according to these rules:

- Nonbonding electrons are assigned to the atom on which they are located.
- Bonding electrons are divided equally between the bonded atoms.

For each atom, we then compute a formal charge:

$$\textit{formal charge} = \underset{\textit{(free atom)}}{\textit{valence } e^-} - \underset{\textit{(atom in Lewis structure)}}{\left(\textit{non-bonding } e^- + \frac{\textit{bonding } e^-}{2}\right)} \text{ (atom in Lewis structure)}$$

To illustrate this method, let's calculate the formal charge on the atoms in ammonia (NH_3) whose Lewis electron structure is as follows:



Ammonia

A neutral nitrogen atom has five valence electrons (it is in group 15). From its Lewis electron structure, the nitrogen atom in ammonia has one lone pair and shares three bonding pairs with hydrogen atoms, so nitrogen itself is assigned a total of five electrons [2 nonbonding e^- +

(6 bonding e⁻/2)]. Substituting into Equation 3.5.1, we obtain

$$formal\ charge\ (N) = 5\ valence\ e^- - \left(2\ non-bonding\ e^- + \frac{6\ bonding\ e^-}{2}\right) = 0 \tag{3.5.1}$$

A neutral hydrogen atom has one valence electron. Each hydrogen atom in the molecule shares one pair of bonding electrons and is therefore assigned one electron [0 nonbonding e^- + (2 bonding e^-/2)]. Using Equation 3.5.1 to calculate the formal charge on hydrogen, we obtain

$$formal\ charge\ (H) = 1\ valence\ e^- - \left(0\ non-bonding\ e^- + \frac{2\ bonding\ e^-}{2}\right) = 0 \tag{3.5.2}$$

The hydrogen atoms in ammonia have the same number of electrons as neutral hydrogen atoms, and so their formal charge is also zero. Adding together the formal charges should give us the overall charge on the molecule or ion. In this example, the nitrogen and each hydrogen has a formal charge of zero. When summed the overall charge is zero, which is consistent with the overall charge on the NH_3 molecule.

> An atom, molecule, or ion has a formal charge of zero if it has the number of bonds that is typical for that species.

Typically, the structure with the most charges on the atoms closest to zero is the more stable Lewis structure. In cases where there are positive or negative formal charges on various atoms, stable structures generally have negative formal charges on the more electronegative atoms and positive formal charges on the less electronegative atoms. The next example further demonstrates how to calculate formal charges.



✔ EXAMPLE 3.5.2: THE AMMONIUM ION

Calculate the formal charges on each atom in the NH_4^+ ion.

Given: chemical species

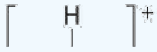
Asked for: formal charges

Strategy:

Identify the number of valence electrons in each atom in the NH_4^+ ion. Use the Lewis electron structure of NH_4^+ to identify the number of bonding and nonbonding electrons associated with each atom and then use Equation 3.5.1 to calculate the formal charge on each atom.

Solution:

The Lewis electron structure for the NH_4^+ ion is as follows:



The central nitrogen is bonded to four hydrogens. The molecule is surrounded by square brackets. Outside the bracket is where the positive charge is placed.

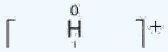
The nitrogen atom shares four bonding pairs of electrons, and a neutral nitrogen atom has five valence electrons. Using Equation ???, the formal charge on the nitrogen atom is therefore

$$formal\ charge\ (N) = 5 - \left(0 + \frac{8}{2}\right) = 0$$

Each hydrogen atom in has one bonding pair. The formal charge on each hydrogen atom is therefore

$$formal\ charge\ (H) = 1 - \left(0 + \frac{2}{2}\right) = 0$$

The formal charges on the atoms in the NH_4^+ ion are thus



In the Lewis structure, each hydrogen has a zero placed nearby while the nitrogen has a +1 placed nearby.

Adding together the formal charges on the atoms should give us the total charge on the molecule or ion. In this case, the sum of the formal charges is 0 + 1 + 0 + 0 + 0 = +1.

? EXERCISE 3.5.2

Write the formal charges on all atoms in BH_4^-.

Answer



Four hydrogens are bonded to a central boron. Each hydrogen has a zero placed nearby while the boron has a -1. The molecule is surrounded by square brackets. Outside of the brackets is a negative charge.

If an atom in a molecule or ion has the number of bonds that is typical for that atom (e.g., four bonds for carbon), its formal charge is zero.

3.5.4 USING FORMAL CHARGES TO DISTINGUISH VIABLE LEWIS STRUCTURES

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3.6: RESONANCE STRUCTURES

LEARNING OBJECTIVES

- To understand the concept of resonance.

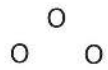
Resonance structures are a set of two or more Lewis Structures that collectively describe the electronic bonding of a single polyatomic species including fractional bonds and fractional charges. Resonance structures are capable of describing delocalized electrons that cannot be expressed by a single Lewis formula with an integral number of covalent bonds.

3.6.1 SOMETIMES ONE LEWIS STRUCTURE IS NOT ENOUGH

Sometimes, even when formal charges are considered, the bonding in some molecules or ions cannot be described by a single Lewis structure. Resonance is a way of describing delocalized electrons within certain molecules or polyatomic ions where the bonding cannot be expressed by a single Lewis formula. A molecule or ion with such delocalized electrons is represented by several contributing structures (also called resonance structures or canonical forms). Such is the case for ozone (O_3), an allotrope of oxygen with a V-shaped structure and an O–O–O angle of 117.5°.

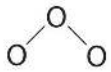
3.6.1.1 OZONE (O_3)

1. We know that ozone has a V-shaped structure, so one O atom is central:



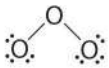
2. Each O atom has 6 valence electrons, for a total of 18 valence electrons.

3. Assigning one bonding pair of electrons to each oxygen–oxygen bond gives



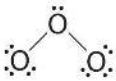
with 14 electrons left over.

4. If we place three lone pairs of electrons on each terminal oxygen, we obtain

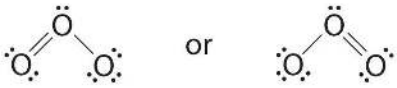


and have 2 electrons left over.

5. At this point, both terminal oxygen atoms have octets of electrons. We therefore place the last 2 electrons on the central atom:

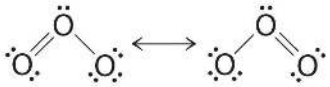


6. The central oxygen has only 6 electrons. We must convert one lone pair on a terminal oxygen atom to a bonding pair of electrons—but which one? Depending on which one we choose, we obtain either



Which is correct? In fact, neither is correct. Both predict one O–O single bond and one O=O double bond. As you will learn, if the bonds were of different types (one single and one double, for example), they would have different lengths. It turns out, however, that both O–O bond distances are identical, 127.2 pm, which is shorter than a typical O–O single bond (148 pm) and longer than the O=O double bond in O_2 (120.7 pm).

Equivalent Lewis dot structures, such as those of ozone, are called **resonance structures**. The position of the *atoms* is the same in the various resonance structures of a compound, but the position of the *electrons* is different. Double-headed arrows link the different resonance structures of a compound:



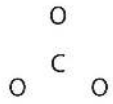
The double-headed arrow indicates that the actual electronic structure is an *average* of those shown, not that the molecule oscillates between the two structures.

> *When it is possible to write more than one equivalent resonance structure for a molecule or ion, the actual structure is the average of the resonance structures.*

3.6.1.2 THE CARBONATE (CO_3^{2-}) ION

Like ozone, the electronic structure of the carbonate ion cannot be described by a single Lewis electron structure. Unlike O_3, though, the actual structure of CO_3^{2-} is an average of *three* resonance structures.

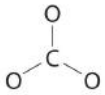
1. Because carbon is the least electronegative element, we place it in the central position:



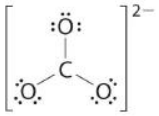
The three oxygens are drawn in the shape of a triangle with the carbon at the center of the triangle.

2. Carbon has 4 valence electrons, each oxygen has 6 valence electrons, and there are 2 more for the −2 charge. This gives 4 + (3 × 6) + 2 = 24 valence electrons.

3. Six electrons are used to form three bonding pairs between the oxygen atoms and the carbon:



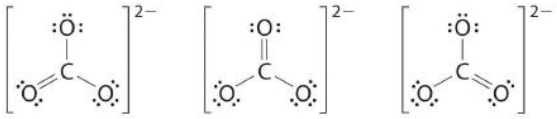
4. We divide the remaining 18 electrons equally among the three oxygen atoms by placing three lone pairs on each and indicating the −2 charge:



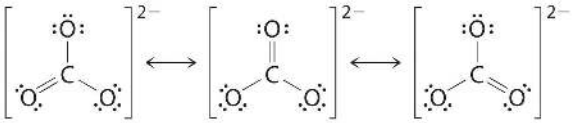
The Lewis dot structure has a central carbon that is bonded to 3 oxygens. Each oxygen has 3 lone pairs. The molecule is inside square brackets and has a charge of minus 2.

5. No electrons are left for the central atom.

6. At this point, the carbon atom has only 6 valence electrons, so we must take one lone pair from an oxygen and use it to form a carbon–oxygen double bond. In this case, however, there are *three* possible choices:



As with ozone, none of these structures describes the bonding exactly. Each predicts one carbon–oxygen double bond and two carbon–oxygen single bonds, but experimentally all C–O bond lengths are identical. We can write resonance structures (in this case, three of them) for the carbonate ion:

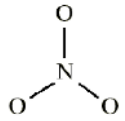


The resonance structure includes all three Lewis dot structures with double headed arrows between them.

The actual structure is an average of these three resonance structures.

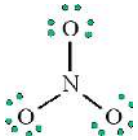
3.6.2 THE NITRATE (NO_3^-) ION

1. Count up the valence electrons: (1*5) + (3*6) + 1(ion) = **24** electrons
2. Draw the bond connectivities:

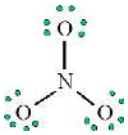


The three oxygens are drawn in the shape of a triangle with the nitrogen at the center of the triangle.

3. Add octet electrons to the atoms bonded to the center atom:

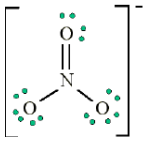


4. Place any leftover electrons (24-24 = **0**) on the center atom:



5. Does the central atom have an octet?

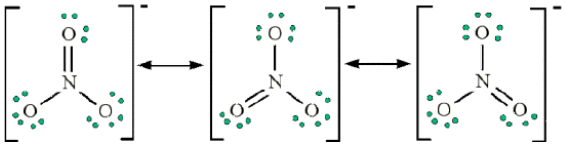
- **NO**, it has 6 electrons
- Add a multiple bond (first try a double bond) to see if the central atom can achieve an octet:



A double bond is added between one oxygen and the central nitrogen. The molecule has a negative charge.

6. Does the central atom have an octet?

- YES
- Are there possible resonance structures? YES



Note: We would expect that the bond lengths in the NO_3^- ion to be somewhat shorter than a single bond.



https://chem.libretexts.org/@go/page/475220

EXAMPLE 3.6.1: BENZENE

Benzene is a common organic solvent that was previously used in gasoline; it is no longer used for this purpose, however, because it is now known to be a carcinogen. The benzene molecule (C_6H_6) consists of a regular hexagon of carbon atoms, each of which is also bonded to a hydrogen atom. Use resonance structures to describe the bonding in benzene.

Given: molecular formula and molecular geometry

Asked for: resonance structures

Strategy:

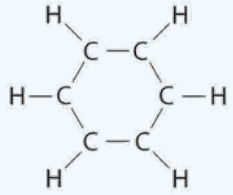
A. Draw a structure for benzene illustrating the bonded atoms. Then calculate the number of valence electrons used in this drawing.

B. Subtract this number from the total number of valence electrons in benzene and then locate the remaining electrons such that each atom in the structure reaches an octet.

C. Draw the resonance structures for benzene.

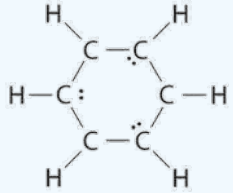
Solution:

A Each hydrogen atom contributes 1 valence electron, and each carbon atom contributes 4 valence electrons, for a total of (6 × 1) + (6 × 4) = 30 valence electrons. If we place a single bonding electron pair between each pair of carbon atoms and between each carbon and a hydrogen atom, we obtain the following:



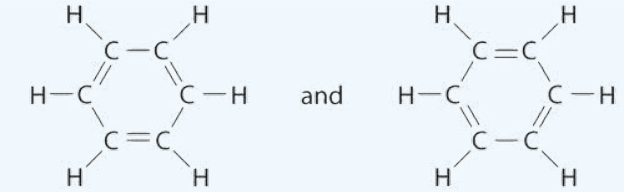
Each carbon atom in this structure has only 6 electrons and has a formal charge of +1, but we have used only 24 of the 30 valence electrons.

B If the 6 remaining electrons are uniformly distributed pairwise on alternate carbon atoms, we obtain the following:

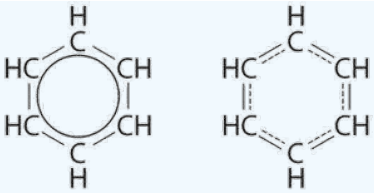


Three carbon atoms now have an octet configuration and a formal charge of −1, while three carbon atoms have only 6 electrons and a formal charge of +1. We can convert each lone pair to a bonding electron pair, which gives each atom an octet of electrons and a formal charge of 0, by making three C=C double bonds.

C There are, however, two ways to do this:



Each structure has alternating double and single bonds, but experimentation shows that each carbon–carbon bond in benzene is identical, with bond lengths (139.9 pm) intermediate between those typically found for a C–C single bond (154 pm) and a C=C double bond (134 pm). We can describe the bonding in benzene using the two resonance structures, but the actual electronic structure is an average of the two. The existence of multiple resonance structures for aromatic hydrocarbons like benzene is often indicated by drawing either a circle or dashed lines inside the hexagon:

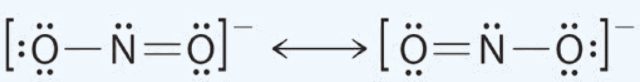


Benzene

EXERCISE 3.6.1: NITRITE ION

The sodium salt of nitrite is used to relieve muscle spasms. Draw two resonance structures for the nitrite ion (NO_2^-).

Answer



There is a double bond between one oxygen and the nitrogen, It can be found on the left oxygen or the right oxygen.

Resonance structures are particularly common in oxoanions of the *p*-block elements, such as sulfate and phosphate, and in aromatic hydrocarbons, such as benzene and naphthalene.

WARNING

If several reasonable resonance forms for a molecule exists, the "actual electronic structure" of the molecule will probably be intermediate between all the forms that you can draw. The classic example is benzene in Example **3.6.1**. One would expect the double bonds to be shorter than the single bonds, but if one overlays the two structures, you see that one structure has a single bond where the other structure has a double bond. The best measurements that we can make of benzene do not show two bond lengths - instead, they show that the bond length is intermediate between the two resonance structures.

Resonance structures is a mechanism that allows us to use all of the possible resonance structures to try to predict what the actual form of the molecule would be. Single bonds, double bonds, triple bonds, +1 charges, -1 charges, these are our limitations in explaining the structures, and the true forms can be in between - a carbon-carbon bond could be mostly single bond with a little bit of double bond character and a partial negative charge, for example.

3.6.3 SUMMARY

Some molecules have two or more chemically equivalent Lewis electron structures, called resonance structures. Resonance is a mental exercise and method within the Valence Bond Theory of bonding that describes the delocalization of electrons within molecules. These structures are written with a **double-headed arrow** between them, indicating that none of the Lewis structures accurately describes the bonding but that the actual structure is an average of the individual resonance structures. Resonance structures are used when one Lewis structure for a single molecule cannot fully describe the bonding that takes place between neighboring atoms relative to the empirical data for the actual bond lengths between those atoms. The net sum of valid resonance structures is defined as a resonance hybrid, which represents the overall delocalization of electrons within the molecule. A molecule that has several resonance structures is more stable than one with fewer. Some resonance structures are more favorable than others.

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3.7: EXCEPTIONS TO THE OCTET RULE

LEARNING OBJECTIVES

- To assign a Lewis dot symbol to elements not having an octet of electrons in their compounds.

Three cases can be constructed that do not follow the octet rule, and as such, they are known as the exceptions to the octet rule. Following the Octet Rule for Lewis Dot Structures leads to the most accurate depictions of stable molecular and atomic structures and because of this we always want to use the octet rule when drawing Lewis Dot Structures. However, it is hard to imagine that one rule could be followed by all molecules. There is always an exception, and in this case, three exceptions:

1. When there are an odd number of valence electrons
2. When there are too few valence electrons
3. When there are too many valence electrons

3.7.1 EXCEPTION 1: SPECIES WITH ODD NUMBERS OF ELECTRONS

The first exception to the Octet Rule is when there are an odd number of valence electrons. An example of this would be Nitrogen (II) Oxide also called nitric oxide (**NO**. Nitrogen has 5 valence electrons while Oxygen has 6. The total would be 11 valence electrons to be used. The Octet Rule for this molecule is fulfilled in the above example, however that is with 10 valence electrons. The last one does not know where to go. The lone electron is called an unpaired electron. But where should the unpaired electron go? The unpaired electron is usually placed in the Lewis Dot Structure so that each element in the structure will have the *lowest* formal charge possible. The formal charge is *the perceived charge on an individual atom in a molecule when atoms do not contribute equal numbers of electrons to the bonds they participate in*.

No formal charge at all is the most ideal situation. An example of a stable molecule with an odd number of valence electrons would be nitric oxide. nitric oxide has 11 valence electrons. If you need more information about formal charges, see Lewis Structures. If we were to imagine nitric oxide had ten valence electrons we would come up with the Lewis Structure (Figure **3.7.1**):

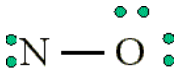


Figure **3.7.1**: This is if nitric oxide has only ten valence electrons, which it does not.

Let's look at the formal charges of Figure **3.7.2** based on this Lewis structure. Nitrogen normally has five valence electrons. In Figure **3.7.1**, it has two lone pair electrons and it participates in two bonds (a double bond) with oxygen. This results in nitrogen having a formal charge of +1. Oxygen normally has six valence electrons. In Figure **3.7.1**, oxygen has four lone pair electrons and it participates in two bonds with nitrogen. Oxygen therefore has a formal charge of 0. The overall molecule here has a formal charge of +1 (+1 for nitrogen, 0 for oxygen. +1 + 0 = +1). However, if we add the eleventh electron to nitrogen (because we want the molecule to have the *lowest* total formal charge), it will bring both the nitrogen and the molecule's overall charges to zero, the most ideal formal charge situation. That is exactly what is done to get the correct Lewis structure for nitric oxide (Figure **3.7.2**):

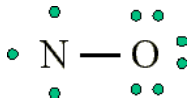


Figure **3.7.2**: The proper Lewis structure for NO molecule

FREE RADICALS

There are actually very few stable molecules with odd numbers of electrons that exist, since that unpaired electron is willing to react with other unpaired electrons. Most odd electron species are highly reactive, which we call Free Radicals. Because of their instability, free radicals bond to atoms in which they can take an electron from in order to become stable, making them very chemically reactive. Radicals are found as both reactants and products, but generally react to form more stable molecules as soon as they can. In order to emphasize the existence of the unpaired electron, radicals are denoted with a dot in front of their chemical symbol as with $\cdot OH$, the hydroxyl radical. An example of a radical you may by familiar with already is the gaseous chlorine atom, denoted $\cdot Cl$. Interestingly, an odd Number of Valence Electrons will result in the molecule being paramagnetic.

3.7.2 EXCEPTION 2: INCOMPLETE OCTETS

The second exception to the Octet Rule is when there are too few valence electrons that results in an incomplete Octet. There are even more occasions where the octet rule does not give the most correct depiction of a molecule or ion. This is also the case with incomplete octets.

Species with incomplete octets are pretty rare and generally are only found in some beryllium, aluminum, and boron compounds including the boron hydrides. Let's take a look at one such hydride, BH_3 (Borane).

If one were to make a Lewis structure for BH_3 following the basic strategies for drawing Lewis structures, one would probably come up with this structure (Figure **3.7.2**):

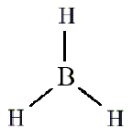


Figure **3.7.3**: The structure of $\boldsymbol{BH_3}$ is square planer.

The problem with this structure is that boron has an incomplete octet; it only has six electrons around it. Hydrogen atoms can naturally only have only 2 electrons in their outermost shell (their version of an octet), and as such there are no spare electrons to form a double bond with boron. One might surmise that the failure of this structure to form complete octets must mean that this bond should be ionic instead of covalent. However, boron has an electronegativity that is very similar to hydrogen, meaning there is likely very little ionic character in the hydrogen to boron bonds, and as such this Lewis structure, though it does not fulfill the octet rule, is likely the best structure possible for depicting BH_3 with Lewis theory. One of the things that may account for BH_3's incomplete octet is that it is commonly a transitory species, formed temporarily in reactions that involve multiple steps.

Let's take a look at another incomplete octet situation dealing with boron, BF_3 (Boron trifluorine). Like with BH_3, the initial drawing of a Lewis structure of BF_3 will form a structure where boron has only six electrons around it (Figure **3.7.4**).

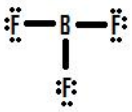


Figure **3.7.4**

If you look Figure **3.7.4**, you can see that the fluorine atoms possess extra lone pairs that they can use to make additional bonds with boron, and you might think that all you have to do is make one lone pair into a bond and the structure will be correct. If we add one double bond between boron and one of the fluorines we get the following Lewis Structure (Figure **3.7.5**):

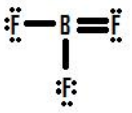


Figure **3.7.5**

Each fluorine has eight electrons, and the boron atom has eight as well! Each atom has a perfect octet, right? Not so fast. We must examine the formal charges of this structure. The fluorine that shares a double bond with boron has six electrons around it (four from its two lone pairs of electrons and one each from its two bonds with boron). This is one less electron than the number of valence electrons it would have naturally (Group Seven elements have seven valence electrons), so it has a formal charge of +1. The two flourines that share single bonds with boron have seven electrons around them (six from their three lone pairs and one from their single bonds with boron). This is the same amount as the number of valence electrons they would have on their own, so they both have a formal charge of zero. Finally, boron has four electrons around it (one from each of its four bonds shared with fluorine). This is one more electron than the number of valence electrons that boron would have on its own, and as such boron has a formal charge of -1.

This structure is supported by the fact that the experimentally determined bond length of the boron to fluorine bonds in BF_3 is less than what would be typical for a single bond (see Bond Order and Lengths). However, this structure contradicts one of the major rules of formal charges: Negative formal charges are supposed to be found on the more electronegative atom(s) in a bond, but in the structure depicted in Figure **3.7.5**, a *positive* formal charge is found on fluorine, which not only is the most electronegative element in the structure, but the most electronegative element in the entire periodic table ($\boldsymbol{\chi = 4.0}$). Boron on the other hand, with the much lower electronegativity of 2.0, has the negative formal charge in this structure. This formal charge-electronegativity disagreement makes this double-bonded structure impossible.

However the large electronegativity difference here, as opposed to in BH_3, signifies significant polar bonds between boron and fluorine, which means there is a high ionic character to this molecule. This suggests the possibility of a semi-ionic structure such as seen in Figure **3.7.6**:

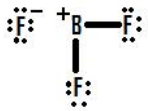


Figure **3.7.6**

A bond is broken between one of the fluorine's and the boron making the free fluorine negatively charged and the boron positively charged.

None of these three structures is the "correct" structure in this instance. The most "correct" structure is most likely a resonance of all three structures: the one with the incomplete octet (Figure **3.7.4**), the one with the double bond (Figure **3.7.5**), and the one with the ionic bond (Figure **3.7.6**). The most contributing structure is probably the incomplete octet structure (due to Figure **3.7.5** being basically impossible and Figure **3.7.6** not matching up with the behavior and properties of BF_3). As you can see even when other possibilities exist, incomplete octets may best portray a molecular structure.

As a side note, it is important to note that BF_3 frequently bonds with a F^- ion in order to form BF_4^- rather than staying as BF_3. This structure completes boron's octet and it is more common in nature. This exemplifies the fact that incomplete octets are rare, and other configurations are typically more favorable, including bonding with additional ions as in the case of BF_3 .

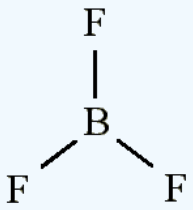
EXAMPLE **3.7.1**: NF_3

Draw the Lewis structure for boron trifluoride (BF_3).

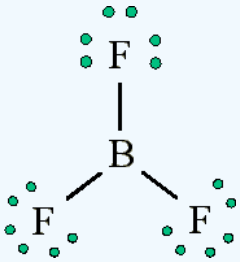
Solution

1. Add electrons (3*7) + 3 = **24**

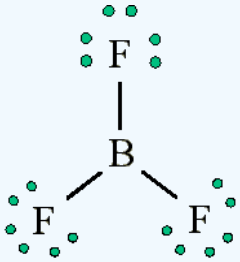
2. Draw connectivities:



3. Add octets to outer atoms:

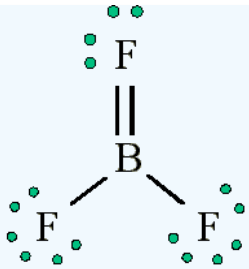


4. Add extra electrons (24-24=0) to central atom:



5. Does central electron have octet?

- NO. It has 6 electrons
- Add a multiple bond (double bond) to see if central atom can achieve an octet:

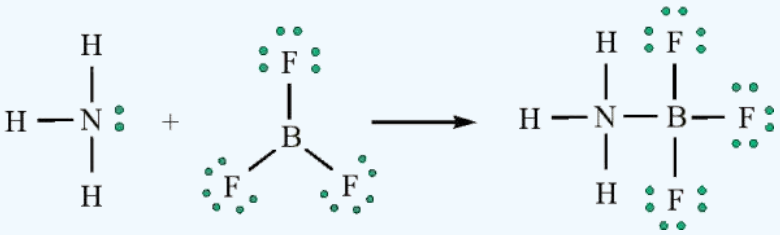


6. The central Boron now has an octet (there would be three resonance Lewis structures)

However...

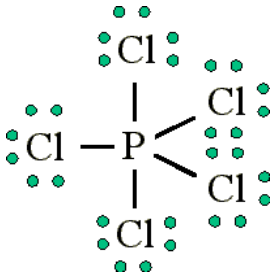
- In this structure with a double bond the fluorine atom is sharing extra electrons with the boron.
- The fluorine would have a '+' partial charge, and the boron a '-' partial charge, this is inconsistent with the electronegativities of fluorine and boron.
- Thus, ***the structure of BF_3, with single bonds, and 6 valence electrons around the central boron is the most likely structure***

BF_3 reacts strongly with compounds which have an unshared pair of electrons which can be used to form a bond with the boron:



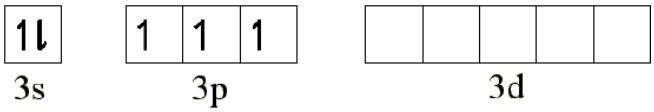
3.7.3 EXCEPTION 3: EXPANDED VALENCE SHELLS

More common than incomplete octets are expanded octets where the central atom in a Lewis structure has more than eight electrons in its valence shell. In expanded octets, the central atom can have ten electrons, or even twelve. *Molecules with expanded octets involve highly electronegative terminal atoms, and a nonmetal central atom found in the third period or below*, which those terminal atoms bond to. For example, PCl_5 is a legitimate compound (whereas NCl_5) is not:



Expanded valence shells are observed **only** for elements in period 3 (i.e. n=3) and beyond

The 'octet' rule is based upon available n*s* and n*p* orbitals for valence electrons (2 electrons in the *s* orbitals, and 6 in the *p* orbitals). Beginning with the n=3 principle quantum number, the d orbitals become available (l=2). The orbital diagram for the valence shell of phosphorous is:



Hence, the third period elements occasionally exceed the octet rule by using their empty d orbitals to accommodate additional electrons. Size is also an important consideration:

- The larger the central atom, the larger the number of electrons which can surround it
- Expanded valence shells occur most often when the central atom is bonded to small electronegative atoms, such as F, Cl and O.

There is currently much scientific exploration and inquiry into the reason why expanded valence shells are found. The top area of interest is figuring out where the extra pair(s) of electrons are found. Many chemists think that there is not a very large energy difference between the 3p and 3d orbitals, and as such it is plausible for extra electrons to easily fill the 3d orbital when an expanded octet is more favorable than having a complete octet. This matter is still under hot debate, however and there is even debate as to what makes an expanded octet more favorable than a configuration that follows the octet rule.

One of the situations where expanded octet structures are treated as more favorable than Lewis structures that follow the octet rule is when the formal charges in the expanded octet structure are smaller than in a structure that adheres to the octet rule, or when there are less formal charges in the expanded octet than in the structure a structure that adheres to the octet rule.



EXAMPLE 3.7.2: THE SO_4^{-2} ION

Such is the case for the sulfate ion, SO_4^{-2}. A strict adherence to the octet rule forms the following Lewis structure:

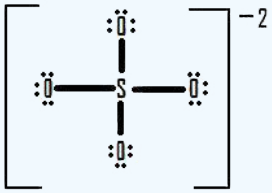


Figure **3.7.12**

Four oxygens are bonded to a central sulfur. Each oxygen has 3 lone pairs. The molecule has a minus 2 charge.

If we look at the formal charges on this molecule, we can see that all of the oxygen atoms have seven electrons around them (six from the three lone pairs and one from the bond with sulfur). This is one more electron than the number of valence electrons then they would have normally, and as such each of the oxygens in this structure has a formal charge of -1. Sulfur has four electrons around it in this structure (one from each of its four bonds) which is two electrons more than the number of valence electrons it would have normally, and as such it carries a formal charge of +2.

If instead we made a structure for the sulfate ion with an expanded octet, it would look like this:

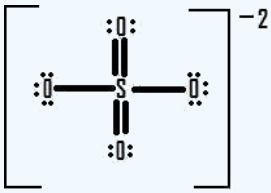


Figure **3.7.13**

Looking at the formal charges for this structure, the sulfur ion has six electrons around it (one from each of its bonds). This is the same amount as the number of valence electrons it would have naturally. This leaves sulfur with a formal charge of zero. The two oxygens that have double bonds to sulfur have six electrons each around them (four from the two lone pairs and one each from the two bonds with sulfur). This is the same amount of electrons as the number of valence electrons that oxygen atoms have on their own, and as such both of these oxygen atoms have a formal charge of zero. The two oxygens with the single bonds to sulfur have seven electrons around them in this structure (six from the three lone pairs and one from the bond to sulfur). That is one electron more than the number of

valence electrons that oxygen would have on its own, and as such those two oxygens carry a formal charge of -1. Remember that with formal charges, the goal is to keep the formal charges (or the difference between the formal charges of each atom) as small as possible. The number of and values of the formal charges on this structure (-1 and 0 (difference of 1) in Figure **3.7.12**, as opposed to +2 and -1 (difference of 3) in Figure **3.7.12**) is significantly lower than on the structure that follows the octet rule, and as such an expanded octet is plausible, and even preferred to a normal octet, in this case.

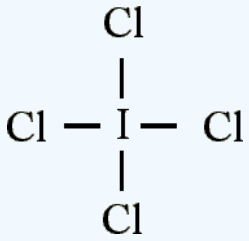
EXAMPLE 3.7.3: THE ICl_4^- ION

Draw the Lewis structure for ICl_4^- ion.

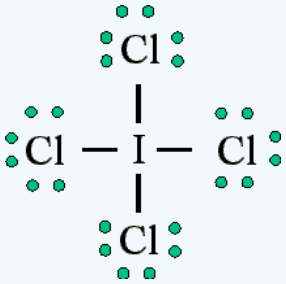
Solution

1. Count up the valence electrons: 7+(4*7)+1 = **36** electrons

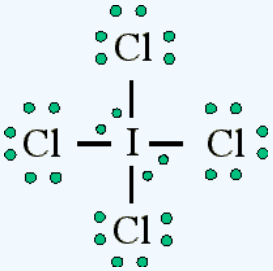
2. Draw the connectivities:



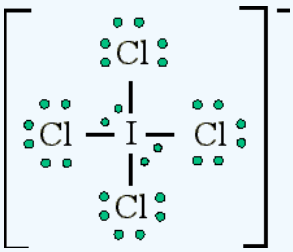
3. Add octet of electrons to outer atoms:



4. Add extra electrons (36-32=**4**) to central atom:



5. The ICl_4^- ion thus has 12 valence electrons around the central Iodine (in the 5*d* orbitals)



Expanded Lewis structures are also plausible depictions of molecules when experimentally determined bond lengths suggest partial double bond characters even when single bonds would already fully fill the octet of the central atom. Despite the cases for expanded octets, as mentioned for incomplete octets, it is important to keep in mind that, in general, the octet rule applies.

3.7.4 SUMMARY

Following the Octet Rule for Lewis Dot Structures leads to the most accurate depictions of stable molecular and atomic structures and because of this we always want to use the octet rule when drawing Lewis Dot Structures. There are three exceptions: (1) When there are an odd number of valence electrons, (2) When there are too few valence electrons, and (3) when there are too many valence electrons

3.7.5 REFERENCES

1. Petrucci, Ralph H.; Harwood, William S.; Herring, F. G.; Madura, Jeffrey D. General Chemistry: Principles & Modern Applications. 9th Ed. New Jersey. Pearson Education, Inc. 2007.
2. Moore, John W.; Stanitski, Conrad L.; Jurs, Peter C. Chemistry; The Molecular Science. 2nd Ed. 2004.

3.7.6 CONTRIBUTORS AND ATTRIBUTIONS

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3.8: STRENGTH OF COVALENT BONDS

LEARNING OBJECTIVES

- The define Bond-dissociation energy (bond energy)
- To correlate bond strength with bond length
- To define and used *average bond energies*

In proposing his theory that octets can be completed by two atoms sharing electron pairs, Lewis provided scientists with the first description of covalent bonding. In this section, we expand on this and describe some of the properties of covalent bonds. The stability of a molecule is a function of the strength of the covalent bonds holding the atoms together.

3.8.1 THE RELATIONSHIP BETWEEN BOND ORDER AND BOND ENERGY

Triple bonds between like atoms are shorter than double bonds, and because more energy is required to completely break all three bonds than to completely break two, a triple bond is also stronger than a double bond. Similarly, double bonds between like atoms are stronger and shorter than single bonds. Bonds of the same order between *different* atoms show a wide range of bond energies, however. Table **3.8.1** lists the average values for some commonly encountered bonds. Although the values shown vary widely, we can observe four trends:

Table **3.8.1**: Average Bond Energies (kJ/mol) for Commonly Encountered Bonds at 273 K

Single Bonds										Multiple Bonds	
H–H	432	C–C	346	N–N	≈167	O–O	≈142	F–F	155	C=C	602
H–C	411	C–Si	318	N–O	201	O–F	190	F–Cl	249	C≡C	835
H–Si	318	C–N	305	N–F	283	O–Cl	218	F–Br	249	C=N	615
H–N	386	C–O	358	N–Cl	313	O–Br	201	F–I	278	C≡N	887
H–P	≈322	C–S	272	N–Br	243	O–I	201	Cl–Cl	240	C=O	749
H–O	459	C–F	485	P–P	201	S–S	226	Cl–Br	216	C≡O	1072
H–S	363	C–Cl	327			S–F	284	Cl–I	208	N=N	418
H–F	565	C–Br	285			S–Cl	255	Br–Br	190	N≡N	942
H–Cl	428	C–I	213			S–Br	218	Br–I	175	N=O	607
H–Br	362	Si–Si	222					I–I	149	O=O	494
H–I	295	Si–O	452							S=O	532

Source: Data from J. E. Huheey, E. A. Keiter, and R. L. Keiter, Inorganic Chemistry, 4th ed. (1993).

1. Bonds between hydrogen and atoms in the same column of the periodic table decrease in strength as we go down the column. Thus an H–F bond is stronger than an H–I bond, H–C is stronger than H–Si, H–N is stronger than H–P, H–O is stronger than H–S, and so forth. The reason for this is that the region of space in which electrons are shared between two atoms becomes proportionally smaller as one of the atoms becomes larger (part (a) in Figure 8.11).
2. Bonds between like atoms usually become *weaker* as we go down a column (important exceptions are noted later). For example, the C–C single bond is stronger than the Si–Si single bond, which is stronger than the Ge–Ge bond, and so forth. As two bonded atoms become larger, the region between them occupied by bonding electrons becomes *proportionally* smaller, as illustrated in part (b) in Figure 8.11. Noteworthy exceptions are single bonds between the period 2 atoms of groups 15, 16, and 17 (i.e., N, O, F), which are unusually weak compared with single bonds between their larger congeners. It is likely that the N–N, O–O, and F–F single bonds are weaker than might be expected due to strong repulsive interactions between lone pairs of electrons on *adjacent* atoms. The trend in bond energies for the halogens is therefore

$$\mathbf{Cl{-}Cl > Br{-}Br > F{-}F > I{-}I}$$

Similar effects are also seen for the O–O versus S–S and for N–N versus P–P single bonds.

> Bonds between hydrogen and atoms in a given column in the periodic table are weaker down the column; bonds between like atoms usually become weaker down a column.

3. Because elements in periods 3 and 4 rarely form multiple bonds with themselves, their multiple bond energies are not accurately known. Nonetheless, they are presumed to be significantly weaker than multiple bonds between lighter atoms of the same families. Compounds

containing an Si=Si double bond, for example, have only recently been prepared, whereas compounds containing C=C double bonds are one of the best-studied and most important classes of organic compounds.

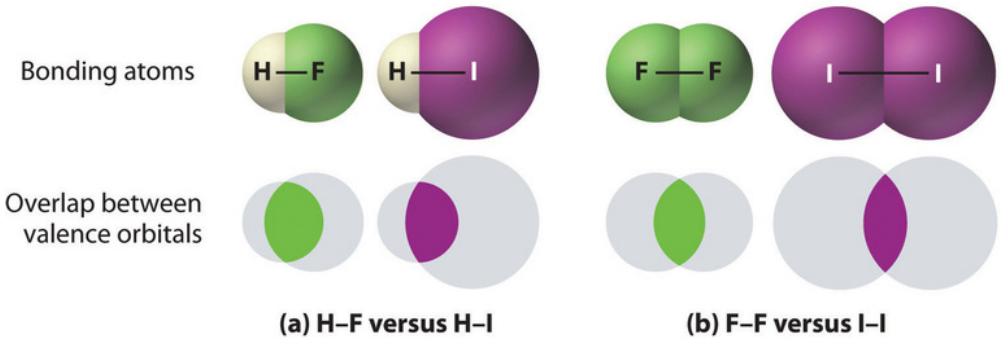


Figure 3.8.1: The Strength of Covalent Bonds Depends on the Overlap between the Valence Orbitals of the Bonded Atoms. The relative sizes of the region of space in which electrons are shared between (a) a hydrogen atom and lighter (smaller) vs. heavier (larger) atoms in the same periodic group; and (b) two lighter versus two heavier atoms in the same group. Although the absolute amount of shared space increases in both cases on going from a light to a heavy atom, the amount of space *relative to the size of the bonded atom* decreases; that is, the *percentage* of total orbital volume decreases with increasing size. Hence the strength of the bond decreases.

4. Multiple bonds between carbon, oxygen, or nitrogen and a period 3 element such as phosphorus or sulfur tend to be unusually strong. In fact, multiple bonds of this type dominate the chemistry of the period 3 elements of groups 15 and 16. Multiple bonds to phosphorus or sulfur occur as a result of *d*-orbital interactions, as we discussed for the SO_4^{2-} ion in Section 8.6. In contrast, silicon in group 14 has little tendency to form discrete silicon–oxygen double bonds. Consequently, SiO_2 has a three-dimensional network structure in which each silicon atom forms four Si–O single bonds, which makes the physical and chemical properties of SiO_2 very different from those of CO_2.

> *Bond strengths increase as bond order* ***increases****, while bond distances* ***decrease****.*

3.8.2 THE RELATIONSHIP BETWEEN MOLECULAR STRUCTURE AND BOND ENERGY

Bond energy is defined as the energy required to break a particular bond in a molecule in the gas phase. Its value depends on not only the identity of the bonded atoms but also their environment. Thus the bond energy of a C–H single bond is *not* the same in all organic compounds. For example, the energy required to break a C–H bond in methane varies by as much as 25% depending on how many other bonds in the molecule have already been broken (Table 3.8.2); that is, the C–H bond energy depends on its molecular environment. Except for diatomic molecules, the bond energies listed in Table 3.8.1 are *average* values for all bonds of a given type in a range of molecules. Even so, they are not likely to differ from the actual value of a given bond by more than about 10%.

Table 3.8.2: Energies for the Dissociation of Successive C–H Bonds in Methane. Source: Data from *CRC Handbook of Chemistry and Physics* (2004).

Reaction	D (kJ/mol)
$CH_4(g) \rightarrow CH_3(g) + H(g)$	439
$CH_3(g) \rightarrow CH_2(g) + H(g)$	462
$CH_2(g) \rightarrow CH(g) + H(g)$	424
$CH(g) \rightarrow C(g) + H(g)$	338

We can estimate the enthalpy change for a chemical reaction by adding together the average energies of the bonds broken in the reactants and the average energies of the bonds formed in the products and then calculating the difference between the two. If the bonds formed in the products are stronger than those broken in the reactants, then energy will be released in the reaction ($\Delta H_{rxn} < 0$):

$$\Delta H_{rxn} \approx \sum(\text{bond energies of bonds broken}) - \sum(\text{bond energies of bonds formed}) \tag{3.8.1}$$

The ≈ sign is used because we are adding together *average* bond energies; hence this approach does not give exact values for ΔH_{rxn}.

Let's consider the reaction of 1 mol of *n*-heptane (C_7H_{16}) with oxygen gas to give carbon dioxide and water. This is one reaction that occurs during the combustion of gasoline:

$$CH_3(CH_2)_5CH_3\,(l) + 11\,O_2\,(g) \rightarrow 7\,CO_2\,(g) + 8\,H_2O\,(g) \tag{3.8.2}$$

In this reaction, 6 C–C bonds, 16 C–H bonds, and 11 O=O bonds are broken per mole of *n*-heptane, while 14 C=O bonds (two for each CO_2) and 16 O–H bonds (two for each H_2O) are formed. The energy changes can be tabulated as follows:

Binds Broken (kJ/mol) and Bonds Formed (kJ/mol)

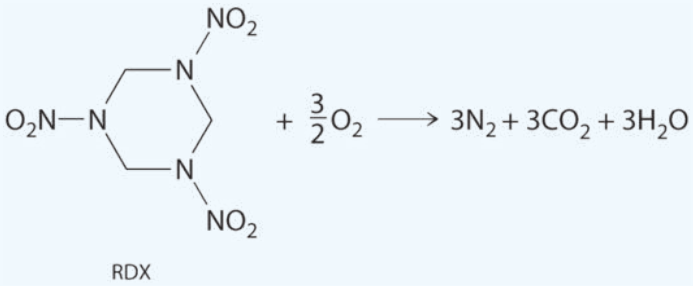
Bonds Broken (kJ/mol)		Bonds Formed (kJ/mol)	
6 C–C	346 × 6 = 2076	14 C=O	799 × 14 = 11,186
16 C–H	411 × 16 = 6576	16 O–H	459 × 16 = 7344
11 O=O	494 × 11 = 5434		**Total** = 18,530
	Total = 14,086		

The bonds in the products are stronger than the bonds in the reactants by about 4444 kJ/mol. This means that ΔH_{rxn} is approximately −4444 kJ/mol, and the reaction is highly exothermic (which is not too surprising for a combustion reaction).

If we compare this approximation with the value obtained from measured ΔH_f^o values ($\Delta H_{rxn} = -481\ 7 kJ/mol$), we find a discrepancy of only about 8%, less than the 10% typically encountered. Chemists find this method useful for calculating approximate enthalpies of reaction for molecules whose actual ΔH_f^o values are unknown. These approximations can be important for predicting whether a reaction is **exothermic** or **endothermic**—and to what degree.

EXAMPLE 3.8.1: EXPLOSIVES

The compound RDX (Research Development Explosive) is a more powerful explosive than dynamite and is used by the military. When detonated, it produces gaseous products and heat according to the following reaction. Use the approximate bond energies in Table 3.8.1 to estimate the ΔH_{rxn} per mole of RDX.



RDX

Given: chemical reaction, structure of reactant, and Table 3.8.1.

Asked for: ΔH_{rxn} per mole

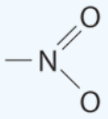
Strategy:

A. List the types of bonds broken in RDX, along with the bond energy required to break each type. Multiply the number of each type by the energy required to break one bond of that type and then add together the energies. Repeat this procedure for the bonds formed in the reaction.

B. Use Equation 3.8.1 to calculate the amount of energy consumed or released in the reaction (ΔH_{rxn}).

Solution:

We must add together the energies of the bonds in the reactants and compare that quantity with the sum of the energies of the bonds in the products. A nitro group (–NO_2) can be viewed as having one N–O single bond and one N=O double bond, as follows:



In fact, however, both N–O distances are usually the same because of the presence of two equivalent resonance structures.

A We can organize our data by constructing a table:

Bonds Broken (kJ/mol)

Bonds Broken (kJ/mol)		Bonds Broken (kJ/mol)	
6 C–H	411 × 6 = 2466	6 C=O	799 × 6 = 4794
3 N–N	167 × 3 = 501	6 O–H	459 × 6 = 2754
3 N–O	201 × 3 = 603		**Total** = 10,374
3 N=O	607 × 3 = 1821		
1.5 O=O	494 × 1.5 = 741		
	Total = 7962		

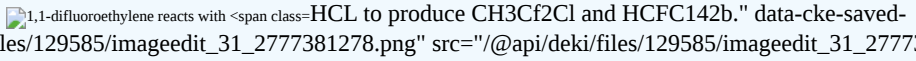
B From Equation **3.8.1**, we have

$$\begin{aligned}\Delta H_{rxn} &\approx \sum(\text{bond energies of bonds broken}) - \sum(\text{bond energies of bonds formed}) \\ &= 7962\ kJ/mol - 10,374\ kJ/mol \\ &= -2412\ kJ/mol\end{aligned}$$

Thus this reaction is also highly exothermic

? EXERCISE 3.8.1: FREON

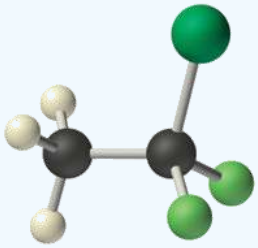
The molecule HCFC-142b is a hydrochlorofluorocarbon that is used in place of chlorofluorocarbons (CFCs) such as the Freons and can be prepared by adding HCl to 1,1-difluoroethylene:



Use tabulated bond energies to calculate ΔH_{rxn}.

Answer

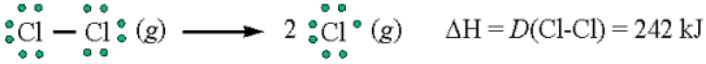
−54 kJ/mol



HCFC-142b

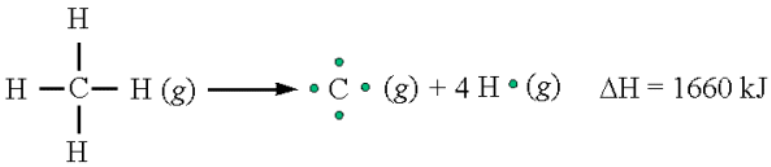
3.8.3 BOND DISSOCIATION ENERGY

Bond Dissociation Energy (also referred to as Bond energy) is the enthalpy change (ΔH, heat input) required to break a bond (in 1 mole of a gaseous substance)



where "D(Cl-Cl)" represents the bond dissociation energy for the Cl-Cl bond

What about when we have a compound which is not a diatomic molecule? Consider the dissociation of ***methane***:



There are four equivalent C-H bonds, thus we can that the dissociation energy for a single C-H bond would be:

$$D(C-H) = (1660/4)\, kJ/mol$$
$$= 415\, kJ/mol$$

> The bond energy for a given bond is influenced by the rest of the molecule. However, this is a relatively small effect (suggesting that bonding electrons are localized between the bonding atoms). Thus, the bond energy for most bonds varies little from the average bonding energy for that type of bond

Bond energy is always a *positive* value - it takes energy to break a covalent bond (conversely energy is released during bond formation)

Table **3.8.4**: Average bond energies:

Bond	(kJ/mol)
C-F	485
C-Cl	328
C-Br	276
C-I	240
C-C	348
C-N	293
C-O	358
C-F	485
C-C	348
C=C	614
C≡C	839

The more stable a molecule (i.e. the stronger the bonds) the less likely the molecule is to undergo a chemical reaction.



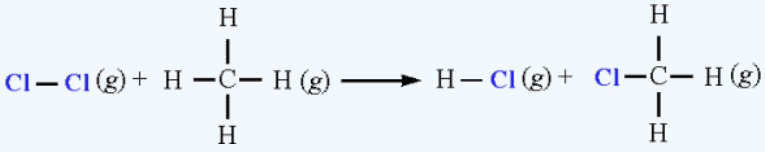
3.8.4 BOND ENERGIES AND THE ENTHALPY OF REACTIONS

If we know which bonds are broken and which bonds are made during a chemical reaction, we can estimate the enthalpy change of the reaction (ΔH_{rxn}) even if we do not know the enthalpies of formation ((ΔH_f°)for the reactants and products:

$$\Delta H = \sum \text{bond energies of broken bonds} - \sum \text{bond energies of formed bonds} \tag{3.8.3}$$

✔ EXAMPLE **3.8.2**: CHLORINATION OF METHANE

What is the enthalpy of reaction between 1 mol of chlorine and 1 mol methane?



Solution

We use Equation 3.8.3, which requires tabulating bonds broken and formed.

- **Bonds broken**: 1 mol of Cl-Cl bonds, 1 mol of C-H bonds
- **Bonds formed**: 1 mol of H-Cl bonds, 1 mol of C-Cl bonds

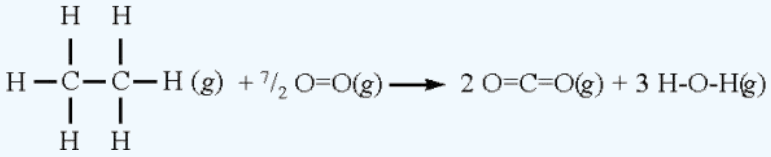
$$\begin{aligned}\Delta H &= [D(Cl-Cl)+D(C-H)]-[D(H-Cl)+D(C-Cl)]\\ &= [242kJ+413kJ]-[431kJ+328kJ]\\ &= -104\,kJ\end{aligned}$$

Thus, the reaction is **exothermic** (because the bonds in the products are stronger than the bonds in the reactants)

EXAMPLE 3.8.3: COMBUSTION OF ETHANE

What is the enthalpy of reaction for the combustion of 1 mol of ethane?

$$C_2H_6(g) + {}^7/_2O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(g)$$



Solution

We use Equation 3.8.3, which requires tabulating bonds broken and formed.

- **bonds broken**: 6 moles C-H bonds, 1 mol C-C bonds, $^7/_2$ moles of O=O bonds
- **bonds formed**: 4 moles C=O bonds, 6 moles O-H bonds

$$\begin{aligned}\Delta H &= [(6\times 413)+(348)+(\frac{7}{2}\times 495)]-[(4\times 799)+(6\times 463)]\\ &= 4558-5974\\ &= -1416\,kJ\end{aligned}$$

Therefor the reaction is exothermic.

Table **3.8.5**: Bond strength and bond length

Bond	Bond Energy (kJ/mol)	Bond Length (Å)
C-C	348	1.54
C=C	614	1.34
C≡C	839	1.

As the number of bonds between two atoms increases, the bond grows shorter and stronger

3.8.5 SUMMARY

Bond order is the number of electron pairs that hold two atoms together. Single bonds have a bond order of one, and multiple bonds with bond orders of two (a double bond) and three (a triple bond) are quite common. In closely related compounds with bonds between the same kinds of atoms, the bond with the highest bond order is both the shortest and the strongest. In bonds with the same bond order between different atoms, trends are observed that, with few exceptions, result in the strongest single bonds being formed between the smallest atoms. Tabulated values of average bond energies can be used to calculate the enthalpy change of many chemical reactions. If the bonds in the products are stronger than those in the reactants, the reaction is exothermic and vice versa.

The breakage and formation of bonds is similar to a relationship: you can either get married or divorced and it is more favorable to be married.

- Energy is always **released** to make bonds, which is why the enthalpy change for breaking bonds is always **positive**.
- Energy is always **required** to break bonds. Atoms are much happier when they are "married" and release energy because it is easier and more stable to be in a relationship (e.g., to generate *octet electronic configurations*). The enthalpy change is always **negative** because the system is releasing energy when forming bond.

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3.E: BASIC CONCEPTS OF CHEMICAL BONDING (EXERCISES)

3.E.1 CHEMICAL BONDS, LEWIS SYMBOLS AND THE OCTET RULE (1~4)

3.E.1.1 CONCEPTUAL PROBLEMS

1. The Lewis electron system is a simplified approach for understanding bonding in covalent and ionic compounds. Why do chemists still find it useful?
2. Is a Lewis dot symbol an exact representation of the valence electrons in an atom or ion? Explain your answer.
3. How can the Lewis electron dot system help to predict the stoichiometry of a compound and its chemical and physical properties?
4. How is a Lewis dot symbol consistent with the quantum mechanical model of the atom? How is it different?

3.E.1.2 CONCEPTUAL ANSWER

3. Lewis dot symbols allow us to predict the number of bonds atoms will form, and therefore the stoichiometry of a compound. The Lewis structure of a compound also indicates the presence or absence of lone pairs of electrons, which provides information on the compound's chemical reactivity and physical properties.

3.E.2 IONIC BONDING (5~16)

3.E.2.1 CONCEPTUAL PROBLEMS

5. Describe the differences in behavior between NaOH and CH_3OH in aqueous solution. Which solution would be a better conductor of electricity? Explain your reasoning.
6. What is the relationship between the strength of the electrostatic attraction between oppositely charged ions and the distance between the ions? How does the strength of the electrostatic interactions change as the size of the ions increases?
7. Which will result in the release of more energy: the interaction of a gaseous sodium ion with a gaseous oxide ion or the interaction of a gaseous sodium ion with a gaseous bromide ion? Why?
8. Which will result in the release of more energy: the interaction of a gaseous chloride ion with a gaseous sodium ion or a gaseous potassium ion? Explain your answer.
9. What are the predominant interactions when oppositely charged ions are
    1. far apart?
    2. at internuclear distances close to r_0?
    3. very close together (at a distance that is *less* than the sum of the ionic radii)?
10. Several factors contribute to the stability of ionic compounds. Describe one type of interaction that *destabilizes* ionic compounds. Describe the interactions that *stabilize* ionic compounds.
11. What is the relationship between the electrostatic attractive energy between charged particles and the distance between the particles?

3.E.2.2 CONCEPTUAL ANSWER

5.

6.

7. The interaction of a sodium ion and an oxide ion. The electrostatic attraction energy between ions of opposite charge is directly proportional to the charge on each ion (Q_1 and Q_2 in Equation 9.1). Thus, more energy is released as the charge on the ions increases (assuming the internuclear distance does not increase substantially). A sodium ion has a +1 charge; an oxide ion, a −2 charge; and a bromide ion, a −1 charge. For the interaction of a sodium ion with an oxide ion, $Q_1 = +1$ and $Q_2 = -2$, whereas for the interaction of a sodium ion with a bromide ion, $Q_1 = +1$ and $Q_2 = -1$. The larger value of $Q_1 \times Q_2$ for the sodium ion–oxide ion interaction means it will release more energy.

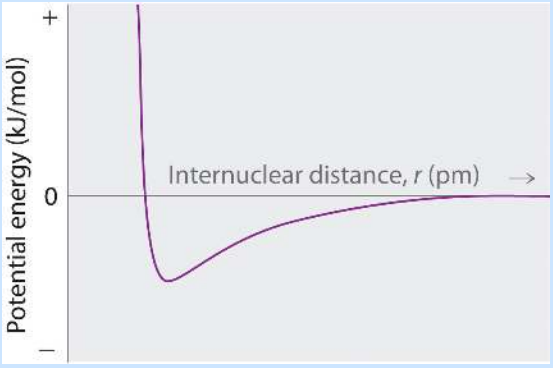
3.E.2.3 NUMERICAL PROBLEMS

12. How does the energy of the electrostatic interaction between ions with charges +1 and −1 compare to the interaction between ions with charges +3 and −1 if the distance between the ions is the same in both cases? How does this compare with the magnitude of the interaction between ions with +3 and −3 charges?

13. How many grams of gaseous $MgCl_2$ are needed to give the same electrostatic attractive energy as 0.5 mol of gaseous LiCl? The ionic radii are Li^+ = 76 pm, Mg^{+2} = 72 pm, and Cl^- = 181 pm.
14. Sketch a diagram showing the relationship between potential energy and internuclear distance (from $r = \infty$ to $r = 0$) for the interaction of a bromide ion and a potassium ion to form gaseous KBr. Explain why the energy of the system increases as the distance between the ions decreases from $r = r_0$ to $r = 0$.
15. Calculate the magnitude of the electrostatic attractive energy (E, in kilojoules) for 85.0 g of gaseous SrS ion pairs. The observed internuclear distance in the gas phase is 244.05 pm.
16. What is the electrostatic attractive energy (E, in kilojoules) for 130 g of gaseous HgI_2? The internuclear distance is 255.3 pm.

3.E.2.4 NUMERICAL ANSWERS

12. According to Equation 9.1, in the first case $Q_1Q_2 = (+1)(-1) = -1$; in the second case, $Q_1Q_2 = (+3)(-1) = -3$. Thus, E will be three times larger for the +3/−1 ions. For +3/−3 ions, $Q_1Q_2 = (+3)(-3) = -9$, so E will be nine times larger than for the +1/−1 ions.
13.
14.



At $r < r_0$, the energy of the system increases due to electron–electron repulsions between the overlapping electron distributions on *adjacent* ions. At very short internuclear distances, electrostatic repulsions between adjacent *nuclei* also become important.

3.E.3 COVALENT BONDING (17~30)

3.E.3.1 CONCEPTUAL PROBLEMS

17. Which would you expect to be stronger—an S–S bond or an Se–Se bond? Why?
18. Which element—nitrogen, phosphorus, or arsenic—will form the strongest multiple bond with oxygen? Why?
19. Why do multiple bonds between oxygen and period 3 elements tend to be unusually strong?
20. What can bond energies tell you about reactivity?
21. Bond energies are typically reported as average values for a range of bonds in a molecule rather than as specific values for a single bond? Why?
22. If the bonds in the products are weaker than those in the reactants, is a reaction exothermic or endothermic? Explain your answer.
23. A student presumed that because heat was required to initiate a particular reaction, the reaction product would be stable. Instead, the product exploded. What information might have allowed the student to predict this outcome?

3.E.3.2 NUMERICAL PROBLEMS

24. What is the bond order about the central atom(s) of hydrazine (N_2H_4), nitrogen, and diimide (N_2H_2)? Draw Lewis electron structures for each compound and then arrange these compounds in order of increasing N–N bond distance. Which of these compounds would you expect to have the largest N–N bond energy? Explain your answer.
25. What is the carbon–carbon bond order in ethylene (C_2H_4), BrH_2CCH_2Br, and FCCH? Arrange the compounds in order of increasing C–C bond distance. Which would you expect to have the largest C–C bond energy? Why?
26. From each pair of elements, select the one with the greater bond strength? Explain your choice in each case.
    1. P–P, Sb–Sb
    2. Cl–Cl, I–I
    3. O–O, Se–Se
    4. S–S, Cl–Cl

5. Al–Cl, B–Cl

27. From each pair of elements, select the one with the greater bond strength? Explain your choice in each case.
    1. Te–Te, S–S
    2. C–H, Ge–H
    3. Si–Si, P–P
    4. Cl–Cl, F–F
    5. Ga–H, Al–H
28. Approximately how much energy per mole is required to completely dissociate acetone [$(CH_3)_2CO$] and urea [$(NH_2)_2CO$] into their constituent atoms?
29. Approximately how much energy per mole is required to completely dissociate ethanol, formaldehyde, and hydrazine into their constituent atoms?
30. Is the reaction of diimine (N_2H_2) with oxygen to produce nitrogen and water exothermic or endothermic? Quantify your answer.

3.E.3.3 NUMERICAL ANSWER

24. N_2H_4, bond order 1; N_2H_2, bond order 2; N_2, bond order 3; N–N bond distance: $N_2 < N_2H_2 < N_2H_4$; Largest bond energy: N_2; Highest bond order correlates with strongest and shortest bond.

3.E.4 BOND POLARITY AND ELECRONEGATIVITY (31~40)

3.E.4.1 CONCEPTUAL PROBLEMS

31. Why do ionic compounds such as KI exhibit substantially less than 100% ionic character in the gas phase?
32. Of the compounds LiI and LiF, which would you expect to behave more like a classical ionic compound? Which would have the greater dipole moment in the gas phase? Explain your answers.

3.E.4.2 NUMERICAL PROBLEMS

33. Predict whether each compound is purely covalent, purely ionic, or polar covalent.
    1. RbCl
    2. S_8
    3. $TiCl_2$
    4. $SbCl_3$
    5. LiI
    6. Br_2
34. Based on relative electronegativities, classify the bonding in each compound as ionic, covalent, or polar covalent. Indicate the direction of the bond dipole for each polar covalent bond.
    1. NO
    2. HF
    3. MgO
    4. $AlCl_3$
    5. SiO_2
    6. the C=O bond in acetone
    7. O_3
35. Based on relative electronegativities, classify the bonding in each compound as ionic, covalent, or polar covalent. Indicate the direction of the bond dipole for each polar covalent bond.
    1. NaBr
    2. OF_2
    3. BCl_3
    4. the S–S bond in $CH_3CH_2SSCH_2CH_3$
    5. the C–Cl bond in CH_2Cl_2
    6. the O–H bond in CH_3OH
    7. $PtCl_4^{2-}$

36. Classify each species as having 0%–40% ionic character, 40%–60% ionic character, or 60%–100% ionic character based on the type of bonding you would expect. Justify your reasoning.
    1. CaO
    2. S_8
    3. $AlBr_3$
    4. ICl
    5. Na_2S
    6. SiO_2
    7. LiBr
37. If the bond distance in HCl (dipole moment = 1.109 D) were double the actual value of 127.46 pm, what would be the effect on the charge localized on each atom? What would be the percent negative charge on Cl? At the actual bond distance, how would doubling the charge on each atom affect the dipole moment? Would this represent more ionic or covalent character?
38. Calculate the percent ionic character of HF (dipole moment = 1.826 D) if the H–F bond distance is 92 pm.
39. Calculate the percent ionic character of CO (dipole moment = 0.110 D) if the C–O distance is 113 pm.
40. Calculate the percent ionic character of PbS and PbO in the gas phase, given the following information: for PbS, r = 228.69 pm and μ = 3.59 D; for PbO, r = 192.18 pm and μ = 4.64 D. Would you classify these compounds as having covalent or polar covalent bonds in the solid state?

3.E.5 DRAWING LEWIS STRUCTURES (41~71)

3.E.5.1 CONCEPTUAL PROBLEMS

41. Compare and contrast covalent and ionic compounds with regard to
    1. volatility.
    2. melting point.
    3. electrical conductivity.
    4. physical appearance.
42. What are the similarities between plots of the overall energy versus internuclear distance for an ionic compound and a covalent compound? Why are the plots so similar?
43. Which atom do you expect to be the central atom in each of the following species?
    1. SO_4^{2-}
    2. NH_4^+
    3. BCl_3
    4. SO_2Cl_2
44. Which atom is the central atom in each of the following species?
    1. PCl_3
    2. $CHCl_3$
    3. SO_2
    4. IF_3
45. What is the relationship between the number of bonds typically formed by the period 2 elements in groups 14, 15, and 16 and their Lewis electron structures?
46. Although formal charges do not represent actual charges on atoms in molecules or ions, they are still useful. Why?

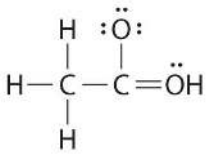
3.E.5.2 NUMERICAL PROBLEMS

47. Give the electron configuration and the Lewis dot symbol for the following. How many more electrons can each atom accommodate?
    1. Se
    2. Kr
    3. Li
    4. Sr
    5. H
48. Give the electron configuration and the Lewis dot symbol for the following. How many more electrons can each atom accommodate?

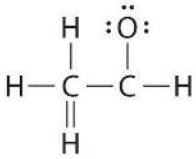
1. Na
2. Br
3. Ne
4. C
5. Ga

49. Based on Lewis dot symbols, predict the preferred oxidation state of Be, F, B, and Cs.
50. Based on Lewis dot symbols, predict the preferred oxidation state of Br, Rb, O, Si, and Sr.
51. Based on Lewis dot symbols, predict how many bonds gallium, silicon, and selenium will form in their neutral compounds.
52. Determine the total number of valence electrons in the following.
    1. Cr
    2. Cu^{+}
    3. NO^{+}
    4. XeF_2
    5. Br_2
    6. CH_2Cl_2
    7. NO_3^{-}
    8. H_3O^{+}
53. Determine the total number of valence electrons in the following.
    1. Ag
    2. Pt^{2+}
    3. H_2S
    4. OH^{-}
    5. I_2
    6. CH_4
    7. SO_4^{2-}
    8. NH_4^{+}.
54. Draw Lewis electron structures for the following.
    1. F_2
    2. SO_2
    3. $AlCl_4^{-}$
    4. SO_3^{2-}
    5. BrCl
    6. XeF_4
    7. NO^{+}
    8. PCl_3
55. Draw Lewis electron structures for the following.
    1. Br_2
    2. CH_3Br
    3. SO_4^{2-}
    4. O_2
    5. S_2^{2-}
    6. BF_3
56. Draw Lewis electron structures for CO_2, NO_2^{-}, SO_2, and NO_2^{+}. From your diagram, predict which pair(s) of compounds have similar electronic structures.
57. Write Lewis dot symbols for each pair of elements. For a reaction between each pair of elements, predict which element is the oxidant, which element is the reductant, and the final stoichiometry of the compound formed.
    1. K, S
    2. Sr, Br
    3. Al, O
    4. Mg, Cl

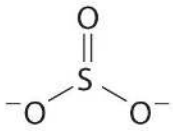
58. Write Lewis dot symbols for each pair of elements. For a reaction between each pair of elements, predict which element is the oxidant, which element is the reductant, and the final stoichiometry of the compound formed.
    1. Li, F
    2. Cs, Br
    3. Ca, Cl
    4. B, F
59. Use Lewis dot symbols to predict whether ICl and NO_4^- are chemically reasonable formulas.
60. Draw a plausible Lewis electron structure for a compound with the molecular formula Cl_3PO.
61. Draw a plausible Lewis electron structure for a compound with the molecular formula CH_4O.
62. While reviewing her notes, a student noticed that she had drawn the following structure in her notebook for acetic acid:



    Why is this structure not feasible? Draw an acceptable Lewis structure for acetic acid. Show the formal charges of all nonhydrogen atoms in both the correct and incorrect structures.
63. A student proposed the following Lewis structure shown for acetaldehyde.



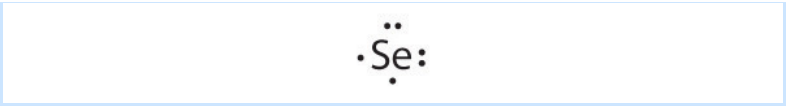
    Why is this structure not feasible? Draw an acceptable Lewis structure for acetaldehyde. Show the formal charges of all nonhydrogen atoms in both the correct and incorrect structures.
64. Draw the most likely structure for HCN based on formal charges, showing the formal charge on each atom in your structure. Does this compound have any plausible resonance structures? If so, draw one.
65. Draw the most plausible Lewis structure for NO_3^-. Does this ion have any other resonance structures? Draw at least one other Lewis structure for the nitrate ion that is not plausible based on formal charges.
66. At least two Lewis structures can be drawn for BCl_3. Using arguments based on formal charges, explain why the most likely structure is the one with three B–Cl single bonds.
67. Using arguments based on formal charges, explain why the most feasible Lewis structure for SO_4^{2-} has two sulfur–oxygen double bonds.
68. At least two distinct Lewis structures can be drawn for N_3^-. Use arguments based on formal charges to explain why the most likely structure contains a nitrogen–nitrogen double bond.
69. Is H–O–N=O a reasonable structure for the compound HNO_2? Justify your answer using Lewis electron dot structures.
70. Is H–O=C–H a reasonable structure for a compound with the formula CH_2O? Use Lewis electron dot structures to justify your answer.
71. Explain why the following Lewis structure for SO_3^{2-} is or is not reasonable.



3.E.5.3 NUMERICAL ANSWERS

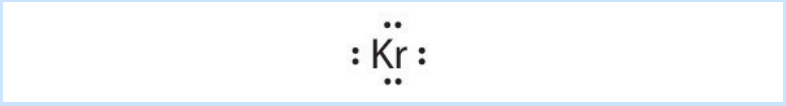
47.
    1. $[Ar]4s^2 3d^{10} 4p^4$

https://chem.libretexts.org/@go/page/475223



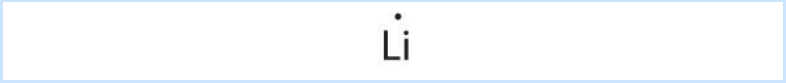
Selenium can accommodate two more electrons, giving the Se^{2-} ion.

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



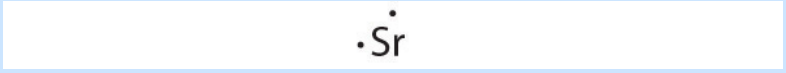
Krypton has a closed shell electron configuration, so it cannot accommodate any additional electrons.

3. $1s^2 2s^1$



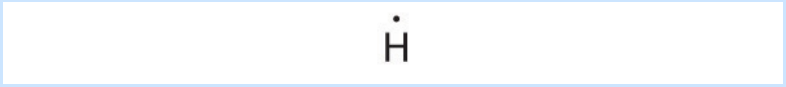
Lithium can accommodate one additional electron in its 2*s* orbital, giving the Li^- ion.

4. $[Kr]5s^2$



Strontium has a filled 5*s* subshell, and additional electrons would have to be placed in an orbital with a higher energy. Thus strontium has no tendency to accept an additional electron.

5. $1s^1$



Hydrogen can accommodate one additional electron in its 1*s* orbital, giving the H^- ion.

48.

49. Be^{2+}, F^-, B^{3+}, Cs^+

50.

51.

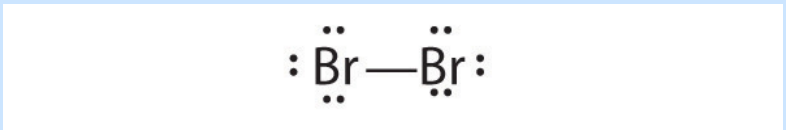
52.

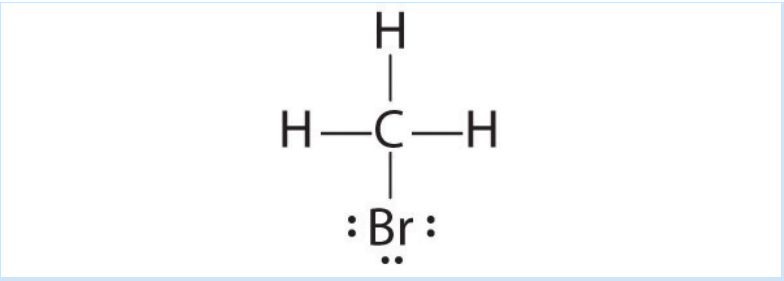
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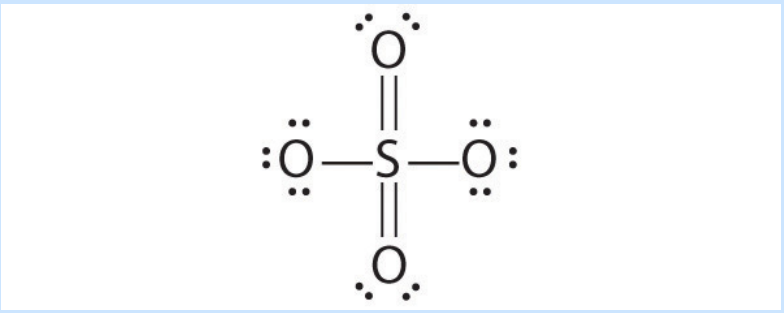
1. 11
2. 8
3. 8
4. 8
5. 14
6. 8
7. 32
8. 8

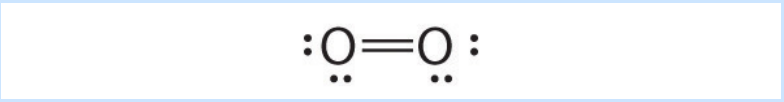
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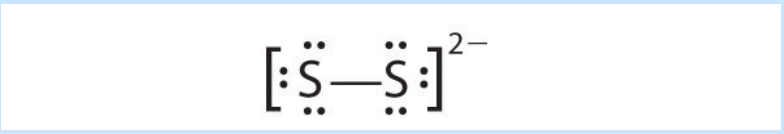
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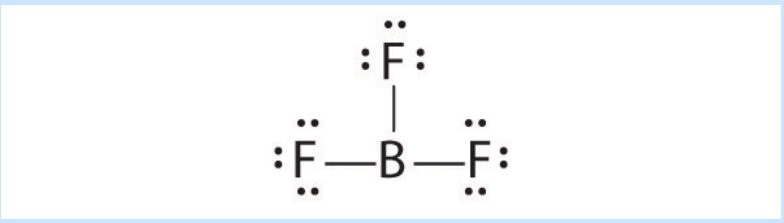
1. 

2. 

3. 

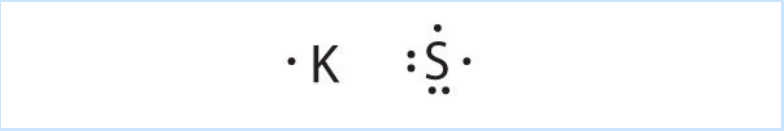
4. 

5. 

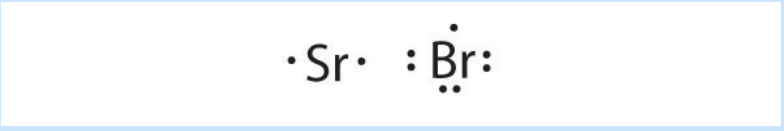
6. 

56.

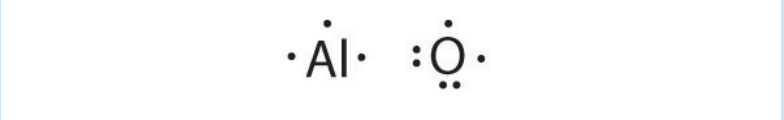
57.

1. 

K is the reductant; S is the oxidant. The final stoichiometry is K_2S.

2. 

Sr is the reductant; Br is the oxidant. The final stoichiometry is $SrBr_2$.

3. 

Al is the reductant; O is the oxidant. The final stoichiometry is Al_2O_3.

4. 

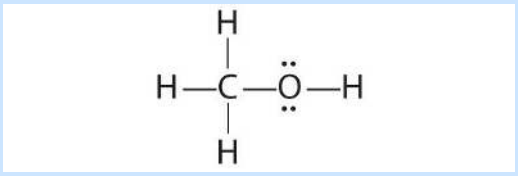
Mg is the reductant; Cl is the oxidant. The final stoichiometry is $MgCl_2$.

58.

59.

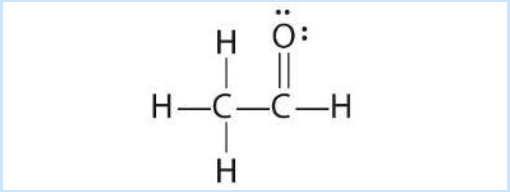
60.

61. The only structure that gives both oxygen and carbon an octet of electrons is the following:

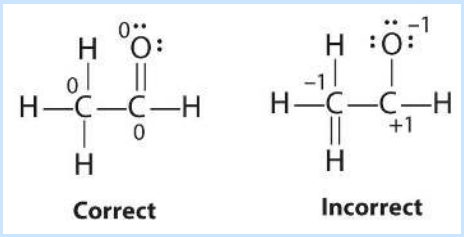


62.

63. The student's proposed structure has two flaws: the hydrogen atom with the double bond has four valence electrons (H can only accommodate two electrons), and the carbon bound to oxygen only has six valence electrons (it should have an octet). An acceptable Lewis structure is

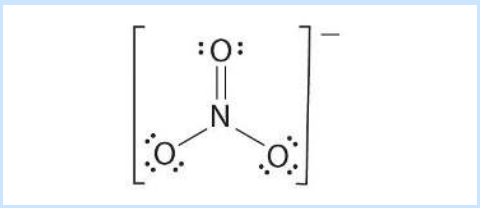


The formal charges on the correct and incorrect structures are as follows:



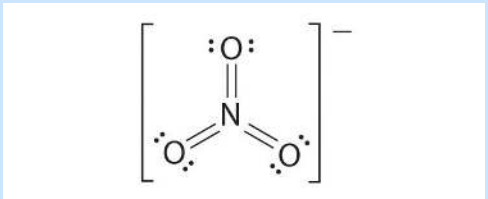
64.

65. The most plausible Lewis structure for NO_3^- is:



There are three equivalent resonance structures for nitrate (only one is shown), in which nitrogen is doubly bonded to one of the three oxygens. In each resonance structure, the formal charge of N is +1; for each singly bonded O, it is −1; and for the doubly bonded oxygen, it is 0.

The following is an example of a Lewis structure that is *not* plausible:



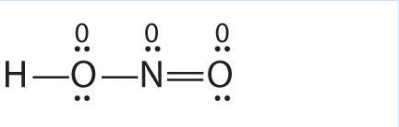
This structure nitrogen has six bonds (nitrogen can form only four bonds) and a formal charge of –1.

66.

67. With four S–O single bonds, each oxygen in SO_4^{2-} has a formal charge of −1, and the central sulfur has a formal charge of +2. With two S=O double bonds, only two oxygens have a formal charge of –1, and sulfur has a formal charge of zero. Lewis structures that minimize formal charges tend to be lowest in energy, making the Lewis structure with two S=O double bonds the most probable.

68.

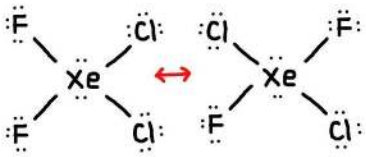
69. Yes. This is a reasonable Lewis structure, because the formal charge on all atoms is zero, and each atom (except H) has an octet of electrons.



3.E.6 RESONANCE STRUCTURES (72~81)

3.E.6.1 CONCEPTUAL PROBLEMS

72. Why are resonance structures important?
73. In what types of compounds are resonance structures particularly common?
74. True or False, The picture below is a resonance structure?

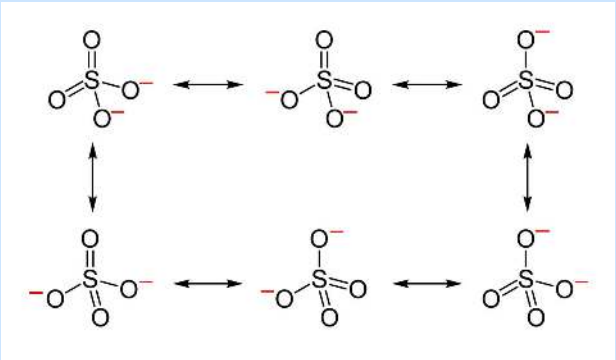


3.E.6.2 NUMERICAL PROBLEMS

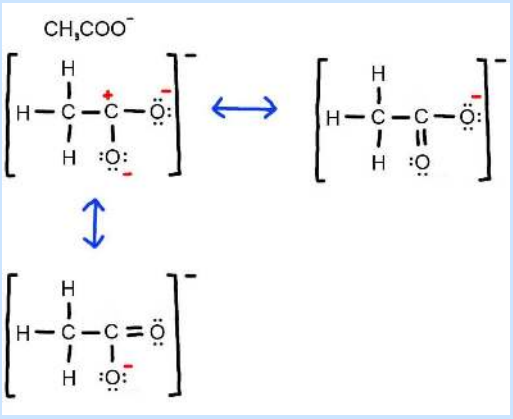
75. Draw all the resonance structures for each ion.
    a. HSO_4^-
    b. HSO_3^-
76. Draw the Lewis Dot Structure for $\mathbf{SO_4^{2-}}$ and all possible resonance structures. Which of the following resonance structure is not favored among the Lewis Structures? Explain why. Assign Formal Charges.
77. Draw the Lewis Dot Structure for $\mathbf{CH_3COO^-}$ and all possible resonance structures. Assign Formal Charges. Choose the most favorable Lewis Structure.
78. Draw the Lewis Dot Structure for $\mathbf{HPO_3^{2-}}$ and all possible resonance structures. Assign Formal Charges.
79. Draw the Lewis Dot Structure for $\mathbf{CHO_2^{1-}}$ and all possible resonance structures. Assign Formal Charges.
80. Draw the Resonance Hybrid Structure for $\mathbf{PO_4^{3-}}$.
81. Draw the Resonance Hybrid Structure for $\mathbf{NO_3^-}$.

3.E.6.3 NUMERICAL ANSWERS

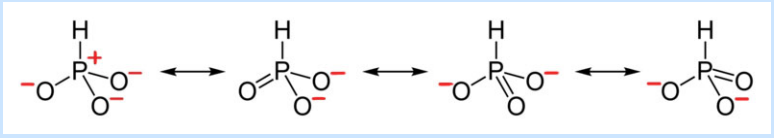
74. False, because the electrons were not moved around, only the atoms (this violates the Resonance Structure Rules).
76. Below are the all Lewis dot structure with formal charges (in red) for Sulfate ($\mathbf{SO_4^{2-}}$). There isn't a most favorable resonance of the Sulfate ion because they are all identical in charge and there is no change in Electronegativity between the Oxygen atoms.



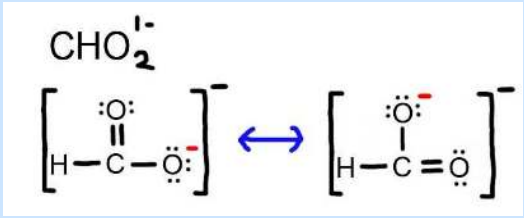
77. Below is the resonance for **CH_3COO^-**, formal charges are displayed in red. The Lewis Structure with the most formal charges is not desirable, because we want the Lewis Structure with the least formal charge.



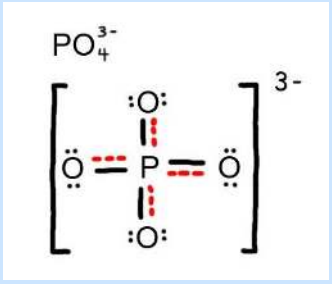
78. The resonance for **HPO_3^{2-}**, and the formal charges (in red).



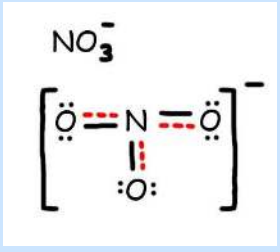
79. The resonance for **CHO_2^{1-}**, and the formal charges (in red).



80. The resonance hybrid for **PO_4^{3-}**, hybrid bonds are in red.



81. The resonance hybrid for **NO_3^-**, hybrid bonds are in red.



3.E.7 EXCEPTIONS TO THE OCTET RULE (82~98)

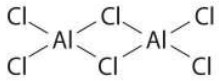
3.E.7.1 CONCEPTUAL PROBLEMS

82. What regions of the periodic table contain elements that frequently form molecules with an odd number of electrons? Explain your answer.

83. How can atoms expand their valence shell? What is the relationship between an expanded valence shell and the stability of an ion or a molecule?
84. What elements are known to form compounds with less than an octet of electrons? Why do electron-deficient compounds form?
85. List three elements that form compounds that do not obey the octet rule. Describe the factors that are responsible for the stability of these compounds.

3.E.7.2 NUMERICAL PROBLEMS

86. What is the major weakness of the Lewis system in predicting the electron structures of PCl_6^- and other species containing atoms from period 3 and beyond?
87. The compound aluminum trichloride consists of Al_2Cl_6 molecules with the following structure (lone pairs of electrons removed for clarity):

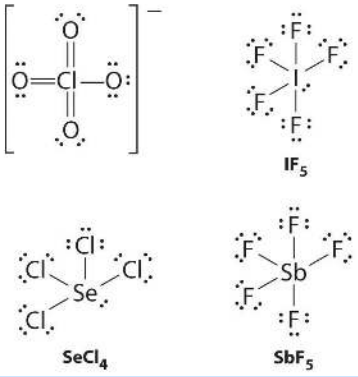


Does this structure satisfy the octet rule? What is the formal charge on each atom? Given the chemical similarity between aluminum and boron, what is a plausible explanation for the fact that aluminum trichloride forms a dimeric structure rather than the monomeric trigonal planar structure of BCl_3?

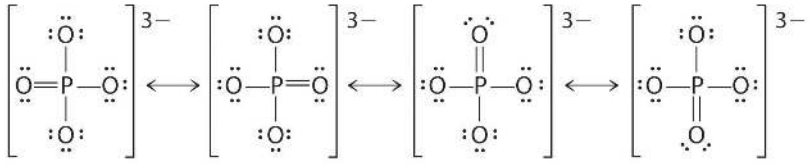
88. Draw Lewis electron structures for ClO_4^-, IF_5, $SeCl_4$, and SbF_5.
89. Draw Lewis electron structures for ICl_3, Cl_3PO, Cl_2SO, and AsF_6^-.
90. Draw plausible Lewis structures for the phosphate ion, including resonance structures. What is the formal charge on each atom in your structures?
91. Draw an acceptable Lewis structure for PCl_5, a compound used in manufacturing a form of cellulose. What is the formal charge of the central atom? What is the oxidation number of the central atom?
92. Using Lewis structures, draw all of the resonance structures for the BrO_3^- ion.
93. Draw an acceptable Lewis structure for xenon trioxide (XeO_3), including all resonance structures.

3.E.7.3 NUMERICAL ANSWERS

86.
87.
88. ClO_4^- (one of four equivalent resonance structures)



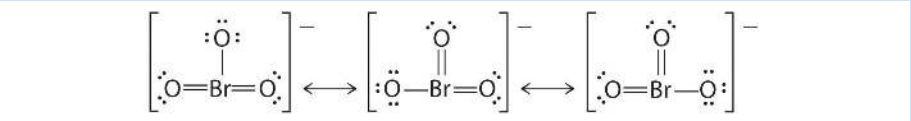
89.
90.



The formal charge on phosphorus is 0, while three oxygen atoms have a formal charge of −1 and one has a formal charge of zero.

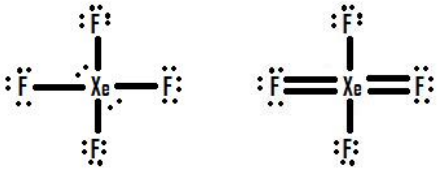
91.

92.



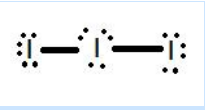
3.E.7.4 PRACTICE PROBLEMS

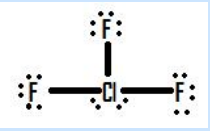
94. Draw the Lewis structure for the molecule I_3^-.
95. Draw the molecule ClF_3.
96. The central atom for an expanded octet must have an atomic number larger than what?
97. Draw the Lewis structure for the molecule NO_2.
98. Which Lewis structure is more likely?



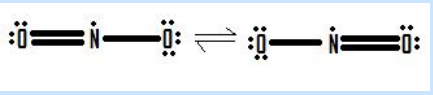
or

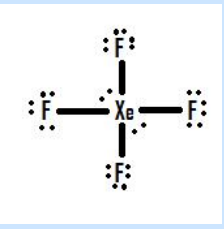
3.E.7.5 PRACTICE ANSWERS

94. 

95. 

96. 10 (Sodium and higher)

97. 

98. 

3.E.8 STRENGTHS OF COVALENT BONDS

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3.S: BASIC CONCEPTS OF CHEMICAL BONDING (SUMMARY)

3.S.1 8.1: CHEMICAL BONDS, LEWIS SYMBOLS AND THE OCTET RULE

Lewis dot symbols can be used to predict the number of bonds formed by most elements in their compounds. Lewis electron dot symbols, which consist of the chemical symbol for an element surrounded by dots that represent its valence electrons, grouped into pairs often placed above, below, and to the left and right of the symbol. The structures reflect the fact that the elements in period 2 and beyond tend to gain, lose, or share electrons to reach a total of 8 valence electrons in their compounds.

- **Ionic bond**: bond formed on the basis of electrostatic forces that exist between oppositely charged ions. The ions are formed from atoms by transfer of one or more electrons
- **Covalent bond**: bond formed between two or more atoms by a sharing of electrons
- **Metallic bond**: bonding in which the bonding electrons are relatively free to move throughout the 3D structure
- **Electron dot symbols**: aka **Lewis symbols**; simple and convenient way of showing the valence electrons of atoms and keeping tack of them in the course of bond formation
- The number of valence electrons of any representative element is the same as the column number of the element in the periodic table
- **Octet rule**: atoms tend to lose or gain electrons until they are surrounded by 8 valence electrons

3.S.2 8.2: IONIC BONDING

The amount of energy needed to separate a gaseous ion pair is its bond energy. Forming ionic compounds is usually extremely exothermic. The strength of the electrostatic attraction between ions with opposite charges is directly proportional to the magnitude of the charges on the ions and inversely proportional to the internuclear distance.

Energies of Ionic Bond Formation

The formation of ionic compounds is very exothermic

Removing an electron from an atom, such as Na, is endothermic because energy needs to be used to overcome the attractive forces within the atom. Adding an electron is the opposite process and releases lots of energy

The principal reason that ionic compounds are stable is the attraction between ions of unlike charge. This attraction draws the ions together, releasing energy and causing the ions to form a solid array (lattice)

Lattice energy: energy required to separate completely a mole of a solid ionic compounds into its gaseous ions

Large values of lattice energy mean that the ions are strongly attracted to one another

Energy released by the attraction between the ions of unlike charges more than makes up for the endothermic nature of ionization energies, making the formation of ionic compounds an exothermic process

$$E = k\frac{Q_1 Q_2}{d}$$

- E = potential energy of two interacting charged particles
- Q_1 and Q_2 = charges on the particles
- D= distance between the particles
- K = constant; 8.99 X 10^9 Jm/C^2

For a given arrangement of ions, the lattice energy increases as the charges of ions increase and as their radii decrease. The magnitude of lattice energies depends primarily on the ionic charges because ionic radii do not vary over a wide range.

Electron Configurations of Ions

Many ions tend to have noble gas electron configurations. This is why Na can have a +1 charge, but not a +2 one. Once an ion has reached noble gas configuration, it wants to stay there.

- Na: $1s^2\ 2s^2\ 2p^6\ 3s^1$ = [Ne] $3s^1$
- Na^+: $1s^2\ 2s^2\ 2p^6$ = [Ne]
- Na^{2+}: $1s^2\ 2s^2\ 2p^5$

Similarly, addition of electrons to nonmetals is either exothermic or slightly endothermic as long as electrons are being added to the valence shell. Further addition of electrons requires tremendous amounts of energy; more than is available form the lattice energy

- Cl: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$ = [Ne] $3s^2\ 3p^5$
- Cl: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ = [Ar]

- Cl^2: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$ = [Ar]

The lattice energies of ionic compounds are generally large enough to compensate for the loss of up to only 3 electrons from atoms. Thus we find cations only having charges of +1, +2, or +3.

Because most transition metals have more than 3 electrons beyond a noble gas core, attainment of a noble gas configuration for these ions is usually impossible.

When a positive ion is formed from an atom, electrons are always lost first from the subshell with the largest value of *n*. Thus, a transition metal always loses the outer *s* electrons before it loses electrons from the underlying *d* subshell.

3.S.3 8.3 SIZES OF IONS

Sizes of ions are important in determining both the way in which the ions pack in a solid and the lattice energy of the solid. It is also a major factor governing the properties of ions in solution

The size of an atom depends on its nuclear charge, the number of electrons it possesses, and the orbitals in which the outer-shell electrons reside

Positive ions are formed by removing 1 or more electrons from the outermost region of the atom. Thus, the formation of a cation not only vacates the most spatially extended orbitals, it also decreases the total electron-electron repulsions. Hence, cations are smaller than the original atoms from which they came.

The opposite happens when speaking of negative ions. An added electron increases electron-electron repulsions and causes the electrons to spread out more in space.

For ions of the same charge, size increases as we go down a group

3.S.4 8.3: COVALENT BONDING

The strength of a covalent bond depends on the overlap between the valence orbitals of the bonded atoms. Bond order is the number of electron pairs that hold two atoms together. Single bonds have a bond order of one, and multiple bonds with bond orders of two (a double bond) and three (a triple bond) are quite common. In closely related compounds with bonds between the same kinds of atoms, the bond with the highest bond order is both the shortest and the strongest.

Ionic substances are usually brittle with high melting points. They are usually crystalline, meaning that they have flat surfaces that make characteristic angles with one another.

- **Covalent bond**: chemical bond formed by sharing a pair of electrons
- **Lewis structure**: structure that represents bonding using dots for unpaired electrons and lines for bonds

For nonmetals, the number of valence electrons is the same as the group number

Knowing this, we can predict that an element in Group 7A would need one covalent bond in order to get an octet, an element in Group 6A would need two, and so on.

Multiple Bonds

- **Single bond**: sharing of one pair of electrons, one covalent bond
- **Double bond**: two shared electrons

Distance between bonded atoms decreases as the number of shared electron pairs increases

3.S.5 8.4: BOND POLARITY AND ELECRONEGATIVITY

Bond polarity and ionic character increase with an increasing difference in electronegativity. The electronegativity (χ) of an element is the relative ability of an atom to attract electrons to itself in a chemical compound and increases diagonally from the lower left of the periodic table to the upper right. The Pauling electronegativity scale is based on measurements of the strengths of covalent bonds between different atoms, whereas the Mulliken electronegativity of an element is the average

- **Bond polarity**: measure of how equally the electrons are shared between the atoms in a chemical bond
- **Nonpolar bond**: one in which the electrons are shared equally between the two atoms
- **Polar covalent bond**: one of the atoms exerts a greater attraction for the electron than the other

Electronegativity

Used to estimate whether a bond will be nonpolar, polar covalent, or ionic

Electronegativity: ability of an atom *in a molecule* to attract electrons to itself

An atom with a very negative electron affinity and high ionization energy will both attract electrons from other atoms and resist having its electrons attracted away; it will be highly electronegative

Highest electronegativity = 4.0 (Fluorine), lowest = 0.7 (Cesium)

Electronegativity increases form left to right, and usually decreases with increasing atomic number in any one group

Electronegativity and Bond Polarity

Differences in electronegativities:

Nonpolar = 0 – 0.4

Polar covalent = 0.4 – 1.6

Ionic = > 1.6 (> 50% = ionic)

δ^+ and δ : "delta sign"; represent partial positive and negative charge. The atom with the δ is the more electronegative one

3.S.6 8.5: DRAWING LEWIS STRUCTURES

Lewis dot symbols provide a simple rationalization of why elements form compounds with the observed stoichiometries. A plot of the overall energy of a covalent bond as a function of internuclear distance is identical to a plot of an ionic pair because both result from attractive and repulsive forces between charged entities. Lewis structures are an attempt to rationalize why certain stoichiometries are commonly observed for the elements of particular families.

1. Sum the valence electrons from all atoms. For an anion, add an electron to the total negative charge. For a cation, subtract an electron.
2. Write the symbols for the atoms to show which atoms are attached to which, and connect them with a single bond.
3. Complete the octets of the atoms bonded to the central atom.
4. Place any leftover electrons on the central atom, even if doing so results in more than an octet
5. If there are not enough electrons to give the central atom an octet, try multiple bonds

3.S.7 8.6: RESONANCE STRUCTURES

Some molecules have two or more chemically equivalent Lewis electron structures, called resonance structures. Resonance is a mental exercise and method within the Valence Bond Theory of bonding that describes the delocalization of electrons within molecules. These structures are written with a double-headed arrow between them, indicating that none of the Lewis structures accurately describes the bonding but that the actual structure is an average of the individual resonance structures.

Resonance structures (resonance forms) are individual Lewis structures in cases where two or more Lewis structures are equally good descriptions of a single molecule. If a molecule (or ion) has two or more resonance structures, the molecule is a blend of these structures. The molecule *does* **not** oscillate rapidly between two or more different forms.

3.S.8 8.7: EXCEPTIONS TO THE OCTET RULE

Following the Octet Rule for Lewis Dot Structures leads to the most accurate depictions of stable molecular and atomic structures and because of this we always want to use the octet rule when drawing Lewis Dot Structures. There are three exceptions: (1) When there are an odd number of valence electrons, (2) When there are too few valence electrons, and (3) when there are too many valence electrons

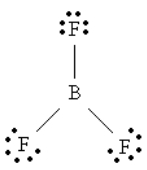
1. Molecules with an odd number of electrons
2. Molecules in which an atom has less than an octet
3. Molecules in which an atom has more than an octet

Odd Number of Electrons

In a few molecules, such as ClO_2, NO, and NO_2, the number of electrons is odd. In NO for example, there are 5+6 = 11 valence electron. Hence, complete pairing of these electrons is impossible and an octet around each atom cannot be achieved.

Less Than an Octet

Second type of exception occurs when there are fewer than eight electrons around an atom in a molecule or ion. Relatively rare situation; most often encountered in compounds of Boron and Beryllium. For example, let's consider Boron Trifluoride, BF_3



There are 6 electrons around the Boron atom. We can form a double bond between Boron and any of the 3 Fluorine atoms (3 possible resonance structures)

However, by doing so, we forced a Fluorine atom to share additional electrons with Boron. This would make the F atom to have a +1 charge, and the Boron atom to have a –1 charge, which is extremely unfavorable.

We then conclude that the structures containing the double bonds are less important than the one illustrated on the right. *Since in this case Boron has only 6 valence electrons, it will react violently with molecules that have an unshared pair of electrons.*

More Than an Octet

The octet rule works as well as it does because the representative elements usually employ only an *ns* and three *np* valence shell orbitals in bonding, and these hold eight electrons.

Because elements of the second period have only 2s and 2p orbitals, they cannot have more than an octet of electrons in their valence shells. However, from the third period on, the elements have unfilled *nd* orbitals that can be used in bonding.

Size also plays an important role in determining whether an atom can accommodate more than eight electrons. The larger the central atom, the larger the number of atoms that can surround it. The size of the surrounding atoms is also important. Expanded valence shells occur most often when the central atom is bonded to the smallest and most electronegative atoms.

3.S.9 8.8: STRENGTHS OF COVALENT BONDS

Bond order is the number of electron pairs that hold two atoms together. Single bonds have a bond order of one, and multiple bonds with bond orders of two (a double bond) and three (a triple bond) are quite common. The bond with the highest bond order is both the shortest and the strongest. In bonds with the same bond order between different atoms, trends are observed that, with few exceptions, result in the strongest single bonds being formed between the smallest atoms.

Bonddissociation energy: aka **bond energy**; enthalpy change, ΔH, required to break a particular bond in a mole of gaseous substance.

For polyatomic molecules, we must often utilize average bond energies.

Bond energy is *always* positive, the greater the bond energy, the stronger the bond

A molecule with strong bonds generally has less tendency to undergo chemical change than does one with weak bonds

Bond Energies and the Enthalpy of Reactions

ΔH = Σ (bond energies of bonds broken) – Σ (bond energies of bonds formed)

If ΔH > 0, the reaction is endothermic

If ΔH < 0, the reaction is exothermic

$Cl – Cl_{(g)} + H – CH_{3\,(g)} \rightarrow H – Cl_{(g)} + Cl – CH_{3\,(g)}$

Bonds broken: 1 mol Cl – Cl, 1 mol C – H

Bonds made: 1 mol H – Cl, 1 mol C – Cl

$$\Delta H = [D(Cl–Cl) + D(C–H)][D(H–Cl) + D(Cl–Cl)]$$

= (242 kJ + 413 kJ) – (431kJ + 328 kJ)

= 104 kJ

Bond Strength and Bond Length

As the number of bonds between a given element increase, the bond energy increases and the bond length decreases. Hence, the atoms are held more tightly and closely together. In general, *as the number of bonds between two atoms increases, the bond grows shorter and stronger.*

3.S.10 8.10 OXIDATION NUMBERS

Oxidation Numbers: aka **Oxidation states**; a positive or negative whole number assigned to an element in a molecule or ion on the basis of a set of normal rules; to some degree it reflects the positive or negative character of an atom

Oxidation numbers do NOT correspond to real charges on the atoms, EXCEPT in the special case of simple ionic substances

1. *The oxidation form of an element in its elemental form is zero.*
2. *The oxidation number of a monoatomic ion is the same as its charge.* For example, the oxidation number of sodium in Na^+ is +1, and that of sulfur in S^2 is –2

3. *In binary compounds (those with two different elements), the element with greater electronegativity is assigned a negative oxidation number equal to its charge in simple ionic compounds the element.* For example, consider the oxidation state of Cl in PCl_3. Cl is more electronegative than P. In its simple ionic compounds, Cl appears as the ion Cl. Thus, in PCl_3, Cl is assigned an oxidation number of –1.
4. *The sum of the oxidation numbers equals zero for an electrically neutral compound and equals the overall charge of the ionic species.* For example, PCl_3 is a neutral molecule. Thus, the sum of oxidation number of the P and Cl atoms must equal zero Because the oxidation number of each Cl in this compound is –1 (rule 3), the oxidation number of P must be +3.

Group 1A elements are +1, Group 2A elements are +2, and Aluminum is +3.

The most electronegative element, F, is always found in the –1 oxidation state. Oxygen is usually in the –2 state, however, it can be –1 in peroxides.

Hydrogen has an oxidation number of +1 when it is bonded to a more electronegative element (most nonmetals), and of –1 when bonded to less electronegative elements (most metals)

Oxidation Numbers and Nomenclature

Name of the less electronegative element is given first, followed by the name of the more electronegative element modified to have an *–ide* ending

Compounds of metals in higher oxidation states tend to be molecular rather than ionic

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CHAPTER OVERVIEW

4: MOLECULAR GEOMETRY AND BONDING THEORIES

A general chemistry Libretexts Textmap organized around the textbook

Chemistry: The Central Science

by Brown, LeMay, Bursten, Murphy, and Woodward

Template:HideTOC

- 4.1: Molecular Shapes
- 4.2: The VSEPR Model
- 4.3: Molecular Shape and Molecular Polarity
- 4.4: Covalent Bonding and Orbital Overlap
- 4.5: Hybrid Orbitals
- 4.6: Multiple Bonds
- 4.7: Molecular Orbitals (Supplementary)
- 4.8: Second-Row Diatomic Molecules (Supplementary)
- 4.E: Exercises
- 4.S: Molecular Geometry and Bonding Theories (Summary)

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4.1: MOLECULAR SHAPES

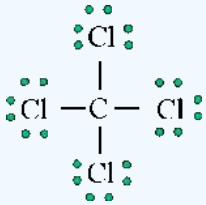
The Lewis electron-pair approach described previously can be used to predict the number and types of bonds between the atoms in a substance, and it indicates which atoms have lone pairs of electrons. This approach gives no information about the actual arrangement of atoms in space, however.

4.1.1 MOLECULAR GEOMETRY

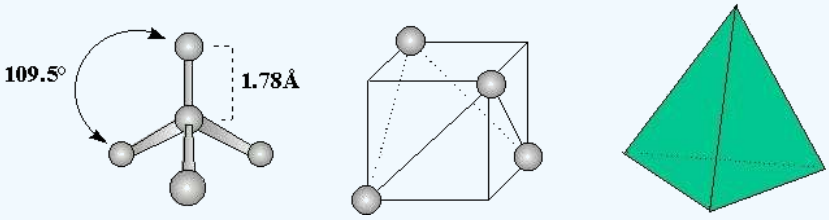
The specific three dimensional arrangement of atoms in molecules is referred to as **molecular geometry**. We also define molecular geometry as the positions of the atomic nuclei in a molecule. There are various instrumental techniques such as X-Ray crystallography and other experimental techniques which can be used to tell us where the atoms are located in a molecule. Using advanced techniques, very complicated structures for proteins, enzymes, DNA, and RNA have been determined. Molecular geometry is associated with the chemistry of vision, smell, taste, drug reactions, and enzyme controlled reactions to name a few.

✔ EXAMPLE 4.1.1: CARBON TETRACHLORIDE

The Lewis structure of carbon tetrachloride provides information about connectivities, provides information about valence orbitals, and provides information about bond character.



However, the Lewis structure provides no information about the shape of the molecule, which is defined by *the bond angles and the bond lengths*. For carbon tetrachloride, each C-Cl bond length is 1.78Å and each Cl-C-Cl bond angle is 109.5°. Hence, carbon tetrachloride is ***tetrahedral*** in structure:



4.1.2 MOLECULAR GEOMETRIES OF AB_n MOLECULES

Molecular geometry is associated with the specific orientation of bonding atoms. A careful analysis of electron distributions in orbitals will usually result in correct molecular geometry determinations. In addition, the simple writing of Lewis diagrams can also provide important clues for the determination of molecular geometry. Molecular shapes, or geometries, are critical to molecular recognition and function. Table **4.1.1** shows some examples of geometries where a central atom ***A*** is bonded to two or more ***X*** atoms. As indicated in several of the geometries below, non-bonding electrons ***E*** can strongly influence the molecular geometry of the molecule; this is discussed in more details in VSEPR Model" data-cke-saved-href="/Bookshelves/General_Chemistry/Map:_Chemistry_-_The_Central_Science_(Brown_et_al.)/09:_Molecular_Geometry_and_Bonding_Theories/9.02:_The_VSEPR_Model" href="/Bookshelves/General_Chemistry/Map:_Chemistry_-_The_Central_Science_(Brown_et_al.)/09:_Molecular_Geometry_and_Bonding_Theories/9.02:_The_VSEPR_Model" data-quail-id="26">Section 9.2.

Table **4.1.1**:

6	5	4	3	2
AX_6  octahedral	AX_5  trigonal bipyramidal	AX_4  tetrahedral	AX_3  trigonal planar	AX_2 Linear linear
1 lone pair of electrons				
AX_5E  square pyramidal	AX_4E  distorted tetrahedron	AX_3E  pyramidal	AX_2E  nonlinear	AXE Linear linear
2 lone pairs of electrons				
AX_4E_2  square planar	AX_3E_2  T-shaped	AX_2E_2  bent	AXE_2 Linear linear	

These structures can generally be predicted, when A is a nonmetal, using the "valence-shell electron-pair repulsion model (VSEPR) discussed in the next section.

4.1.3 CONTRIBUTORS AND ATTRIBUTIONS

- Mike Blaber (Florida State University)
- Robyn Rindge (Class of '98) who now works for PDI Dreamworks (look for his name in the credits of Shrek2.). Robyn drew these rotating molecules using Infini-D (MetaCreations).
- Paul Groves, chemistry teacher at South Pasadena High School and Chemmy Bear(opens in new window)

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4.2: THE VSEPR MODEL

LEARNING OBJECTIVES

- To use the VSEPR model to predict molecular geometries.
- To predict whether a molecule has a dipole moment.

The Lewis electron-pair approach can be used to predict the number and types of bonds between the atoms in a substance, and it indicates which atoms have lone pairs of electrons. This approach gives no information about the actual arrangement of atoms in space, however. We continue our discussion of structure and bonding by introducing the **valence-shell electron-pair repulsion** (VSEPR) model (pronounced "vesper"), which can be used to predict the shapes of many molecules and polyatomic ions. Keep in mind, however, that the VSEPR model, like any model, is a limited representation of reality; the model provides no information about bond lengths or the presence of multiple bonds.

4.2.1 THE VSEPR MODEL

The VSEPR model can predict the structure of nearly any molecule or polyatomic ion in which the central atom is a nonmetal, as well as the structures of many molecules and polyatomic ions with a central metal atom. The premise of the VSEPR theory is that electron pairs located in bonds and lone pairs repel each other and will therefore adopt the geometry that places electron pairs as far apart from each other as possible. This theory is very simplistic and does not account for the subtleties of orbital interactions that influence molecular shapes; however, the simple VSEPR counting procedure accurately predicts the three-dimensional structures of a large number of compounds, which cannot be predicted using the Lewis electron-pair approach.

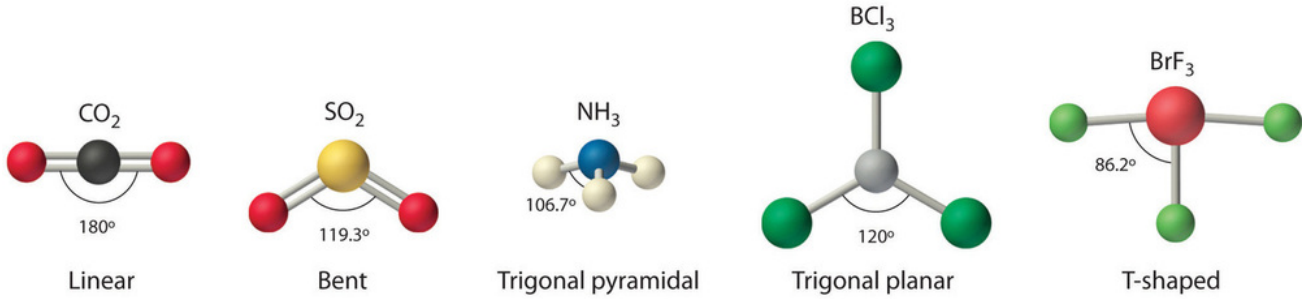


Figure 4.2.1: Common Structures for Molecules and Polyatomic Ions That Consist of a Central Atom Bonded to Two or Three Other Atoms. (CC BY-NC-SA; anonymous)

We can use the VSEPR model to predict the geometry of most polyatomic molecules and ions by focusing only on the number of electron pairs around the *central atom*, ignoring all other valence electrons present. According to this model, valence electrons in the Lewis structure form *groups*, which may consist of a single bond, a double bond, a triple bond, a lone pair of electrons, or even a single unpaired electron, which in the VSEPR model is counted as a lone pair. Because electrons repel each other electrostatically, the most stable arrangement of electron groups (i.e., the one with the lowest energy) is the one that minimizes repulsions. Groups are positioned around the central atom in a way that produces the molecular structure with the lowest energy, as illustrated in Figures 4.2.1 and 4.2.2.

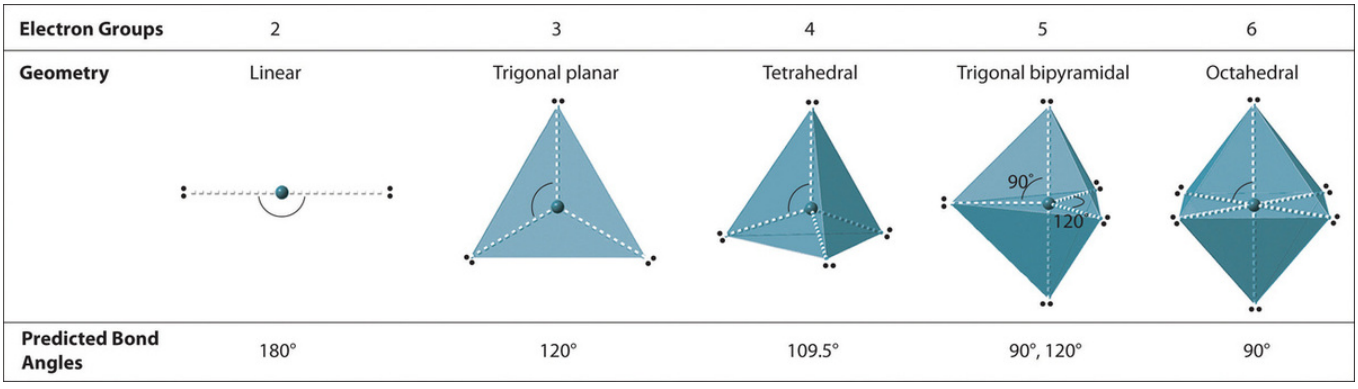


Figure 4.2.2: Electron Geometries for Species with Two to Six Electron Groups. Groups are placed around the central atom in a way that produces a molecular structure with the lowest energy, that is, the one that minimizes repulsions. (CC BY-NC-SA; anonymous)

In the VSEPR model, the molecule or polyatomic ion is given an AX_mE_n designation, where A is the central atom, X is a bonded atom, E is a nonbonding valence electron group (usually a lone pair of electrons), and *m* and *n* are integers. Each group around the central atom is designated as a bonding pair (BP) or lone (nonbonding) pair (LP). From the BP and LP interactions we can predict both the relative positions of the atoms and the angles between the bonds, called the bond angles. Using this information, we can describe the molecular geometry, the arrangement of the *bonded atoms* in a molecule or polyatomic ion.

VESPR PRODUCE TO PREDICT MOLECULAR GEOMETRY

This VESPR procedure is summarized as follows:

1. Draw the Lewis electron structure of the molecule or polyatomic ion.
2. Determine the electron group arrangement around the central atom that minimizes repulsions.
3. Assign an AX_mE_n designation; then identify the LP–LP, LP–BP, or BP–BP interactions and predict deviations from ideal bond angles.
4. Describe the molecular geometry.

We will illustrate the use of this procedure with several examples, beginning with atoms with two electron groups. In our discussion we will refer to Figure **4.2.2** and Figure **4.2.3**, which summarize the common molecular geometries and idealized bond angles of molecules and ions with two to six electron groups.

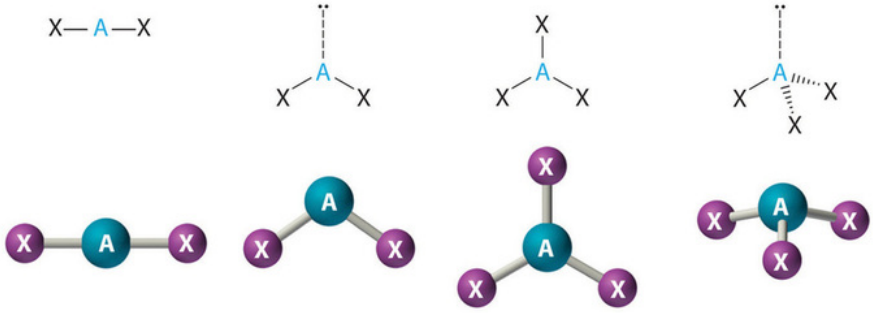
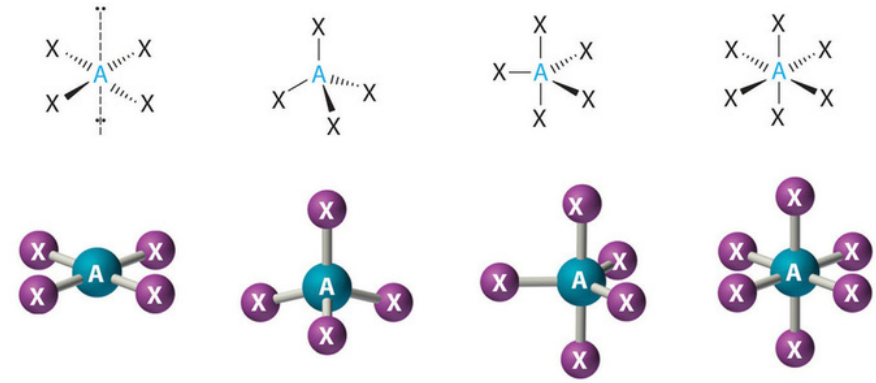
AX_mE_n Notation	AX_2	AX_2E	AX_3	AX_3E
Geometry	Linear	Bent (V-shaped)	Trigonal planar	Trigonal pyramidal
				
Idealized Bond Angles	180°	<180°	120°	<120°
AX_mE_n Notation	AX_4E_2	AX_4	AX_5	AX_6
Geometry	Square planar	Tetrahedral	Trigonal bipyramidal	Octahedral
				
Idealized Bond Angles	90°	109.5°	90°, 120°	90°

Figure **4.2.3**: Common Molecular Geometries for Species with Two to Six Electron Groups. Lone pairs are shown using a dashed line. (CC BY-NC-SA; anonymous)

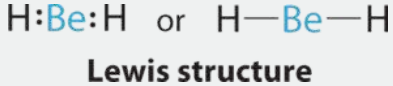
Linear, bent, trigonal planar, trigonal pyramidal, square planar, tetrahedral, trigonal bipyramidal, octahedral.

4.2.2 TWO ELECTRON GROUPS

Our first example is a molecule with two bonded atoms and no lone pairs of electrons, BeH_2.

AX_2 MOLECULES: BEH_2

1. The central atom, beryllium, contributes two valence electrons, and each hydrogen atom contributes one. The Lewis electron structure is



Lewis structure

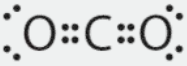
Figure **4.2.2** that the arrangement that minimizes repulsions places the groups 180° apart. (CC BY-NC-SA; anonymous)

3. Both groups around the central atom are bonding pairs (BP). Thus BeH_2 is designated as AX_2.

4. From Figure **4.2.3** we see that with two bonding pairs, the molecular geometry that minimizes repulsions in BeH_2 is *linear*.

AX_2 MOLECULES: CO_2

1. The central atom, carbon, contributes four valence electrons, and each oxygen atom contributes six. The Lewis electron structure is



2. The carbon atom forms two double bonds. Each double bond is a group, so there are two electron groups around the central atom. Like BeH_2, the arrangement that minimizes repulsions places the groups 180° apart.

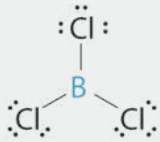
3. Once again, both groups around the central atom are bonding pairs (BP), so CO_2 is designated as AX_2.

4. VSEPR only recognizes groups around the *central* atom. Thus the lone pairs on the oxygen atoms do not influence the molecular geometry. With two bonding pairs on the central atom and no lone pairs, the molecular geometry of CO_2 is linear (Figure **4.2.3**). The structure of $\mathbf{CO_2}$ is shown in Figure **4.2.1**.

4.2.3 THREE ELECTRON GROUPS

AX_3 MOLECULES: BCL_3

1. The central atom, boron, contributes three valence electrons, and each chlorine atom contributes seven valence electrons. The Lewis electron structure is



Lewis structure

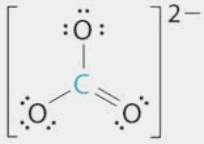
Figure **4.2.2**): (CC BY-NC-SA; anonymous)

3. All electron groups are bonding pairs (BP), so the structure is designated as AX_3.

4. From Figure **4.2.3** we see that with three bonding pairs around the central atom, the molecular geometry of BCl_3 is *trigonal planar*, as shown in Figure **4.2.2**.

AX_3 MOLECULES: CO_3^{2-}

1. The central atom, carbon, has four valence electrons, and each oxygen atom has six valence electrons. As you learned previously, the Lewis electron structure of one of three resonance forms is represented as



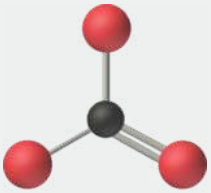
Lewis structure

Figure **4.2.2**).

The three oxygens are arranged in a triangular shape with carbon at the center. Two of the oxygens have three lone pairs. One ocht oxygens has 2 lone pairs and is double bonded to the carbon. The molecule has a minus 2 charge.

3. All electron groups are bonding pairs (BP). With three bonding groups around the central atom, the structure is designated as AX_3.

4. We see from Figure **4.2.3** that the molecular geometry of CO_3^{2-} is trigonal planar with bond angles of 120°.



Molecular geometry
(trigonal planar)

In our next example we encounter the effects of lone pairs and multiple bonds on molecular geometry for the first time.

AX_2E MOLECULES: SO_2

1. The central atom, sulfur, has 6 valence electrons, as does each oxygen atom. With 18 valence electrons, the Lewis electron structure is shown below.

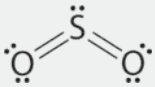


Figure **4.2.2**): (CC BY-NC-SA; anonymous)

The two oxygens are double bonded to the sulfur. The oxygens have 2 lone pairs while sulfur had one lone pair.

3. There are two bonding pairs and one lone pair, so the structure is designated as AX_2E. This designation has a total of three electron pairs, two X and one E. Because a lone pair is not shared by two nuclei, it occupies more space near the central atom than a bonding pair (Figure **4.2.4**). Thus bonding pairs and lone pairs repel each other electrostatically in the order BP–BP < LP–BP < LP–LP. In SO_2, we have one BP–BP interaction and two LP–BP interactions.

4. The molecular geometry is described only by the positions of the nuclei, *not* by the positions of the lone pairs. Thus with two nuclei and one lone pair the shape is *bent*, or *V shaped*, which can be viewed as a trigonal planar arrangement with a missing vertex (Figures **4.2.2** and **4.2.3**). The O-S-O bond angle is expected to be *less than* 120° because of the extra space taken up by the lone pair.

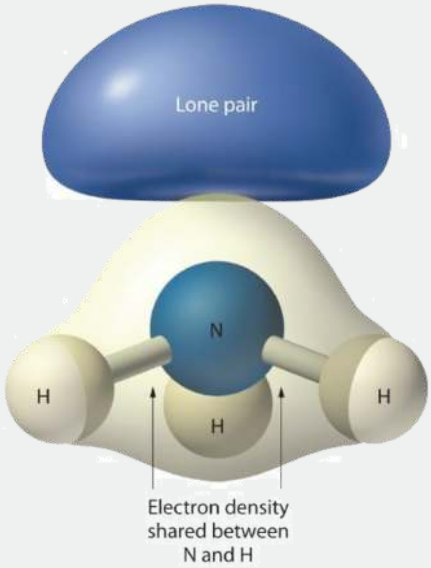
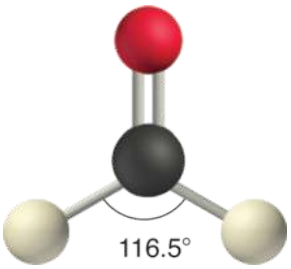


Figure **4.2.4**: The Difference in the Space Occupied by a Lone Pair of Electrons and by a Bonding Pair. (CC BY-NC-SA; anonymous)

As with SO_2, this composite model of electron distribution and negative electrostatic potential in ammonia shows that a lone pair of electrons occupies a larger region of space around the nitrogen atom than does a bonding pair of electrons that is shared with a hydrogen atom.

Like lone pairs of electrons, multiple bonds occupy more space around the central atom than a single bond, which can cause other bond angles to be somewhat smaller than expected. This is because a multiple bond has a higher electron density than a single bond, so its electrons occupy more space than those of a single bond. For example, in a molecule such as CH_2O (AX_3), whose structure is shown below, the double bond repels the single bonds more strongly than the single bonds repel each other. This causes a deviation from ideal geometry (an H–C–H bond angle of 116.5° rather than 120°).

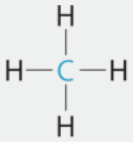


4.2.4 FOUR ELECTRON GROUPS

One of the limitations of Lewis structures is that they depict molecules and ions in only two dimensions. With four electron groups, we must learn to show molecules and ions in three dimensions.

AX_4 MOLECULES: CH_4

1. The central atom, carbon, contributes four valence electrons, and each hydrogen atom has one valence electron, so the full Lewis electron structure is

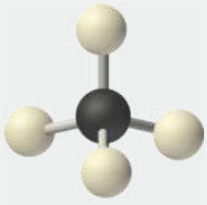


Lewis structure

2. There are four electron groups around the central atom. As shown in Figure **4.2.2**, repulsions are minimized by placing the groups in the corners of a tetrahedron with bond angles of 109.5°.

3. All electron groups are bonding pairs, so the structure is designated as AX_4.

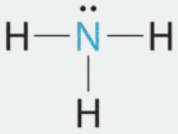
4. With four bonding pairs, the molecular geometry of methane is *tetrahedral* (Figure **4.2.3**).



Molecular geometry
(tetrahedral)

AX_3E MOLECULES: NH_3

1. In ammonia, the central atom, nitrogen, has five valence electrons and each hydrogen donates one valence electron, producing the Lewis electron structure



Lewis structure

2. There are four electron groups around nitrogen, three bonding pairs and one lone pair. Repulsions are minimized by directing each hydrogen atom and the lone pair to the corners of a tetrahedron.

3. With three bonding pairs and one lone pair, the structure is designated as AX_3E. This designation has a total of four electron pairs, three X and one E. We expect the LP–BP interactions to cause the bonding pair angles to deviate significantly from the angles of a perfect tetrahedron.

4. There are three nuclei and one lone pair, so the molecular geometry is *trigonal pyramidal*. In essence, this is a tetrahedron with a vertex missing (Figure **4.2.3**). However, the H–N–H bond angles are less than the ideal angle of 109.5° because of LP–BP repulsions (Figure **4.2.3** and Figure **4.2.4**).

AX_2E_2 MOLECULES: H_2O

1. Oxygen has six valence electrons and each hydrogen has one valence electron, producing the Lewis electron structure

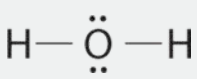
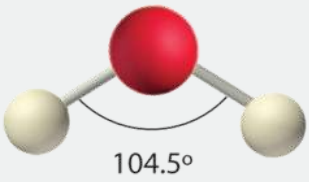


Figure **4.2.2**: (CC BY-NC-SA; anonymous)

3. With two bonding pairs and two lone pairs, the structure is designated as AX_2E_2 with a total of four electron pairs. Due to LP–LP, LP–BP, and BP–BP interactions, we expect a significant deviation from idealized tetrahedral angles.

4. With two hydrogen atoms and two lone pairs of electrons, the structure has significant lone pair interactions. There are two nuclei about the central atom, so the molecular shape is *bent*, or *V shaped*, with an H–O–H angle that is even less than the H–N–H angles in NH_3, as we would expect because of the presence of two lone pairs of electrons on the central atom rather than one. This molecular shape is essentially a tetrahedron with two missing vertices.



4.2.5 FIVE ELECTRON GROUPS

In previous examples it did not matter where we placed the electron groups because all positions were equivalent. In some cases, however, the positions are not equivalent. We encounter this situation for the first time with five electron groups.

AX_5 MOLECULES: PCL_5

1. Phosphorus has five valence electrons and each chlorine has seven valence electrons, so the Lewis electron structure of PCl_5 is

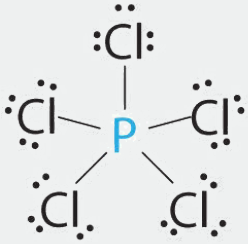
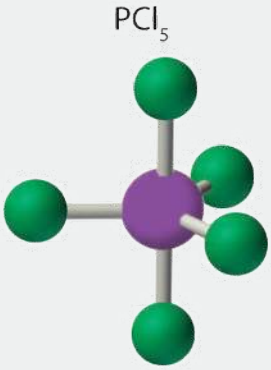


Figure **4.2.2**): (CC BY-NC-SA; anonymous)

3. All electron groups are bonding pairs, so the structure is designated as AX_5. There are no lone pair interactions.

4. The molecular geometry of PCl_5 is *trigonal bipyramidal*, as shown in Figure **4.2.3**. The molecule has three atoms in a plane in *equatorial* positions and two atoms above and below the plane in *axial* positions. The three equatorial positions are separated by 120° from one another, and the two axial positions are at 90° to the equatorial plane. The axial and equatorial positions are not chemically equivalent, as we will see in our next example.



AX_4E MOLECULES: SF_4

1. The sulfur atom has six valence electrons and each fluorine has seven valence electrons, so the Lewis electron structure is



Lewis structure

Four fluorenes are bonded to a central sulfur. Each fluorine has three lone pairs. Sulfur has one lone pair.

With an expanded valence, this species is an exception to the octet rule.

2. There are five groups around sulfur, four bonding pairs and one lone pair. With five electron groups, the lowest energy arrangement is a trigonal bipyramid, as shown in Figure **4.2.2**.

3. We designate SF_4 as AX_4E; it has a total of five electron pairs. However, because the axial and equatorial positions are not chemically equivalent, where do we place the lone pair? If we place the lone pair in the axial position, we have three LP–BP repulsions at 90°. If we place it in the equatorial position, we have two 90° LP–BP repulsions at 90°. With fewer 90° LP–BP repulsions, we can predict that the structure with the lone pair of electrons in the *equatorial position is more stable than the one with the lone pair in the axial position*. We also expect a deviation from ideal geometry because a lone pair of electrons occupies more space than a bonding pair.

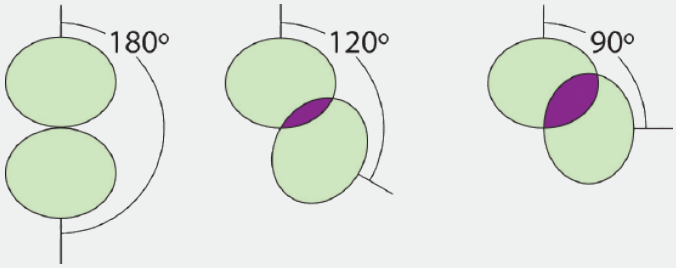
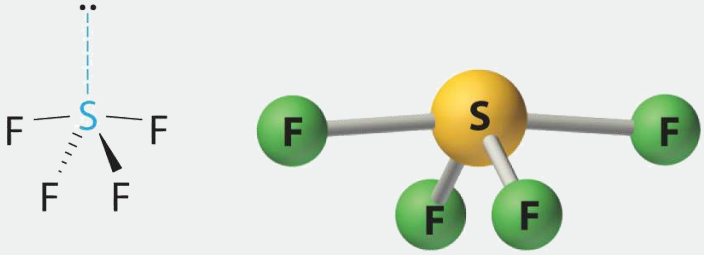


Figure **4.2.5**: Illustration of the Area Shared by Two Electron Pairs versus the Angle between Them

180 degree angle has no shared space between teo electron pair, 120 degree angle has some shared area between two electron pairs. 90 degree angle has more shared space than 120.

At 90°, the two electron pairs share a relatively large region of space, which leads to strong repulsive electron–electron interactions.

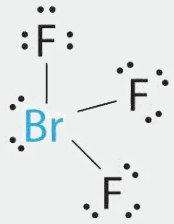
4. With four nuclei and one lone pair of electrons, the molecular structure is based on a trigonal bipyramid with a missing equatorial vertex; it is described as a *seesaw*. The F_{axial}–S–F_{axial} angle is 173° rather than 180° because of the lone pair of electrons in the equatorial plane.



Molecular geometry (seesaw)

AX_3E_2 MOLECULES: BRF_3

1. The bromine atom has seven valence electrons, and each fluorine has seven valence electrons, so the Lewis electron structure is



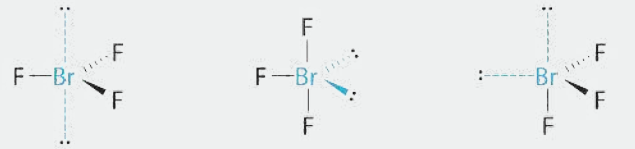
Lewis structure

Three fluorines are bonded to a central bromine. Each fluorine has three lone pairs, Bromine has two lone pairs.

Once again, we have a compound that is an exception to the octet rule.

2. There are five groups around the central atom, three bonding pairs and two lone pairs. We again direct the groups toward the vertices of a trigonal bipyramid.

3. With three bonding pairs and two lone pairs, the structural designation is AX_3E_2 with a total of five electron pairs. Because the axial and equatorial positions are not equivalent, we must decide how to arrange the groups to minimize repulsions. If we place both lone pairs in the axial positions, we have six LP–BP repulsions at 90°. If both are in the equatorial positions, we have four LP–BP repulsions at 90°. If one lone pair is axial and the other equatorial, we have one LP–LP repulsion at 90° and three LP–BP repulsions at 90°:



	Lone pairs axial (a)	Lone pairs equatorial (b)	Lone pairs axial and equatorial (c)
Interactions			
90° LP–LP	0	0	1
90° LP–BP	6	4	3

If the lone pairs are axiam, the 90 degree LP-LP interactions are o and the 90 degree LP-BP interaction is zero. If the Lone pares are equatorial there are zero 90 degree LP-LP interactions and four 90 degree LP-BP intereactions. If the lone pairs are axial and equatorial there is one 90 degree LP-LP interaction and three 90 degree LP-BP interaction.

Structure (c) can be eliminated because it has a LP–LP interaction at 90°. Structure (b), with fewer LP–BP repulsions at 90° than (a), is lower in energy. However, we predict a deviation in bond angles because of the presence of the two lone pairs of electrons.

4. The three nuclei in BrF_3 determine its molecular structure, which is described as *T shaped*. This is essentially a trigonal bipyramid that is missing two equatorial vertices. The F_{axial}–Br–F_{axial} angle is 172°, less than 180° because of LP–BP repulsions (Figure **4.2.2**.1).

Because lone pairs occupy more space around the central atom than bonding pairs, electrostatic repulsions are more important for lone pairs than for bonding pairs.

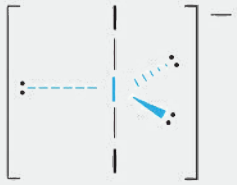
AX_2E_3 MOLECULES: I_3^-

1. Each iodine atom contributes seven electrons and the negative charge one, so the Lewis electron structure is



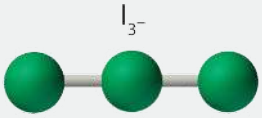
2. There are five electron groups about the central atom in I_3^-, two bonding pairs and three lone pairs. To minimize repulsions, the groups are directed to the corners of a trigonal bipyramid.

3. With two bonding pairs and three lone pairs, I_3^- has a total of five electron pairs and is designated as AX_2E_3. We must now decide how to arrange the lone pairs of electrons in a trigonal bipyramid in a way that minimizes repulsions. Placing them in the axial positions eliminates 90° LP–LP repulsions and minimizes the number of 90° LP–BP repulsions.



The three lone pairs of electrons have equivalent interactions with the three iodine atoms, so we do not expect any deviations in bonding angles.

4. With three nuclei and three lone pairs of electrons, the molecular geometry of I_3^- is linear. This can be described as a trigonal bipyramid with three equatorial vertices missing. The ion has an I–I–I angle of 180°, as expected.

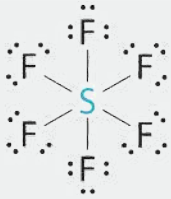


4.2.6 SIX ELECTRON GROUPS

Six electron groups form an *octahedron*, a polyhedron made of identical equilateral triangles and six identical vertices (Figure **4.2.2**.)

AX_6 MOLECULES: SF_6

1. The central atom, sulfur, contributes six valence electrons, and each fluorine atom has seven valence electrons, so the Lewis electron structure is



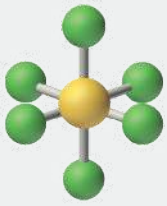
Lewis structure

With an expanded valence, this species is an exception to the octet rule.

2. There are six electron groups around the central atom, each a bonding pair. We see from Figure **4.2.2** that the geometry that minimizes repulsions is *octahedral*.

3. With only bonding pairs, SF_6 is designated as AX_6. All positions are chemically equivalent, so all electronic interactions are equivalent.

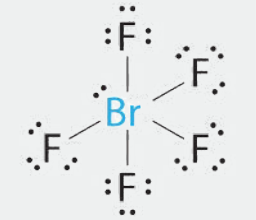
4. There are six nuclei, so the molecular geometry of SF_6 is octahedral.



Molecular geometry
(octahedral)

AX_5E MOLECULES: BRF_5

1. The central atom, bromine, has seven valence electrons, as does each fluorine, so the Lewis electron structure is

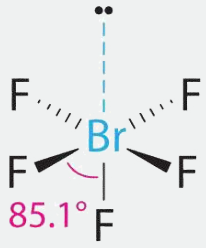


Lewis structure

Five fluorines are bonded to a central bromine. Each fluorine has three lone pairs, Bromine has one lone pair.

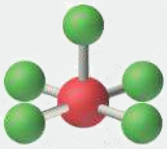
With its expanded valence, this species is an exception to the octet rule.

2. There are six electron groups around the Br, five bonding pairs and one lone pair. Placing five F atoms around Br while minimizing BP–BP and LP–BP repulsions gives the following structure:



3. With five bonding pairs and one lone pair, BrF_5 is designated as AX_5E; it has a total of six electron pairs. The BrF_5 structure has four fluorine atoms in a plane in an equatorial position and one fluorine atom and the lone pair of electrons in the axial positions. We expect all F_{axial}–Br–$F_{equatorial}$ angles to be less than 90° because of the lone pair of electrons, which occupies more space than the bonding electron pairs.

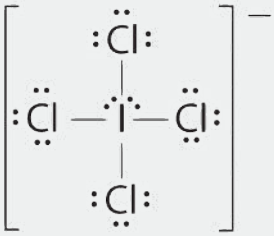
4. With five nuclei surrounding the central atom, the molecular structure is based on an octahedron with a vertex missing. This molecular structure is *square pyramidal*. The F_{axial}–B–$F_{equatorial}$ angles are 85.1°, less than 90° because of LP–BP repulsions.



Molecular geometry
(square pyramidal)

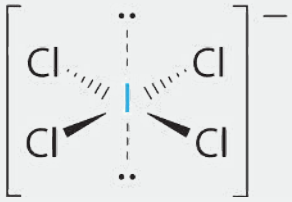
AX_4E_2 MOLECULES: ICl_4^-

1. The central atom, iodine, contributes seven electrons. Each chlorine contributes seven, and there is a single negative charge. The Lewis electron structure is



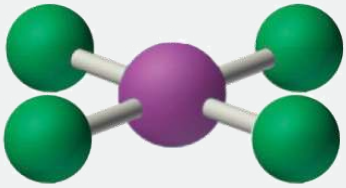
Four chlorines are bonded to a central iodine. Each chlorine has three electron pairs. The iodine has two electron pairs. The molecule is negatively charged.

2. There are six electron groups around the central atom, four bonding pairs and two lone pairs. The structure that minimizes LP–LP, LP–BP, and BP–BP repulsions is



3. ICl_4^- is designated as AX_4E_2 and has a total of six electron pairs. Although there are lone pairs of electrons, with four bonding electron pairs in the equatorial plane and the lone pairs of electrons in the axial positions, all LP–BP repulsions are the same. Therefore, we do not expect any deviation in the Cl–I–Cl bond angles.

4. With five nuclei, the ICl4− ion forms a molecular structure that is *square planar*, an octahedron with two opposite vertices missing.



The relationship between the number of electron groups around a central atom, the number of lone pairs of electrons, and the molecular geometry is summarized in Figure **4.2.6**.

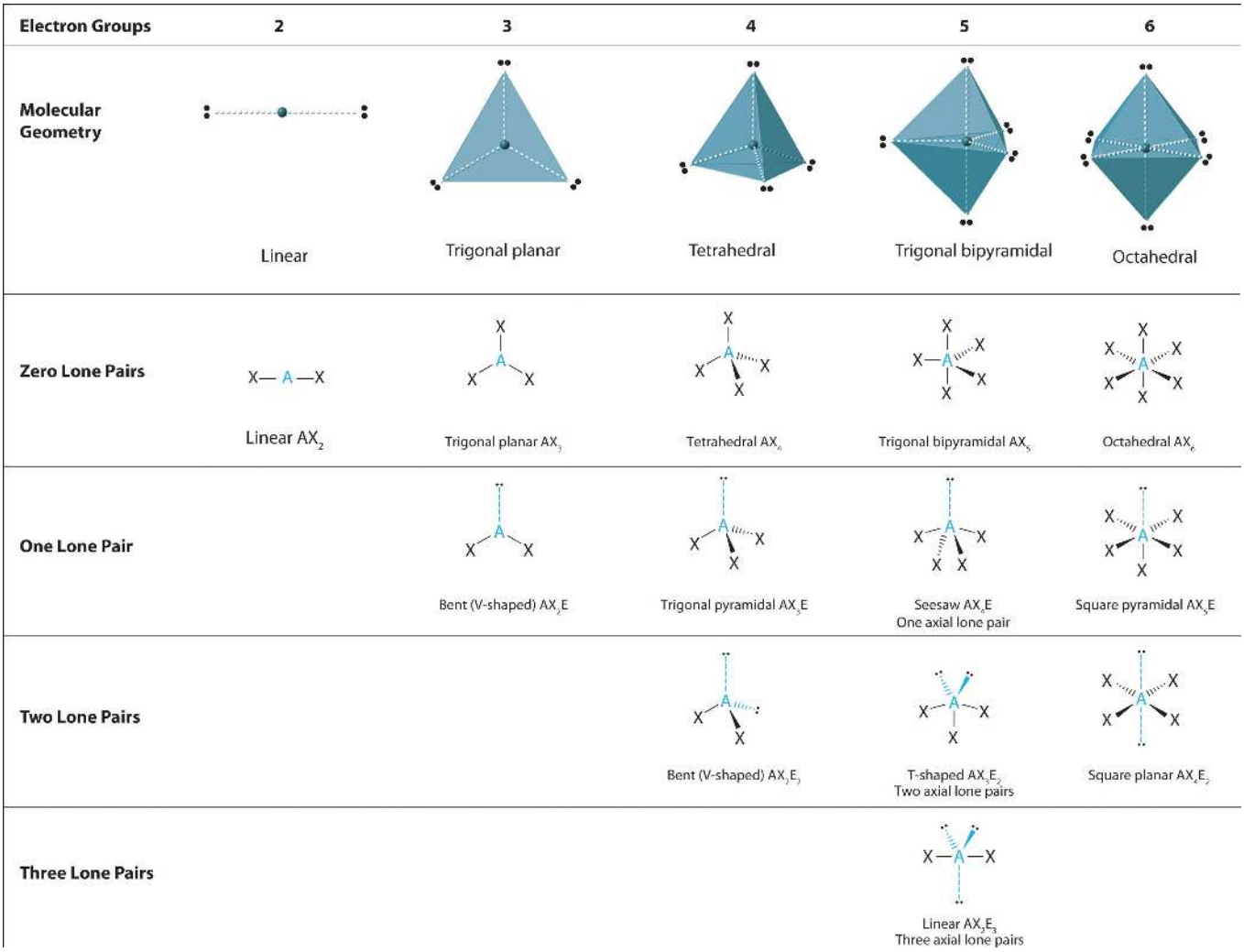


***Figure* 4.2.6:** *Overview of Molecular Geometries*

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EXAMPLE 4.2.1

Using the VSEPR model, predict the molecular geometry of each molecule or ion.

1. PF_5 (phosphorus pentafluoride, a catalyst used in certain organic reactions)
2. H_3O^+ (hydronium ion)

Given: two chemical species

Asked for: molecular geometry

Strategy:

A. Draw the Lewis electron structure of the molecule or polyatomic ion.
B. Determine the electron group arrangement around the central atom that minimizes repulsions.
C. Assign an AX_mE_n designation; then identify the LP–LP, LP–BP, or BP–BP interactions and predict deviations in bond angles.
D. Describe the molecular geometry.

Solution:

1. **A** The central atom, P, has five valence electrons and each fluorine has seven valence electrons, so the Lewis structure of PF_5 is

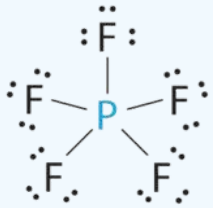


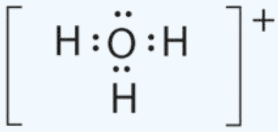
Figure **4.2.6**): (CC BY-NC-SA; anonymous)

C All electron groups are bonding pairs, so PF_5 is designated as AX_5. Notice that this gives a total of five electron pairs. With no lone pair repulsions, we do not expect any bond angles to deviate from the ideal.

D The PF_5 molecule has five nuclei and no lone pairs of electrons, so its molecular geometry is trigonal bipyramidal.



2. **A** The central atom, O, has six valence electrons, and each H atom contributes one valence electron. Subtracting one electron for the positive charge gives a total of eight valence electrons, so the Lewis electron structure is

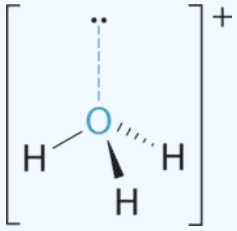


Three hydrogens are bonded to a central oxygen. The oxygen has two lone pairs. The molecule has a charge of plus one.

B There are four electron groups around oxygen, three bonding pairs and one lone pair. Like NH_3, repulsions are minimized by directing each hydrogen atom and the lone pair to the corners of a tetrahedron.

C With three bonding pairs and one lone pair, the structure is designated as AX_3E and has a total of four electron pairs (three X and one E). We expect the LP–BP interactions to cause the bonding pair angles to deviate significantly from the angles of a perfect tetrahedron.

D There are three nuclei and one lone pair, so the molecular geometry is *trigonal pyramidal*, in essence a tetrahedron missing a vertex. However, the H–O–H bond angles are less than the ideal angle of 109.5° because of LP–BP repulsions:



EXERCISE 4.2.1

Using the VSEPR model, predict the molecular geometry of each molecule or ion.

a. XeO_3
b. PF_6^-
c. NO_2^+

Answer a

trigonal pyramidal

Answer b

octahedral

Answer c

linear

EXAMPLE 4.2.2

Predict the molecular geometry of each molecule.

1. XeF_2
2. $SnCl_2$

Given: two chemical compounds

Asked for: molecular geometry

Strategy:

Use the strategy given in Example **4.2.1**.

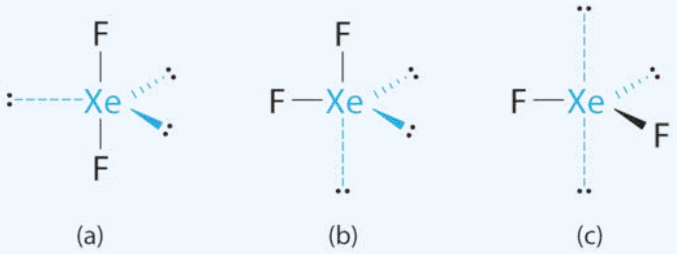
Solution:

1. **A** Xenon contributes eight electrons and each fluorine seven valence electrons, so the Lewis electron structure is



B There are five electron groups around the central atom, two bonding pairs and three lone pairs. Repulsions are minimized by placing the groups in the corners of a trigonal bipyramid.

C From B, XeF_2 is designated as AX_2E_3 and has a total of five electron pairs (two X and three E). With three lone pairs about the central atom, we can arrange the two F atoms in three possible ways: both F atoms can be axial, one can be axial and one equatorial, or both can be equatorial:



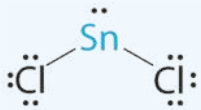
Interactions			
90 LP–LP	0	2	2

If the two F atoms are axial ther are zero 90 LP-LP interactions. If the two F atoms are axial and equatorial or just equatorial, there are 2 90 LP-LP interactions.

The structure with the lowest energy is the one that minimizes LP–LP repulsions. Both (b) and (c) have two 90° LP–LP interactions, whereas structure (a) has none. Thus both F atoms are in the axial positions, like the two iodine atoms around the central iodine in I_3^-. All LP–BP interactions are equivalent, so we do not expect a deviation from an ideal 180° in the F–Xe–F bond angle.

D With two nuclei about the central atom, the molecular geometry of XeF_2 is linear. It is a trigonal bipyramid with three missing equatorial vertices.

2. **A** The tin atom donates 4 valence electrons and each chlorine atom donates 7 valence electrons. With 18 valence electrons, the Lewis electron structure is



Two chlorines are bonded to a central tin. Each chlorine has three lone pairs. Tin has one lone pair.

B There are three electron groups around the central atom, two bonding groups and one lone pair of electrons. To minimize repulsions the three groups are initially placed at 120° angles from each other.

C From B we designate $SnCl_2$ as AX_2E. It has a total of three electron pairs, two X and one E. Because the lone pair of electrons occupies more space than the bonding pairs, we expect a decrease in the Cl–Sn–Cl bond angle due to increased LP–BP repulsions.

D With two nuclei around the central atom and one lone pair of electrons, the molecular geometry of $SnCl_2$ is bent, like SO_2, but with a Cl–Sn–Cl bond angle of 95°. The molecular geometry can be described as a trigonal planar arrangement with one vertex missing.

? EXERCISE 4.2.2

Predict the molecular geometry of each molecule.

a. SO_3
b. XeF_4

Answer a

trigonal planar

Answer b

square planar

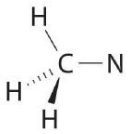
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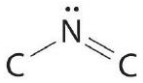
4.2.7 MOLECULES WITH NO SINGLE CENTRAL ATOM

The VSEPR model can be used to predict the structure of somewhat more complex molecules with no single central atom by treating them as linked AX_mE_n fragments. We will demonstrate with methyl isocyanate (CH_3–N=C=O), a volatile and highly toxic molecule that is used to produce the pesticide Sevin. In 1984, large quantities of Sevin were accidentally released in Bhopal, India, when water leaked into storage tanks. The resulting highly exothermic reaction caused a rapid increase in pressure that ruptured the tanks, releasing large amounts of methyl isocyanate that killed approximately 3800 people and wholly or partially disabled about 50,000 others. In addition, there was significant damage to livestock and crops.

We can treat methyl isocyanate as linked AX_mE_n fragments beginning with the carbon atom at the left, which is connected to three H atoms and one N atom by single bonds. The four bonds around carbon mean that it must be surrounded by four bonding electron pairs in a configuration similar to AX_4. We can therefore predict the CH_3–N portion of the molecule to be roughly tetrahedral, similar to methane:



The nitrogen atom is connected to one carbon by a single bond and to the other carbon by a double bond, producing a total of three bonds, C–N=C. For nitrogen to have an octet of electrons, it must also have a lone pair:



One carbon bonded to nitrogen and another carbon double bonded to the nitrogen. The nitrogen has one lone pair.

Because multiple bonds are not shown in the VSEPR model, the nitrogen is effectively surrounded by three electron pairs. Thus according to the VSEPR model, the C–N=C fragment should be bent with an angle less than 120°.

The carbon in the –N=C=O fragment is doubly bonded to both nitrogen and oxygen, which in the VSEPR model gives carbon a total of two electron pairs. The N=C=O angle should therefore be 180°, or linear. The three fragments combine to give the following structure:

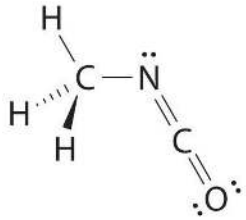


Figure **4.2.7**).

Three hydrogens are bonded to a carbon. The carbon is also bonded to a nitrogen. The nitrogen is double bonded to another carbon. The second carbon is double bonded to an oxygen. The nitrogen has one lone pair. The oxygen has two lone pairs.

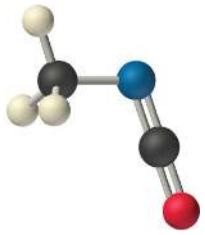


Figure **4.2.7**: The Experimentally Determined Structure of Methyl Isocyanate

Certain patterns are seen in the structures of moderately complex molecules. For example, carbon atoms with four bonds (such as the carbon on the left in methyl isocyanate) are generally tetrahedral. Similarly, the carbon atom on the right has two double bonds that are similar to those in CO_2, so its geometry, like that of CO_2, is linear. Recognizing similarities to simpler molecules will help you predict the molecular geometries of more complex molecules.

✔ EXAMPLE 4.2.3

Use the VSEPR model to predict the molecular geometry of propyne ($H_3C–C≡CH$), a gas with some anesthetic properties.

Given: chemical compound

Asked for: molecular geometry

Strategy:

Count the number of electron groups around each carbon, recognizing that in the VSEPR model, a multiple bond counts as a single group. Use Figure **4.2.3** to determine the molecular geometry around each carbon atom and then deduce the structure of the molecule as a whole.

Solution:

Because the carbon atom on the left is bonded to four other atoms, we know that it is approximately tetrahedral. The next two carbon atoms share a triple bond, and each has an additional single bond. Because a multiple bond is counted as a single bond in the VSEPR model, each carbon atom behaves as if it had two electron groups. This means that both of these carbons are linear, with C–C≡C and C≡C–H angles of 180°.

? EXERCISE 4.2.3

Predict the geometry of allene ($H_2C=C=CH_2$), a compound with narcotic properties that is used to make more complex organic molecules.

Answer

The terminal carbon atoms are trigonal planar, the central carbon is linear, and the C–C–C angle is 180°.

4.2.8 MOLECULAR DIPOLE MOMENTS

You previously learned how to calculate the **dipole moments** of simple diatomic molecules. In more complex molecules with polar covalent bonds, the three-dimensional geometry and the compound's symmetry determine whether there is a net dipole moment. Mathematically, dipole moments are *vectors*; they possess both a *magnitude* and a *direction*. The dipole moment of a molecule is therefore the *vector sum* of the dipole moments of the individual bonds in the molecule. If the individual bond dipole moments cancel one another, there is no net dipole moment. Such is the case for CO_2, a linear molecule (Figure **4.2.8*a***). Each C–O bond in CO_2 is polar, yet experiments show that the CO_2 molecule has no dipole moment. Because the two C–O bond dipoles in CO_2 are equal in magnitude and oriented at 180° to each other, they cancel. As a result, the CO_2 molecule has no *net* dipole moment even though it has a substantial separation of charge. In contrast, the H_2O molecule is not linear (Figure **4.2.8*b***); it is bent in three-dimensional space, so the dipole moments do not cancel each other. Thus a molecule such as H_2O has a net dipole moment. We expect the concentration of negative charge to be on the oxygen, the more electronegative atom, and positive charge on the two hydrogens. This charge polarization allows H_2O to hydrogen-bond to other polarized or charged species, including other water molecules.

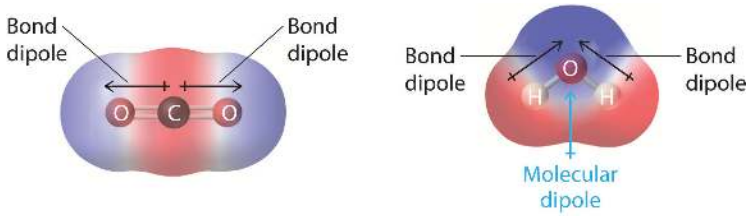


Figure **4.2.8**: How Individual Bond Dipole Moments Are Added Together to Give an Overall Molecular Dipole Moment for Two Triatomic Molecules with Different Structures. (a) In CO_2, the C–O bond dipoles are equal in magnitude but oriented in opposite directions (at 180°). Their vector sum is zero, so CO_2 therefore has no net dipole. (b) In H_2O, the O–H bond dipoles are also equal in magnitude, but they are oriented at 104.5° to each other. Hence the vector sum is not zero, and H_2O has a net dipole moment.

Other examples of molecules with polar bonds are shown in Figure **4.2.9**. In molecular geometries that are highly symmetrical (most notably tetrahedral and square planar, trigonal bipyramidal, and octahedral), individual bond dipole moments completely cancel, and there is no net dipole moment. Although a molecule like $CHCl_3$ is best described as tetrahedral, the atoms bonded to carbon are not identical. Consequently, the bond dipole moments cannot cancel one another, and the molecule has a dipole moment. Due to the arrangement of the bonds in molecules that have V-shaped, trigonal pyramidal, seesaw, T-shaped, and square pyramidal geometries, the bond dipole moments cannot cancel one another. Consequently, molecules with these geometries always have a nonzero dipole moment. Molecules with asymmetrical charge distributions have a net dipole moment.

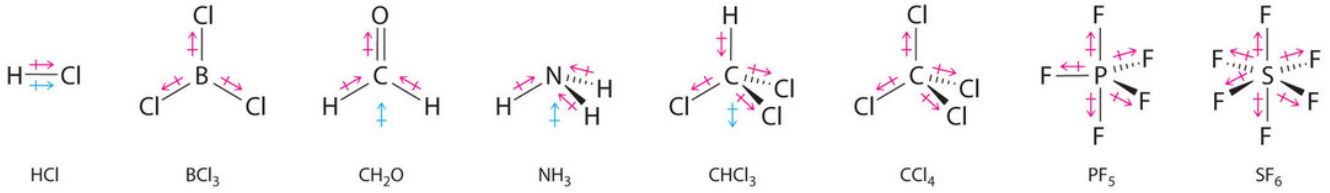


Figure **4.2.9**: Molecules with Polar Bonds. Individual bond dipole moments are indicated in red. Due to their different three-dimensional structures, some molecules with polar bonds have a net dipole moment (HCl, CH_2O, NH_3, and $CHCl_3$), indicated in blue, whereas others do not because the bond dipole moments cancel (BCl_3, CCl_4, PF_5, and SF_6).



EXAMPLE 4.2.4

Which molecule(s) has a net dipole moment?

a. **H_2S**
b. **NHF_2**
c. **BF_3**

Given: three chemical compounds

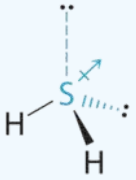
Asked for: net dipole moment

Strategy:

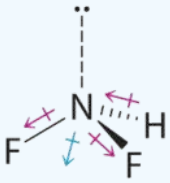
For each three-dimensional molecular geometry, predict whether the bond dipoles cancel. If they do not, then the molecule has a net dipole moment.

Solution:

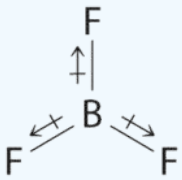
1. The total number of electrons around the central atom, S, is eight, which gives four electron pairs. Two of these electron pairs are bonding pairs and two are lone pairs, so the molecular geometry of H_2S is bent (Figure **4.2.6**). The bond dipoles cannot cancel one another, so the molecule has a net dipole moment.



2. Difluoroamine has a trigonal pyramidal molecular geometry. Because there is one hydrogen and two fluorines, and because of the lone pair of electrons on nitrogen, the molecule is not symmetrical, and the bond dipoles of NHF_2 cannot cancel one another. This means that NHF_2 has a net dipole moment. We expect polarization from the two fluorine atoms, the most electronegative atoms in the periodic table, to have a greater affect on the net dipole moment than polarization from the lone pair of electrons on nitrogen.



3. The molecular geometry of BF_3 is trigonal planar. Because all the B–F bonds are equal and the molecule is highly symmetrical, the dipoles cancel one another in three-dimensional space. Thus BF_3 has a net dipole moment of zero:



? EXERCISE 4.2.4

Which molecule(s) has a net dipole moment?

- CH_3Cl
- SO_3
- XeO_3

Answer

CH_3Cl and XeO_3

4.2.9 SUMMARY

Lewis electron structures give no information about **molecular geometry**, the arrangement of bonded atoms in a molecule or polyatomic ion, which is crucial to understanding the chemistry of a molecule. The **valence-shell electron-pair repulsion (VSEPR) model** allows us to predict which of the possible structures is actually observed in most cases. It is based on the assumption that pairs of electrons occupy space, and the lowest-energy structure is the one that minimizes electron pair–electron pair repulsions. In the VSEPR model, the molecule or polyatomic ion is given an AX_mE_n designation, where A is the central atom, X is a bonded atom, E is a nonbonding valence electron group (usually a lone pair of electrons), and m and n are integers. Each group around the central atom is designated as a bonding pair (BP) or lone (nonbonding) pair (LP). From the BP and LP interactions we can predict both the relative positions of the atoms and the angles between the bonds, called the **bond angles**. From this we can describe the **molecular geometry**. The VSEPR model can be used to predict the shapes of many molecules and polyatomic ions, but it gives no information about bond lengths and the presence of multiple bonds. A combination of VSEPR and a bonding model, such as Lewis electron structures, is necessary to understand the presence of multiple bonds.

Molecules with polar covalent bonds can have a *dipole moment*, an asymmetrical distribution of charge that results in a tendency for molecules to align themselves in an applied electric field. Any diatomic molecule with a polar covalent bond has a dipole moment, but in

polyatomic molecules, the presence or absence of a net dipole moment depends on the structure. For some highly symmetrical structures, the individual bond dipole moments cancel one another, giving a dipole moment of zero.

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4.3: MOLECULAR SHAPE AND MOLECULAR POLARITY

LEARNING OBJECTIVES

- To calculate the percent ionic character of a covalent polar bond

Previously, we described the two idealized extremes of chemical bonding:

- **ionic bonding**—in which one or more electrons are transferred completely from one atom to another, and the resulting ions are held together by purely electrostatic forces—and
- **covalent bonding**, in which electrons are shared *equally* between two atoms.

Most compounds, however, have polar covalent bonds, which means that electrons are shared *unequally* between the bonded atoms. Figure **4.3.1** compares the electron distribution in a polar covalent bond with those in an ideally covalent and an ideally ionic bond. Recall that a lowercase Greek delta (δ) is used to indicate that a bonded atom possesses a partial positive charge, indicated by δ^+, or a partial negative charge, indicated by δ^-, and a bond between two atoms that possess partial charges is a *polar bond*.

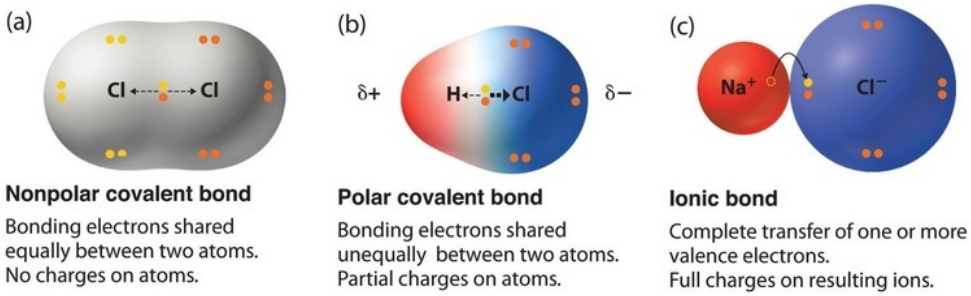


Figure **4.3.1**: The Electron Distribution in a Nonpolar Covalent Bond, a Polar Covalent Bond, and an Ionic Bond Using Lewis Electron Structures. In a purely covalent bond (a), the bonding electrons are shared equally between the atoms. In a purely ionic bond (c), an electron has been transferred completely from one atom to the other. A polar covalent bond (b) is intermediate between the two extremes: the bonding electrons are shared unequally between the two atoms, and the electron distribution is asymmetrical with the electron density being greater around the more electronegative atom. Electron-rich (negatively charged) regions are shown in blue; electron-poor (positively charged) regions are shown in red.

4.3.1 BOND POLARITY

The polarity of a bond—the extent to which it is polar—is determined largely by the relative electronegativities of the bonded atoms. *Electronegativity* (χ) was defined as the ability of an atom in a molecule or an ion to attract electrons to itself. Thus there is a direct correlation between electronegativity and bond polarity. A bond is *nonpolar* if the bonded atoms have equal electronegativities. If the electronegativities of the bonded atoms are not equal, however, the bond is *polarized* toward the more electronegative atom. A bond in which the electronegativity of B (χ_B) is greater than the electronegativity of A (χ_A), for example, is indicated with the partial negative charge on the more electronegative atom:

$$\underset{\delta^+}{\overset{\text{less electronegative}}{A}} - \underset{\delta^-}{\overset{\text{more electronegative}}{B}} \tag{4.3.1}$$

One way of estimating the ionic character of a bond—that is, the magnitude of the charge separation in a polar covalent bond—is to calculate the difference in electronegativity between the two atoms:

$$\Delta\chi = \chi_B - \chi_A.$$

To predict the polarity of the bonds in Cl_2, HCl, and NaCl, for example, we look at the electronegativities of the relevant atoms (Table A2): $\chi_{Cl} = 3.16$, $\chi_H = 2.20$, and $\chi_{Na} = 0.93$. Cl_2 must be nonpolar because the electronegativity difference ($\Delta\chi$) is zero; hence the two chlorine atoms share the bonding electrons equally. In NaCl, $\Delta\chi$ is 2.23. This high value is typical of an ionic compound ($\Delta\chi \geq\approx 1.5$) and means that the valence electron of sodium has been completely transferred to chlorine to form Na^+ and Cl^- ions. In HCl, however, $\Delta\chi$ is only 0.96. The bonding electrons are more strongly attracted to the more electronegative chlorine atom, and so the charge distribution is

$$\underset{}{\overset{\delta^+}{H}} - \underset{}{\overset{\delta^-}{Cl}}$$

Remember that electronegativities are difficult to measure precisely and different definitions produce slightly different numbers. In practice, the polarity of a bond is usually estimated rather than calculated.

> Bond polarity and ionic character increase with an increasing difference in electronegativity.

As with bond energies, the electronegativity of an atom depends to some extent on its chemical environment. It is therefore unlikely that the reported electronegativities of a chlorine atom in NaCl, $\mathrm{Cl_2}$, $\mathrm{ClF_5}$, and $\mathrm{HClO_4}$ would be exactly the same.

4.3.2 DIPOLE MOMENTS

The asymmetrical charge distribution in a polar substance such as HCl produces a dipole moment where Qr in meters (m). is abbreviated by the Greek letter mu (μ). The dipole moment is defined as the product of the partial charge Q on the bonded atoms and the distance r between the partial charges:

$$\mu = Qr \tag{4.3.2}$$

where Q is measured in coulombs (C) and r in meters. The unit for dipole moments is the debye (D):

$$1\ D = 3.3356 \times 10^{-30}\ C \cdot m \tag{4.3.3}$$

When a molecule with a dipole moment is placed in an electric field, it tends to orient itself with the electric field because of its asymmetrical charge distribution (Figure 4.3.2).

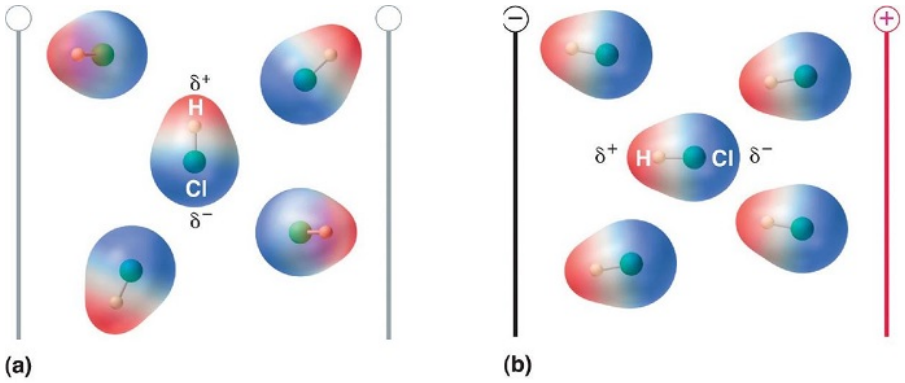


Figure 4.3.2: Molecules That Possess a Dipole Moment Partially Align Themselves with an Applied Electric Field In the absence of a field (a), theHClmolecules are randomly oriented. When an electric field is applied (b), the molecules tend to align themselves with the field, such that the positive end of the molecular dipole points toward the negative terminal and vice versa.

We can measure the partial charges on the atoms in a molecule such as HCl using Equation 4.3.2. If the bonding in HCl were purely ionic, an electron would be transferred from H to Cl, so there would be a full +1 charge on the H atom and a full −1 charge on the Cl atom. The dipole moment of HCl is 1.109 D, as determined by measuring the extent of its alignment in an electric field, and the reported gas-phase H–Cl distance is 127.5 pm. Hence the charge on each atom is

$$\begin{aligned} Q &= \frac{\mu}{r} \\ &= 1.109\ \cancel{D}\left(\frac{3.3356 \times 10^{-30}\ C \cdot \cancel{m}}{1\ \cancel{D}}\right)\left(\frac{1}{127.8\ \cancel{pm}}\right)\left(\frac{1\ \cancel{pm}}{10^{-12}\ \cancel{m}}\right) \\ &= 2.901 \times 10^{-20}\ C \end{aligned}$$

By dividing this calculated value by the charge on a single electron (1.6022×10^{-19} C), we find that the electron distribution inHCl is asymmetric and that effectively it appears that there is a net negative charge on the Cl of about −0.18, effectively corresponding to about 0.18 e^-. This certainly does not mean that there is a fraction of an electron on the Cl atom, but that the distribution of electron probability favors the Cl atom side of the molecule by about this amount.

$$\frac{2.901 \times 10^{-20}\ \cancel{C}}{1.6022 \times 10^{-19}\ \cancel{C}} = 0.1811\ e^- \tag{4.3.4}$$

To form a neutral compound, the charge on the H atom must be equal but opposite. Thus the measured dipole moment of HCl indicates that the H–Cl bond has approximately 18% ionic character (0.1811 × 100), or 82% covalent character. Instead of writingHCl as

$$\overset{\delta+}{H} - \overset{\delta-}{Cl}$$

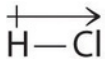
we can therefore indicate the charge separation quantitatively as

$$\overset{0.18\delta+}{H} - \overset{0.18\delta-}{Cl}$$

Our calculated results are in agreement with the electronegativity difference between hydrogen and chlorine ($\chi_H = 2.20$ and $\chi_{Cl} = 3.16$) so

$$\chi_{Cl} - \chi_H = 0.96$$

This is a value well within the range for polar covalent bonds. We indicate the dipole moment by writing an arrow above the molecule.Mathematically, dipole moments are vectors, and they possess both a magnitude and a direction. The dipole moment of a molecule is the vector sum of the dipoles of the individual bonds. In HCl, for example, the dipole moment is indicated as follows:



The arrow shows the direction of electron flow by pointing toward the more electronegative atom.



A WARNING ABOUT DIPOLE MOMENT ARROWS

As the figure above shows, we represent dipole moments by an arrow with a length proportional to μ and pointing from the positive charge to the negative charge. However, the **opposite** convention is still widely used especially among physicists.

The charge on the atoms of many substances in the gas phase can be calculated using measured dipole moments and bond distances. Figure **4.3.2** shows a plot of the percent ionic character versus the difference in electronegativity of the bonded atoms for several substances. According to the graph, the bonding in species such as $NaCl_{(g)}$ and $CsF_{(g)}$ is substantially less than 100% ionic in character. As the gas condenses into a solid, however, dipole–dipole interactions between polarized species increase the charge separations. In the crystal, therefore, an electron is transferred from the metal to the nonmetal, and these substances behave like classic ionic compounds. The data in Figure **4.3.2** show that diatomic species with an electronegativity difference of less than 1.5 are less than 50% ionic in character, which is consistent with our earlier description of these species as containing polar covalent bonds. The use of dipole moments to determine the ionic character of a polar bond is illustrated in Example **4.3.1**.

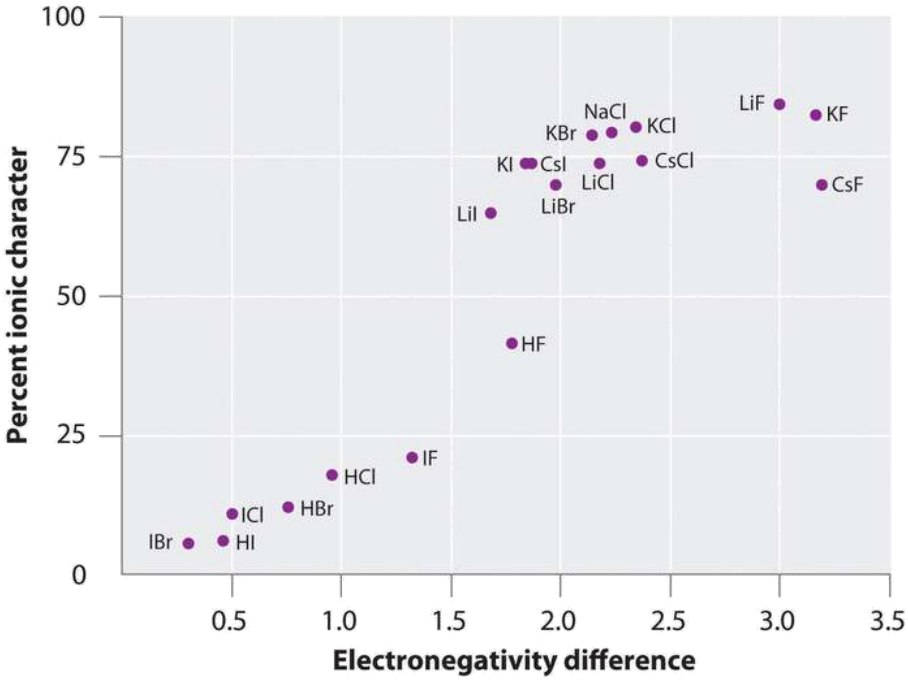


Figure **4.3.2**: A Plot of the Percent Ionic Character of a Bond as Determined from Measured Dipole Moments versus the Difference in Electronegativity of the Bonded Atoms. In the gas phase, even CsF, which has the largest possible difference in electronegativity between atoms, is not 100% ionic. Solid CsF, however, is best viewed as 100% ionic because of the additional electrostatic interactions in the lattice.

EXAMPLE 4.3.1: PERCENT IONIC CHARACTER

In the gas phase, NaCl has a dipole moment of 9.001 D and an Na–Cl distance of 236.1 pm. Calculate the percent ionic character in NaCl.

Given: chemical species, dipole moment, and internuclear distance

Asked for: percent ionic character

Strategy:

A. Compute the charge on each atom using the information given and Equation 4.3.2

B. Find the percent ionic character from the ratio of the actual charge to the charge of a single electron.

Solution:

A The charge on each atom is given by

$$\begin{aligned} Q &= \frac{\mu}{r} \\ &= 9.001 \cancel{D} \left(\frac{3.3356 \times 10^{-30}\ C \cdot \cancel{m}}{1\ \cancel{D}} \right) \left(\frac{1}{236.1\ \cancel{pm}} \right) \left(\frac{1\ \cancel{pm}}{10^{-12}\ \cancel{m}} \right) \\ &= 1.272 \times 10^{-19}\ C \end{aligned}$$

Thus NaCl behaves as if it had charges of 1.272×10^{-19} C on each atom separated by 236.1 pm.

B The percent ionic character is given by the ratio of the actual charge to the charge of a single electron (the charge expected for the complete transfer of one electron):

$$\begin{aligned} \text{ionic character} &= \left(\frac{1.272 \times 10^{-19}\ \cancel{C}}{1.6022 \times 10^{-19}\ \cancel{C}} \right) (100) \\ &= 79.39\% \simeq 79\% \end{aligned}$$

? EXERCISE 4.3.1

In the gas phase, silver chloride (AgCl) has a dipole moment of 6.08 D and an Ag–Cl distance of 228.1 pm. What is the percent ionic character in silver chloride?

Answer

55.5%

4.3.3 SUMMARY

Bond polarity and ionic character increase with an increasing difference in electronegativity.

$$\mu = Qr$$

Compounds with **polar covalent bonds** have electrons that are shared unequally between the bonded atoms. The polarity of such a bond is determined largely by the relative electronegativites of the bonded atoms. The asymmetrical charge distribution in a polar substance produces a **dipole moment**, which is the product of the partial charges on the bonded atoms and the distance between them.

4.3.4 CONTRIBUTORS AND ATTRIBUTIONS

- Modified by Joshua Halpern (Howard University)

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4.4: COVALENT BONDING AND ORBITAL OVERLAP

LEARNING OBJECTIVES

- To describe the bonding in simple compounds using valence bond theory.

Although the VSEPR model is a simple and useful method for qualitatively predicting the structures of a wide range of compounds, it is *not* infallible. It predicts, for example, that H_2S and PH_3 should have structures similar to those of $\mathbf{H_2O}$ and $\mathbf{NH_3}$, respectively. In fact, structural studies have shown that the H–S–H and H–P–H angles are more than 12° smaller than the corresponding bond angles in $\mathbf{H_2O}$ and $\mathbf{NH_3}$. More disturbing, the VSEPR model predicts that the simple group 2 halides (MX_2), which have four valence electrons, should all have linear X–M–X geometries. Instead, many of these species, including $\mathbf{SrF_2}$ and $\mathbf{BaF_2}$, are significantly bent. A more sophisticated treatment of bonding is needed for systems such as these. In this section, we present a quantum mechanical description of bonding, in which bonding electrons are viewed as being localized between the nuclei of the bonded atoms. The overlap of bonding orbitals is substantially increased through a process called *hybridization*, which results in the formation of stronger bonds.

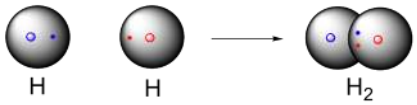
4.4.1 INTRODUCTION

As we have talked about using Lewis structures to depict the bonding in covalent compounds, we have been very vague in our language about the actual nature of the chemical bonds themselves. We know that a covalent bond involves the 'sharing' of a pair of electrons between two atoms - but how does this happen, and how does it lead to the formation of a bond holding the two atoms together?

The **valence bond theory** is introduced to describe bonding in covalent molecules. In this model, bonds are considered to form from the overlapping of two atomic orbitals on different atoms, each orbital containing a single electron. In looking at simple inorganic molecules such as H_2 or HF, our present understanding of s and p atomic orbitals will suffice. To explain the bonding in organic molecules, however, we will need to introduce the concept of **hybrid orbitals**.

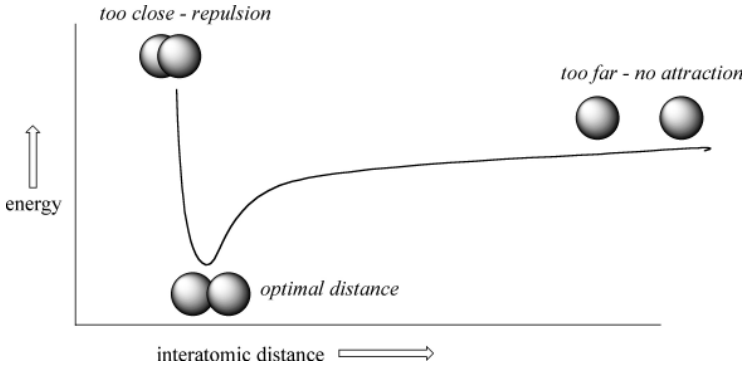
4.4.2 EXAMPLE: THE H_2 MOLECULE

The simplest case to consider is the hydrogen molecule, H_2. When we say that the two electrons from each of the hydrogen atoms are shared to form a covalent bond between the two atoms, what we mean in valence bond theory terms is that the two spherical 1*s* orbitals overlap, allowing the two electrons to form a pair within the two overlapping orbitals. In simple terms, we can say that both electrons now spend more time *between* the two nuclei and thus hold the atoms together. As we will see, the situation is not quite so simple as that, because the electron pair must still obey quantum mechanics - that is, the two electrons must now occupy a *shared orbital space*. This will be the essential principle of valence bond theory.



These two electrons are now attracted to the positive charge of both of the hydrogen nuclei, with the result that they serve as a sort of 'chemical glue' holding the two nuclei together.

How far apart are the two nuclei? That is a very important issue to consider. If they are too far apart, their respective 1*s* orbitals cannot overlap, and thus no covalent bond can form - they are still just two separate hydrogen atoms. As they move closer and closer together, orbital overlap begins to occur, and a bond begins to form. This lowers the potential energy of the system, as new, *attractive* positive-negative electrostatic interactions become possible between the nucleus of one atom and the electron of the second. However, something else is happening at the same time: as the atoms get closer, the *repulsive* positive-positive interaction between the two nuclei also begins to increase.



Graph of increasing energy against increasting interatomic distance. If the two are too close there is repulsion, if the two are too far there is no attraction. There is an optimal distance.

At first this repulsion is more than offset by the attraction between nuclei and electrons, but at a certain point, as the nuclei get even closer, the repulsive forces begin to overcome the attractive forces, and the potential energy of the system rises quickly. When the two nuclei are 'too close', we have a very unstable, high-energy situation. There is a defined optimal distance between the nuclei in which the potential energy is at a minimum, meaning that the combined attractive and repulsive forces add up to the greatest overall attractive force. This optimal internuclear distance is the **bond length**. For the H_2 molecule, this distance is 74 x 10^{-12} meters, or 0.74 Å (Å means angstrom, or 10^{-10} meters). Likewise, the difference in potential energy between the lowest state (at the optimal internuclear distance) and the state where the two atoms are completely separated is called the **bond energy**. For the hydrogen molecule, this energy is equal to about 104 kcal/mol.

Every covalent bond in a given molecule has a characteristic length and strength. In general, carbon-carbon single bonds are about 1.5 Å long (Å means angstrom, or 10^{-10} meters) while carbon-carbon double bonds are about 1.3 Å, carbon-oxygen double bonds are about 1.2 Å, and carbon-hydrogen bonds are in the range of 1.0 – 1.1 Å. Most covalent bonds in organic molecules range in strength from just under 100 kcal/mole (for a carbon-hydrogen bond in ethane, for example) up to nearly 200 kcal/mole. You can refer to tables in reference books such as the CRC Handbook of Chemistry and Physics for extensive lists of bond lengths, strengths, and many other data for specific organic compounds.

BALLS AND SPRINGS

Although we tend to talk about "bond length" as a specific distance, it is not accurate to picture covalent bonds as rigid sticks of unchanging length - rather, it is better to picture them as *springs* which have a defined length when relaxed, but which can be compressed, extended, and bent. This 'springy' picture of covalent bonds will become very important, when we study the analytical technique known as infrared (IR) spectroscopy.

4.4.3 VALENCE BOND THEORY: A LOCALIZED BONDING APPROACH

You learned that as two hydrogen atoms approach each other from an infinite distance, the energy of the system reaches a minimum. This region of minimum energy in the energy diagram corresponds to the formation of a covalent bond between the two atoms at an H–H distance of 74 pm (Figure **4.4.1**). According to quantum mechanics, bonds form between atoms because their atomic orbitals overlap, with each region of overlap accommodating a *maximum of two electrons with opposite spin*, in accordance with the Pauli principle. In this case, a bond forms between the two hydrogen atoms when the singly occupied 1*s* atomic orbital of one hydrogen atom overlaps with the singly occupied 1*s* atomic orbital of a second hydrogen atom. Electron density between the nuclei is increased because of this orbital overlap and results in a *localized electron-pair bond* (Figure **4.4.1**).

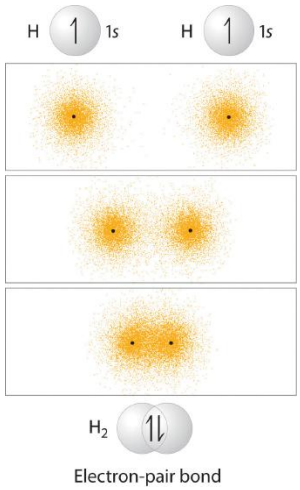


Figure **4.4.1**: Overlap of Two Singly Occupied Hydrogen 1*s* Atomic Orbitals Produces an H–H Bond in H_2. The formation of H_2 from two hydrogen atoms, each with a single electron in a 1*s* orbital, occurs as the electrons are shared to form an electron-pair bond, as indicated schematically by the gray spheres and black arrows. The orange electron density distributions show that the formation of an H_2 molecule increases the electron density in the region between the two positively charged nuclei.

Although Lewis and VSEPR structures also contain localized electron-pair bonds, neither description uses an atomic orbital approach to predict the stability of the bond. Doing so forms the basis for a description of chemical bonding known as valence bond theory, which is built on two assumptions:

1. The strength of a covalent bond is proportional to the amount of overlap between atomic orbitals; that is, the greater the overlap, the more stable the bond.
2. An atom can use different combinations of atomic orbitals to maximize the overlap of orbitals used by bonded atoms.

Figure **4.4.2** shows an electron-pair bond formed by the overlap of two *ns* atomic orbitals, two *np* atomic orbitals, and an *ns* and an *np* orbital where $n = 2$. Notice that bonding overlap occurs when the interacting atomic orbitals have the correct orientation (are "pointing at" each other) and are *in phase* (represented by colors in Figure **4.4.2**).

> Maximum overlap occurs between orbitals with the same spatial orientation and similar energies.

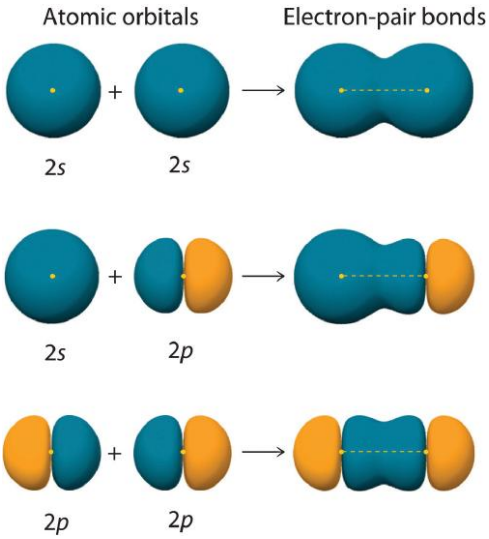


Figure **4.4.2** : Three Different Ways to Form an Electron-Pair Bond. An electron-pair bond can be formed by the overlap of any of the following combinations of two singly occupied atomic orbitals: two *ns* atomic orbitals (a), an *ns* and an *np* atomic orbital (b), and two *np* atomic orbitals (c) where $n = 2$. The positive lobe is indicated in yellow, and the negative lobe is in blue.

Let's examine the bonds in BeH_2, for example. According to the VSEPR model, BeH_2 is a linear compound with four valence electrons and two Be–H bonds. Its bonding can also be described using an atomic orbital approach. Beryllium has a $1s^2 2s^2$ electron configuration, and each H atom has a $1s^1$ electron configuration. Because the Be atom has a filled 2*s* subshell, however, it has no singly occupied orbitals available to overlap with the singly occupied 1*s* orbitals on the H atoms. If a singly occupied 1*s* orbital on hydrogen were to overlap with a filled 2*s* orbital on beryllium, the resulting bonding orbital would contain *three* electrons, but the maximum allowed by quantum mechanics

is *two*. How then is beryllium able to bond to two hydrogen atoms? One way would be to add enough energy to excite one of its 2*s* electrons into an empty 2*p* orbital and reverse its spin, in a process called promotion:



The ground state of beryllium has one electron pair in the 2s orbital. The excited state of beryllium takes one of the electrons from the 2s orbital and moves it to the 2p orbital.

In this excited state, the Be atom would have two singly occupied atomic orbitals (the 2*s* and one of the 2*p* orbitals), each of which could overlap with a singly occupied 1*s* orbital of an H atom to form an electron-pair bond. Although this would produce $\mathbf{BeH_2}$, the two Be–H bonds would not be equivalent: the 1*s* orbital of one hydrogen atom would overlap with a Be 2*s* orbital, and the 1*s* orbital of the other hydrogen atom would overlap with an orbital of a different energy, a Be 2*p* orbital. Experimental evidence indicates, however, that the two Be–H bonds have identical energies. To resolve this discrepancy and explain how molecules such as $\mathbf{BeH_2}$ form, scientists developed the concept of hybridization.

4.4.4 CONTRIBUTORS AND ATTRIBUTIONS

- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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4.5: HYBRID ORBITALS

The localized **valence bond theory** uses a process called **hybridization**, in which atomic orbitals that are similar in energy but not equivalent are combined mathematically to produce sets of equivalent orbitals that are properly oriented to form bonds. These new combinations are called hybrid atomic orbitals because they are produced by combining (*hybridizing*) two or more atomic orbitals from the same atom.

4.5.1 HYBRIDIZATION OF *S* AND *P* ORBITALS

In BeH_2, we can generate two equivalent orbitals by combining the 2*s* orbital of beryllium and any one of the three degenerate 2*p* orbitals. By taking the sum and the difference of Be 2*s* and $2p_z$ atomic orbitals, for example, we produce two new orbitals with major and minor lobes oriented along the *z*-axes, as shown in Figure **4.5.1**.

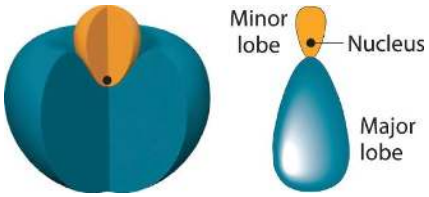


Figure **4.5.1:** The position of the atomic nucleus with respect to an sp hybrid orbital. The nucleus is actually located slightly inside the minor lobe, not at the node separating the major and minor lobes.

Because the difference A − B can also be written as A + (−B), in Figure **4.5.2** and subsequent figures we have reversed the phase(s) of the orbital being subtracted, which is the same as multiplying it by −1 and adding. This gives us Equation **4.5.2**, where the value $\frac{1}{\sqrt{2}}$ is needed mathematically to indicate that the 2*s* and 2*p* orbitals contribute equally to each hybrid orbital.

$$sp = \frac{1}{\sqrt{2}}(2s + 2p_z) \tag{4.5.1}$$

and

$$sp = \frac{1}{\sqrt{2}}(2s - 2p_z) \tag{4.5.2}$$

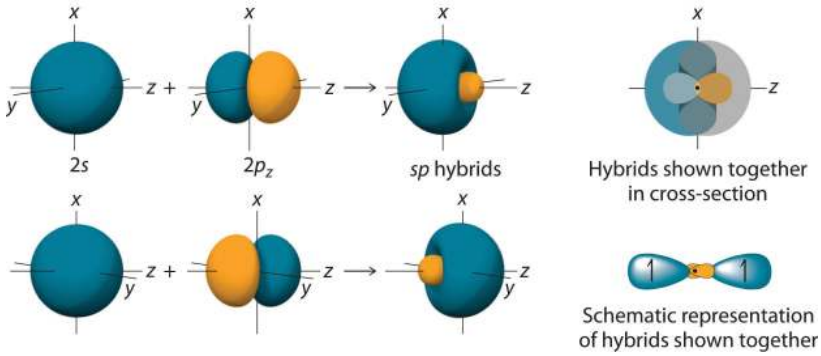


Figure **4.5.2**: The Formation of *sp* Hybrid Orbitals. Taking the sum and difference of an *ns* and an *np* atomic orbital where *n* = 2 gives two equivalent *sp* hybrid orbitals oriented at 180° to each other.

The nucleus resides just inside the minor lobe of each orbital. In this case, the new orbitals are called *sp hybrids* because they are formed from one *s* and one *p* orbital. The two new orbitals are equivalent in energy, and their energy is between the energy values associated with pure *s* and *p* orbitals, as illustrated in this diagram:

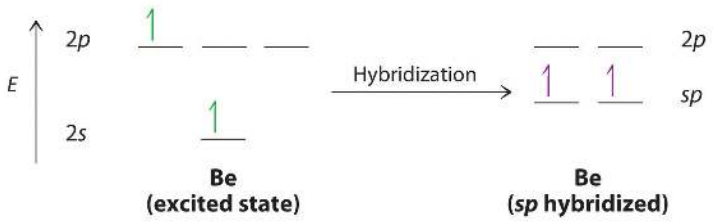


Figure **4.5.3**. each *sp* orbital on Be has the correct orientation for the major lobes to overlap with the 1*s* atomic orbital of an H atom. The formation of two energetically equivalent Be–H bonds produces a linear $\boldsymbol{BeH_2}$ molecule. Thus valence bond theory does what neither the Lewis electron structure nor the VSEPR model is able to do; it explains why the bonds in $\boldsymbol{BeH_2}$ are equivalent in energy and why $\boldsymbol{BeH_2}$ has a linear geometry.

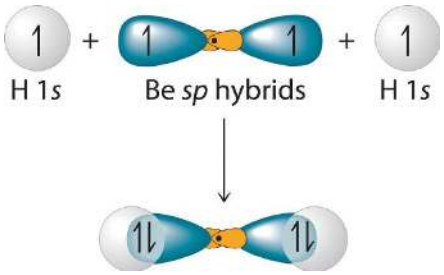


Figure **4.5.3**: Explanation of the Bonding in BeH_2 Using *sp* Hybrid Orbitals. Each singly occupied *sp* hybrid orbital on beryllium can form an electron-pair bond with the singly occupied 1*s* orbital of a hydrogen atom. Because the two *sp* hybrid orbitals are oriented at a 180° angle, the BeH_2 molecule is linear.

Because both promotion and hybridization require an input of energy, the formation of a set of singly occupied hybrid atomic orbitals is energetically uphill. The overall process of forming a compound with hybrid orbitals will be energetically favorable *only* if the amount of energy released by the formation of covalent bonds is greater than the amount of energy used to form the hybrid orbitals (Figure **4.5.4**). As we will see, some compounds are highly unstable or do not exist because the amount of energy required to form hybrid orbitals is greater than the amount of energy that would be released by the formation of additional bonds.

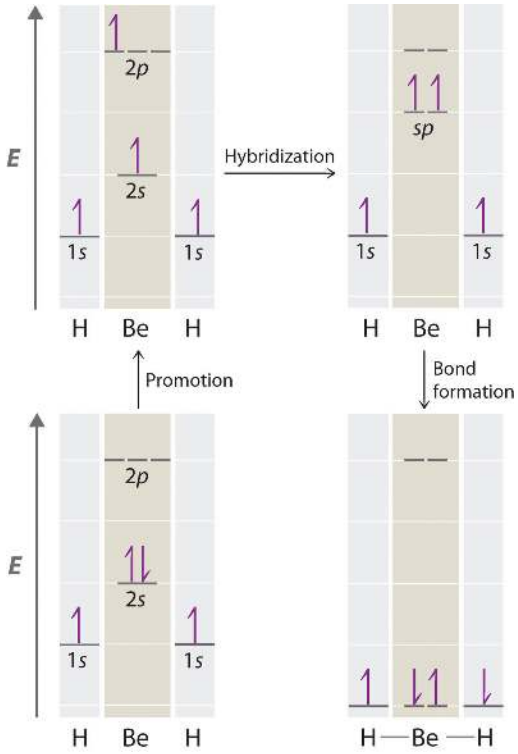


Figure **4.5.4**: A Hypothetical Stepwise Process for the Formation of BeH_2 from a Gaseous Be Atom and Two Gaseous H Atoms. The promotion of an electron from the 2*s* orbital of beryllium to one of the 2*p* orbitals is energetically uphill. The overall process of forming a BeH_2 molecule from a Be atom and two H atoms will therefore be energetically favorable *only* if the amount of energy released by the formation of the two Be–H bonds is greater than the amount of energy required for promotion and hybridization.

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The concept of hybridization also explains why boron, with a $2s^2 2p^1$ valence electron configuration, forms three bonds with fluorine to produce BF_3, as predicted by the Lewis and VSEPR approaches. With only a single unpaired electron in its ground state, boron should form only a single covalent bond. By the promotion of one of its 2*s* electrons to an unoccupied 2*p* orbital, however, followed by the hybridization of the three singly occupied orbitals (the 2*s* and two 2*p* orbitals), boron acquires a set of three equivalent hybrid orbitals with one electron each, as shown here:

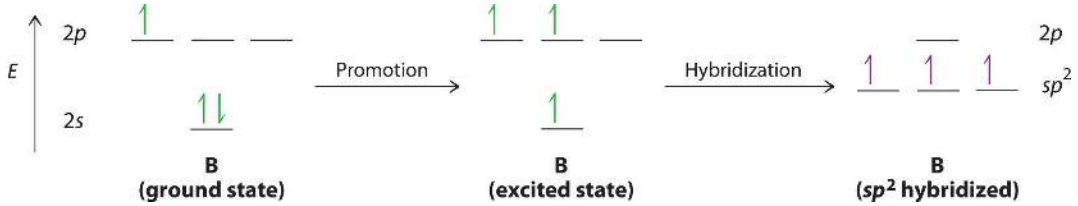


Figure **4.5.5**). Because the hybrid atomic orbitals are formed from one *s* and two *p* orbitals, boron is said to be sp^2 *hybridized* (pronounced "s-p-two" or "s-p-squared"). The singly occupied sp^2 hybrid atomic orbitals can overlap with the singly occupied orbitals on each of the three F atoms to form a trigonal planar structure with three energetically equivalent B–F bonds.

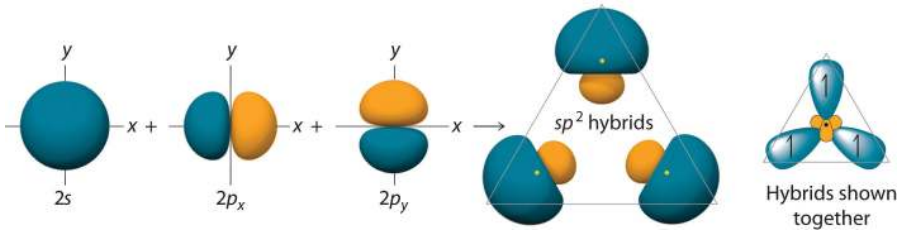


Figure **4.5.5**: Formation of sp^2 Hybrid Orbitals. Combining one *ns* and two *np* atomic orbitals gives three equivalent sp^2 hybrid orbitals in a trigonal planar arrangement; that is, oriented at 120° to one another.



Looking at the $2s^2 2p^2$ valence electron configuration of carbon, we might expect carbon to use its two unpaired 2*p* electrons to form compounds with only two covalent bonds. We know, however, that carbon typically forms compounds with four covalent bonds. We can

explain this apparent discrepancy by the hybridization of the 2*s* orbital and the three 2*p* orbitals on carbon to give a set of four degenerate sp^3 ("s-p-three" or "s-p-cubed") hybrid orbitals, each with a single electron:

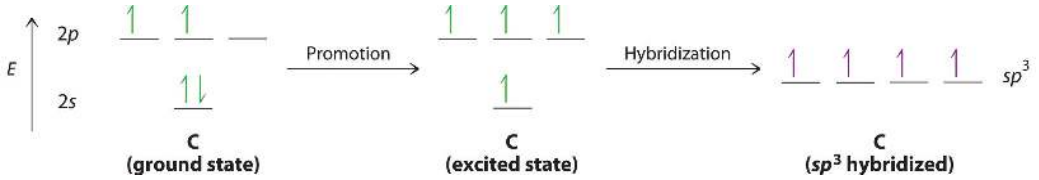


Figure **4.5.6**). Like all the hybridized orbitals discussed earlier, the sp^3 hybrid atomic orbitals are predicted to be equal in energy. Thus, methane (CH_4) is a tetrahedral molecule with four equivalent C-H bonds.

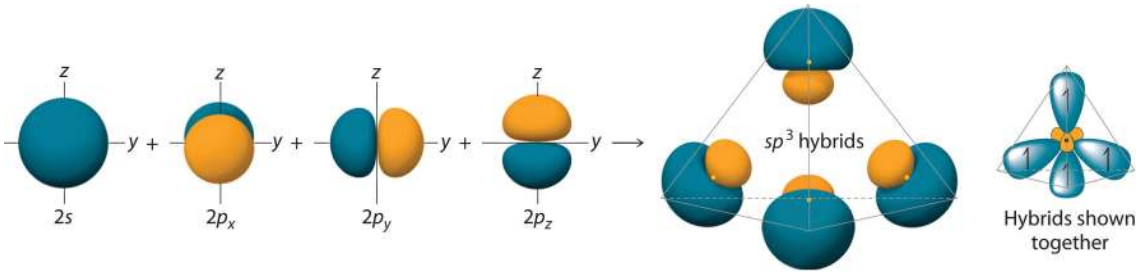


Figure **4.5.6**: Formation of sp^3 Hybrid Orbitals. Combining one *ns* and three *np* atomic orbitals results in four sp^3 hybrid orbitals oriented at 109.5° to one another in a tetrahedral arrangement.

In addition to explaining why some elements form more bonds than would be expected based on their valence electron configurations, and why the bonds formed are equal in energy, valence bond theory explains why these compounds are so stable: the amount of energy released increases with the number of bonds formed. In the case of carbon, for example, much more energy is released in the formation of four bonds than two, so compounds of carbon with four bonds tend to be more stable than those with only two. Carbon does form compounds with only two covalent bonds (such as CH_2 or CF_2), but these species are highly reactive, unstable intermediates that only form in certain chemical reactions.

> *Valence bond theory explains the number of bonds formed in a compound and the relative bond strengths.*

The bonding in molecules such as NH_3 or H_2O, which have lone pairs on the central atom, can also be described in terms of hybrid atomic orbitals. In NH_3, for example, N, with a $2s^2 2p^3$ valence electron configuration, can hybridize its 2*s* and 2*p* orbitals to produce four sp^3 hybrid orbitals. Placing five valence electrons in the four hybrid orbitals, we obtain three that are singly occupied and one with a pair of electrons:



The three singly occupied sp^3 lobes can form bonds with three H atoms, while the fourth orbital accommodates the lone pair of electrons. Similarly, H_2O has an sp^3 hybridized oxygen atom that uses two singly occupied sp^3 lobes to bond to two H atoms, and two to accommodate the two lone pairs predicted by the VSEPR model. Such descriptions explain the approximately tetrahedral distribution of electron pairs on the central atom in NH_3 and H_2O. Unfortunately, however, recent experimental evidence indicates that in NH_3 and H_2O, the hybridized orbitals are *not* entirely equivalent in energy, making this bonding model an active area of research.



EXAMPLE 4.5.1

Use the VSEPR model to predict the number of electron pairs and molecular geometry in each compound and then describe the hybridization and bonding of all atoms except hydrogen.

a. H_2S
b. $CHCl_3$

Given: two chemical compounds

Asked for: number of electron pairs and molecular geometry, hybridization, and bonding

Strategy:

A. Using the VSEPR approach to determine the number of electron pairs and the molecular geometry of the molecule.
B. From the valence electron configuration of the central atom, predict the number and type of hybrid orbitals that can be produced. Fill these hybrid orbitals with the total number of valence electrons around the central atom and describe the hybridization.

Solution:

1. **A** H_2S has four electron pairs around the sulfur atom with two bonded atoms, so the VSEPR model predicts a molecular geometry that is bent, or V shaped. **B** Sulfur has a $3s^2 3p^4$ valence electron configuration with six electrons, but by hybridizing its 3*s* and 3*p* orbitals, it can produce four sp^3 hybrids. If the six valence electrons are placed in these orbitals, two have electron pairs and two are singly occupied. The two sp^3 hybrid orbitals that are singly occupied are used to form S–H bonds, whereas the other two have lone pairs of electrons. Together, the four sp^3 hybrid orbitals produce an approximately tetrahedral arrangement of electron pairs, which agrees with the molecular geometry predicted by the VSEPR model.
2. **A** The $CHCl_3$ molecule has four valence electrons around the central atom. In the VSEPR model, the carbon atom has four electron pairs, and the molecular geometry is tetrahedral. **B** Carbon has a $2s^2 2p^2$ valence electron configuration. By hybridizing its 2*s* and 2*p* orbitals, it can form four sp^3 hybridized orbitals that are equal in energy. Eight electrons around the central atom (four from C, one from H, and one from each of the three Cl atoms) fill three sp^3 hybrid orbitals to form C–Cl bonds, and one forms a C–H bond. Similarly, the Cl atoms, with seven electrons each in their 3*s* and 3*p* valence subshells, can be viewed as sp^3 hybridized. Each Cl atom uses a singly occupied sp^3 hybrid orbital to form a C–Cl bond and three hybrid orbitals to accommodate lone pairs.

EXERCISE 4.5.1

Use the VSEPR model to predict the number of electron pairs and molecular geometry in each compound and then describe the hybridization and bonding of all atoms except hydrogen.

a. the BF_4^- ion
b. hydrazine ($H_2N–NH_2$)

Answer a

B is sp^3 hybridized; F is also sp^3 hybridized so it can accommodate one B–F bond and three lone pairs. The molecular geometry is tetrahedral.

Answer b

Each N atom is sp^3 hybridized and uses one sp^3 hybrid orbital to form the N–N bond, two to form N–H bonds, and one to accommodate a lone pair. The molecular geometry about each N is trigonal pyramidal.

The number of hybrid orbitals used by the central atom is the same as the number of electron pairs around the central atom.

4.5.2 HYBRIDIZATION USING D ORBITALS

Hybridization is not restricted to the *ns* and *np* atomic orbitals. The bonding in compounds with central atoms in the period 3 and below can also be described using hybrid atomic orbitals. In these cases, the central atom can use its valence $(n - 1)d$ orbitals as well as its *ns* and *np* orbitals to form hybrid atomic orbitals, which allows it to accommodate five or more bonded atoms (as in PF_5 and SF_6). Using the *ns* orbital, all three *np* orbitals, and one $(n - 1)d$ orbital gives a set of five sp^3d hybrid orbitals that point toward the vertices of a trigonal bipyramid (part (a) in Figure **4.5.7**). In this case, the five hybrid orbitals are *not* all equivalent: three form a triangular array oriented at 120° angles, and the other two are oriented at 90° to the first three and at 180° to each other.

Similarly, the combination of the *ns* orbital, all three *np* orbitals, and *two nd* orbitals gives a set of six equivalent sp^3d^2 hybrid orbitals oriented toward the vertices of an octahedron (part (b) in Figure 9.5.6). In the VSEPR model, PF_5 and SF_6 are predicted to be trigonal bipyramidal and octahedral, respectively, which agrees with a valence bond description in which sp^3d or sp^3d^2 hybrid orbitals are used for bonding.

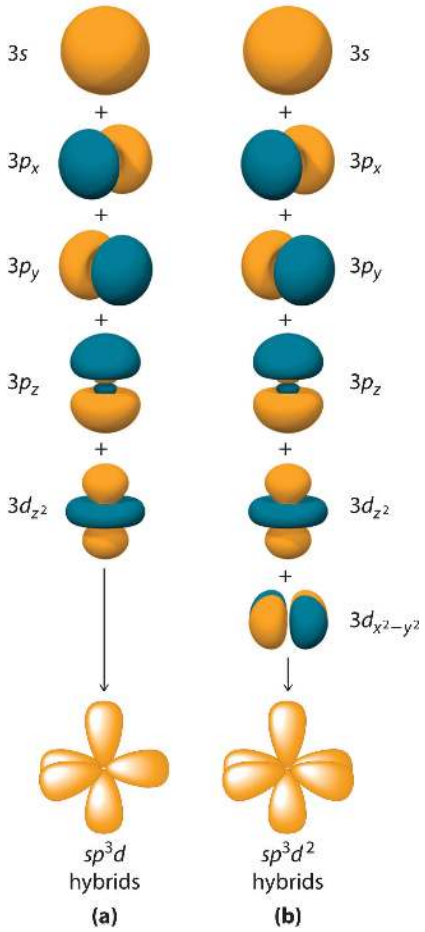


Figure **4.5.7**: Hybrid Orbitals Involving *d* Orbitals. The formation of a set of (a) five sp^3d hybrid orbitals and (b) six sp^3d^2 hybrid orbitals from *ns*, *np*, and *nd* atomic orbitals where $n = 4$.

✔ EXAMPLE 4.5.2

What is the hybridization of the central atom in each species? Describe the bonding in each species.

a. XeF_4
b. SO_4^{2-}
c. SF_4

Given: three chemical species

Asked for: hybridization of the central atom

Strategy:

A. Determine the geometry of the molecule using the strategy in Example **4.5.1**. From the valence electron configuration of the central atom and the number of electron pairs, determine the hybridization.

B. Place the total number of electrons around the central atom in the hybrid orbitals and describe the bonding.

Solution:

a. **A** Using the VSEPR model, we find that Xe in XeF_4 forms four bonds and has two lone pairs, so its structure is square planar and it has six electron pairs. The six electron pairs form an octahedral arrangement, so the Xe must be sp^3d^2 hybridized. **B** With 12 electrons around Xe, four of the six sp^3d^2 hybrid orbitals form Xe–F bonds, and two are occupied by lone pairs of electrons.

b. **A** The S in the SO_4^{2-} ion has four electron pairs and has four bonded atoms, so the structure is tetrahedral. The sulfur must be sp^3 hybridized to generate four S–O bonds. **B** Filling the sp^3 hybrid orbitals with eight electrons from four bonds produces four filled sp^3 hybrid orbitals.

c. **A** The S atom in SF_4 contains five electron pairs and four bonded atoms. The molecule has a seesaw structure with one lone pair:



To accommodate five electron pairs, the sulfur atom must be sp^3d hybridized. **B** Filling these orbitals with 10 electrons gives four sp^3d hybrid orbitals forming S–F bonds and one with a lone pair of electrons.

? EXERCISE 4.5.2

What is the hybridization of the central atom in each species? Describe the bonding.

a. PCl_4^+

b. BrF_3

c. SiF_6^{2-}

Answer a

sp^3 with four P–Cl bonds

Answer a

sp^3d with three Br–F bonds and two lone pairs

Answer a

sp^3d^2 with six Si–F bonds

Hybridization using *d* orbitals allows chemists to explain the structures and properties of many molecules and ions. Like most such models, however, it is not universally accepted. Nonetheless, it does explain a fundamental difference between the chemistry of the elements in the period 2 (C, N, and O) and those in period 3 and below (such as Si, P, and S).

Period 2 elements do not form compounds in which the central atom is covalently bonded to five or more atoms, although such compounds are common for the heavier elements. Thus whereas carbon and silicon both form tetrafluorides (CF_4 and SiF_4), only SiF_4 reacts with F^- to give a stable hexafluoro dianion, SiF_6^{2-}. Because there are no 2*d* atomic orbitals, the formation of octahedral CF_6^{2-} would require hybrid orbitals created from 2*s*, 2*p*, and 3*d* atomic orbitals. The 3*d* orbitals of carbon are so high in energy that the amount of energy needed to form a set of sp^3d^2 hybrid orbitals cannot be equaled by the energy released in the formation of two additional C–F bonds. These additional bonds are expected to be weak because the carbon atom (and other atoms in period 2) is so small that it cannot accommodate five or six F atoms at normal C–F bond lengths due to repulsions between electrons on adjacent fluorine atoms. Perhaps not surprisingly, then, species such as CF_6^{2-} have never been prepared.



EXAMPLE 4.5.3: OF_4

What is the hybridization of the oxygen atom in OF_4? Is OF_4 likely to exist?

Given: chemical compound

Asked for: hybridization and stability

Strategy:

A. Predict the geometry of OF_4 using the VSEPR model.

B. From the number of electron pairs around O in OF_4, predict the hybridization of O. Compare the number of hybrid orbitals with the number of electron pairs to decide whether the molecule is likely to exist.

Solution:

A The VSEPR model predicts that OF_4 will have five electron pairs, resulting in a trigonal bipyramidal geometry with four bonding pairs and one lone pair. **B** To accommodate five electron pairs, the O atom would have to be sp^3d hybridized. The only *d* orbital available for forming a set of sp^3d hybrid orbitals is a 3*d* orbital, which is *much* higher in energy than the 2*s* and 2*p* valence orbitals of oxygen. As a result, the OF_4 molecule is unlikely to exist. In fact, it has not been detected.

EXERCISE 4.5.3

What is the hybridization of the boron atom in BF_6^{3-}? Is this ion likely to exist?

Answer a

sp^3d^2 hybridization; no

4.5.3 SUMMARY

Hybridization increases the overlap of bonding orbitals and explains the molecular geometries of many species whose geometry cannot be explained using a VSEPR approach. The *localized bonding* model (called **valence bond theory**) assumes that covalent bonds are formed when atomic orbitals overlap and that the strength of a covalent bond is proportional to the amount of overlap. It also assumes that atoms use combinations of atomic orbitals (*hybrids*) to maximize the overlap with adjacent atoms. The formation of **hybrid atomic orbitals** can be viewed as occurring via **promotion** of an electron from a filled ns^2 subshell to an empty *np* or $(n - 1)d$ valence orbital, followed by **hybridization**, the combination of the orbitals to give a new set of (usually) equivalent orbitals that are oriented properly to form bonds. The combination of an *ns* and an *np* orbital gives rise to two equivalent **sp hybrids** oriented at 180°, whereas the combination of an *ns* and two or three *np* orbitals produces three equivalent sp^2 **hybrids** or four equivalent sp^3 **hybrids**, respectively. The bonding in molecules with more than an octet of electrons around a central atom can be explained by invoking the participation of one or two $(n - 1)d$ orbitals to give sets of five sp^3d or six sp^3d^2 **hybrid** orbitals, capable of forming five or six bonds, respectively. The spatial orientation of the hybrid atomic orbitals is consistent with the geometries predicted using the VSEPR model.

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4.6: MULTIPLE BONDS

LEARNING OBJECTIVES

- To explain resonance structures using molecular orbitals.

So far in our valence bond orbital descriptions we have not dealt with polyatomic systems with multiple bonds. To do so, we can use an approach in which we describe σ bonding using localized electron-pair bonds formed by hybrid atomic orbitals, and π bonding using **molecular orbitals** formed by unhybridized *np* atomic orbitals.

4.6.1 MULTIPLE BONDING

We begin our discussion by considering the bonding in ethylene (C_2H_4). Experimentally, we know that the H–C–H and H–C–C angles in ethylene are approximately 120°. This angle suggests that the carbon atoms are sp^2 hybridized, which means that a singly occupied sp^2 orbital on one carbon overlaps with a singly occupied *s* orbital on each H and a singly occupied sp^2 lobe on the other C. The sp^2 hybridization can be represented as follows:

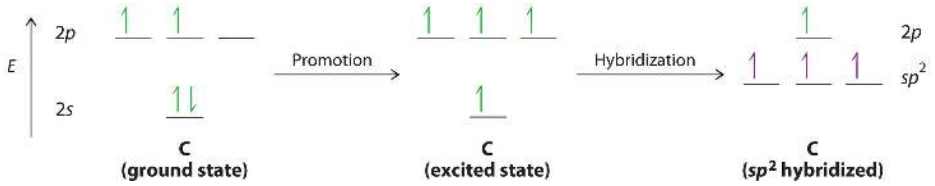


Figure **4.6.1**). These two singly occupied $2p_z$ orbitals can overlap in a side-to-side fashion to form a π bond. The orbitals overlap both above and below the plane of the molecule but form just one bonding orbital space. The C–C π bond plus the hybridized C–C σ bond together form a double bond.

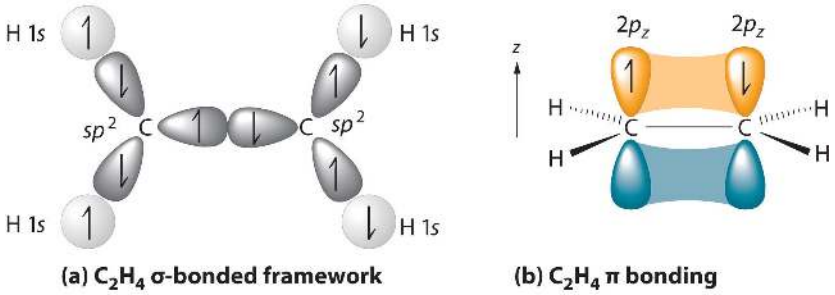
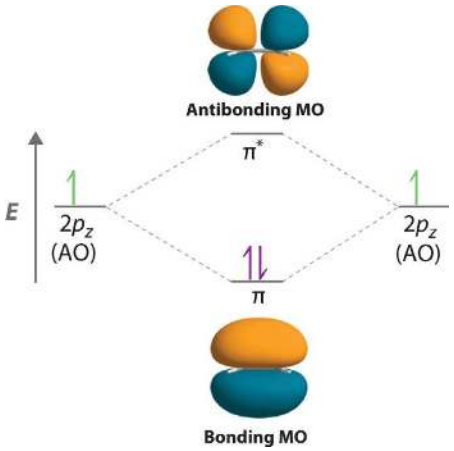


Figure **4.6.1**: Bonding in Ethylene. (a) The σ-bonded framework is formed by the overlap of two sets of singly occupied carbon sp^2 hybrid orbitals and four singly occupied hydrogen 1*s* orbitals to form electron-pair bonds. This uses 10 of the 12 valence electrons to form a total of five σ bonds (four C–H bonds and one C–C bond). (b) One singly occupied unhybridized $2p_z$ orbital remains on each carbon atom to form a carbon–carbon π bond. (Note: by convention, in planar molecules the axis perpendicular to the molecular plane is the *z*-axis.)

When considering multiple bonds, we can introduce the more sophisticated **molecular orbital theory** to better understand how orbital overlap creates bonding orbitals. Recall that atomic orbitals represent *electron wavefunctions*; this implies that "orbital overlap" actually involves the combination of those wavefunctions, which can occur via both constructive and destructive interference. Thus, when the two singly occupied $2p_z$ orbitals in ethylene overlap, they actually create both a π bonding orbital (constructive combination) and a π^* antibonding orbital (destructive combination), which produces the energy-level diagram shown in Figure **4.6.2**. With the formation of a π bonding orbital, electron density increases in the plane between the carbon nuclei. Electrons occupying this orbital lower the potential energy of the combination and tend to hold the two nuclei together (i.e., they form a bond.) The π^* orbital lies outside the internuclear region and has a nodal plane perpendicular to the internuclear axis; electrons in this orbital would tend to push the nuclei apart, so it is called an antibonding orbital. Because each $2p_z$ orbital has a single electron, there are only two electrons, enough to fill only the bonding (π) level, leaving the π^* orbital empty. Consequently, the C–C bond in ethylene consists of a σ bond and a π bond, which together give a C=C double bond. Our model is supported by the facts that the measured carbon–carbon bond is shorter than that in ethane (133.9 pm versus 153.5 pm) and the bond is stronger (728 kJ/mol versus 376 kJ/mol in ethane). The two CH_2 fragments are coplanar, which maximizes the overlap of the two singly occupied $2p_z$ orbitals.



IFigure **4.6.2**: Molecular Orbital Energy-Level Diagram for π Bonding in Ethylene. As in the diatomic molecules discussed previously, the singly occupied $2p_z$ orbitals in ethylene can overlap to form a bonding/antibonding pair of π molecular orbitals. The two electrons remaining are enough to fill only the bonding π orbital. With one σ bond plus one π bond, the carbon–carbon bond order in ethylene is 2.

Triple bonds, as in acetylene (C_2H_2), can also be explained using a combination of hybrid atomic orbitals and molecular orbitals. The four atoms of acetylene are collinear, which suggests that each carbon is *sp* hybridized. If one *sp* lobe on each carbon atom is used to form a C–C σ bond and one is used to form the C–H σ bond, then each carbon will still have two unhybridized 2*p* orbitals (a $2p_{x,y}$ pair), each with one electron (part (a) in Figure **4.6.3**).

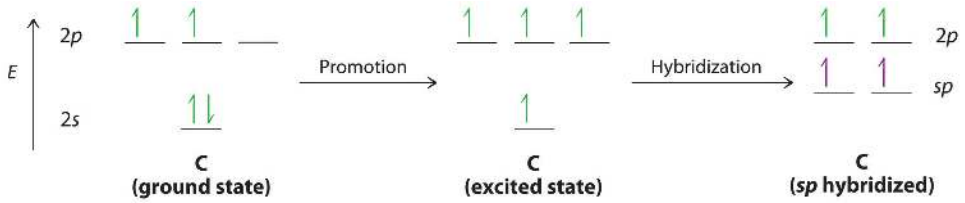


Figure **4.6.2**). Because each of the unhybridized 2*p* orbitals has a single electron, four electrons are available for π bonding, which is enough to occupy only the bonding molecular orbitals. Acetylene must therefore have a carbon–carbon triple bond, which consists of a C–C σ bond and two mutually perpendicular π bonds. Acetylene does in fact have a shorter carbon–carbon bond (120.3 pm) and a higher bond energy (965 kJ/mol) than ethane and ethylene, as we would expect for a triple bond.

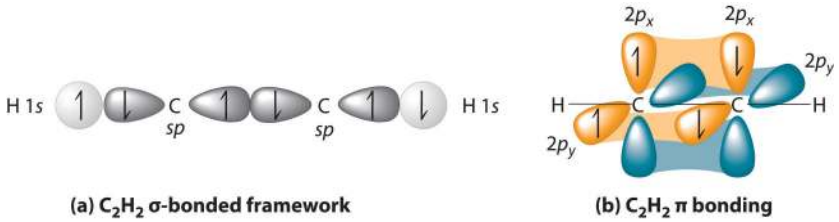


Figure **4.6.3**: Bonding in Acetylene (a) In the formation of the σ-bonded framework, two sets of singly occupied carbon *sp* hybrid orbitals and two singly occupied hydrogen 1*s* orbitals overlap. (b) In the formation of two carbon–carbon π bonds in acetylene, two singly occupied unhybridized $2p_{x,y}$ orbitals on each carbon atom overlap. With one σ bond plus two π bonds, the carbon–carbon bond order in acetylene is 3.

In complex molecules, *hybrid orbitals* and *valence bond theory* can be used to describe σ bonding, and unhybridized π orbitals and *molecular orbital theory* can be used to describe π bonding.

✔ EXAMPLE 4.6.1

Describe the bonding in HCN using a combination of hybrid atomic orbitals and molecular orbitals. The HCN molecule is linear.

Given: chemical compound and molecular geometry

Asked for: bonding description using hybrid atomic orbitals and molecular orbitals

Strategy:

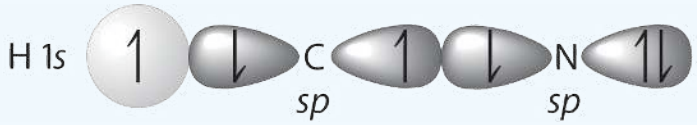
A. From the geometry given, predict the hybridization in HCN. Use the hybrid orbitals to form the σ-bonded framework of the molecule and determine the number of valence electrons that are used for σ bonding.

B. Determine the number of remaining valence electrons. Use any remaining unhybridized *p* orbitals to form π and π^* orbitals.

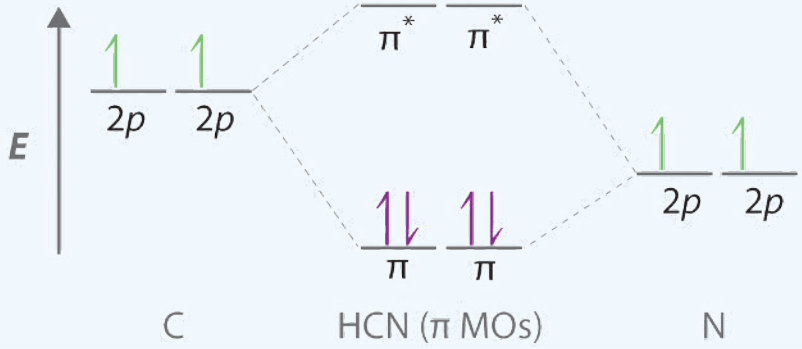
C. Fill the orbitals with the remaining electrons in order of increasing energy. Describe the bonding in HCN.

Solution:

A Because HCN is a linear molecule, it is likely that the bonding can be described in terms of *sp* hybridization at carbon. Because the nitrogen atom can also be described as *sp* hybridized, we can use one *sp* hybrid on each atom to form a C–N σ bond. This leaves one *sp* hybrid on each atom to either bond to hydrogen (C) or hold a lone pair of electrons (N). Of 10 valence electrons (5 from N, 4 from C, and 1 from H), 4 are used for σ bonding:



B We are now left with 2 electrons on N (5 valence electrons minus 1 bonding electron minus 2 electrons in the lone pair) and 2 electrons on C (4 valence electrons minus 2 bonding electrons). We have two unhybridized 2*p* atomic orbitals left on carbon and two on nitrogen, each occupied by a single electron. These four 2*p* atomic orbitals can be combined to give four molecular orbitals: two π (bonding) orbitals and two π* (antibonding) orbitals. **C** With 4 electrons available, only the π orbitals are filled. The overall result is a triple bond (1 σ and 2 π) between C and N.



EXERCISE 4.6.1

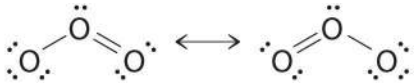
Describe the bonding in formaldehyde ($H_2C{=}O$), a trigonal planar molecule, using a combination of hybrid atomic orbitals and molecular orbitals.

Answer

- σ-bonding framework: Carbon and oxygen are sp^2 hybridized. Two sp^2 hybrid orbitals on oxygen have lone pairs, two sp^2 hybrid orbitals on carbon form C–H bonds, and one sp^2 hybrid orbital on C and O forms a C–O σ bond.
- π bonding: Unhybridized, singly occupied 2*p* atomic orbitals on carbon and oxygen interact to form π (bonding) and π* (antibonding) molecular orbitals. With two electrons, only the π (bonding) orbital is occupied.

4.6.2 MOLECULAR ORBITALS AND RESONANCE STRUCTURES

Resonance structures can be used to describe the bonding in molecules such as ozone (O_3) and the nitrite ion (NO_2^-). Ozone can be represented by either of these Lewis electron structures:



Although the VSEPR model correctly predicts that both species are bent, it gives no information about their bond orders.

Experimental evidence indicates that ozone has a bond angle of 117.5°. Because this angle is close to 120°, it is likely that the central oxygen atom in ozone is trigonal planar and sp^2 hybridized. If we assume that the terminal oxygen atoms are also sp^2 hybridized, then we obtain the σ-bonded framework shown in Figure **4.6.4**. Two of the three sp^2 lobes on the central O are used to form O–O sigma bonds, and the third has a lone pair of electrons. Each terminal oxygen atom has two lone pairs of electrons that are also in sp^2 lobes. In addition, each oxygen atom has one unhybridized 2*p* orbital perpendicular to the molecular plane. The σ bonds and lone pairs account for a total of 14 electrons (five lone pairs and two σ bonds, each containing 2 electrons). Each oxygen atom in ozone has 6 valence electrons, so O_3 has a total of 18 valence electrons. Subtracting 14 electrons from the total gives us 4 electrons that must occupy the three unhybridized 2*p* orbitals.

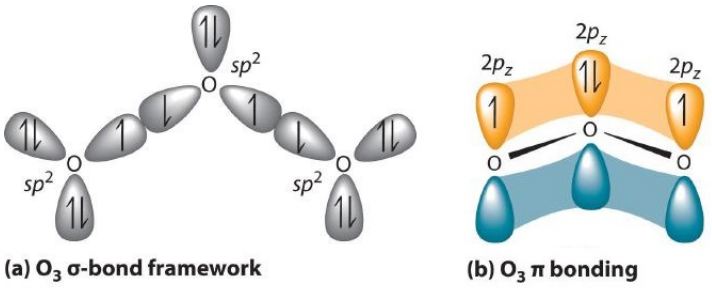


Figure 4.6.4: Bonding in Ozone. (a) In the formation of the σ-bonded framework, three sets of oxygen sp^2 hybrid orbitals overlap to give two O–O σ bonds and five lone pairs, two on each terminal O and one on the central O. The σ bonds and lone pairs account for 14 of the 18 valence electrons of O_3. (b) One unhybridized $2p_z$ orbital remains on each oxygen atom that is available for π bonding. The unhybridized $2p_z$ orbital on each terminal O atom has a single electron, whereas the unhybridized $2p_z$ orbital on the central O atom has 2 electrons.

With a molecular orbital approach to describe the π bonding, three $2p$ atomic orbitals give us three molecular orbitals, as shown in Figure 4.6.5. One of the molecular orbitals is a π bonding molecular orbital, which is shown as a banana-shaped region of electron density above and below the molecular plane. This region has *no* nodes perpendicular to the O_3 plane. The molecular orbital with the highest energy has two nodes that bisect the O–O σ bonds; it is a π^* antibonding orbital. The third molecular orbital contains a single node that is perpendicular to the O_3 plane and passes through the central O atom; because the orbital nodes do not directly touch, this is a *nonbonding* molecular orbital. Because electrons in nonbonding orbitals are neither bonding nor antibonding, they are ignored in calculating bond orders.

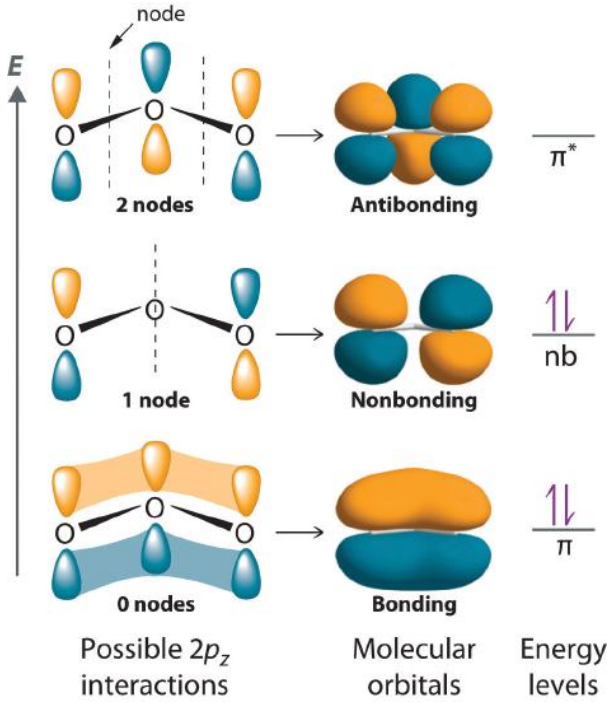


Figure 4.6.5: π Bonding in Ozone. The three unhybridized $2p_z$ atomic orbitals interact with one another to form three molecular orbitals: one π bonding orbital at lower energy, one π^* antibonding orbital at higher energy, and a nonbonding orbital in between. Placing four electrons in this diagram fills the bonding and nonbonding orbitals. With one filled π bonding orbital holding three atoms together, the net π bond order is ½ per O–O bond. The combined σ/π bond order is thus 1 ½) for each O–O bond.

We can now place the remaining four electrons in the three energy levels shown in Figure 4.6.5, thereby filling the π bonding and the nonbonding levels. The result is a single π bond holding three oxygen atoms together, or ½π bond per O–O. We therefore predict the overall O–O bond order to be ½π bond plus 1 σ bond), just as predicted using resonance structures. The molecular orbital description, however, makes it more clear that resonance really means that electrons are *delocalized* over all three atoms at once. The molecular orbital approach also shows that the π nonbonding orbital is localized on the terminal O atoms, which suggests that they are more electron rich than the central O atom (corresponding to the "extra" lone pair seen on one of the terminal O atoms in the Lewis resonance structures). The reactivity of ozone is consistent with the predicted charge localization.

> *Resonance structures are a crude way of describing molecular orbitals that extend over more than two atoms.*

EXAMPLE 4.6.2

Describe the bonding in the nitrite ion in terms of a combination of hybrid atomic orbitals and molecular orbitals. Lewis dot structures and the VSEPR model predict that the NO_2^- ion is bent.

Given: chemical species and molecular geometry

Asked for: bonding description using hybrid atomic orbitals and molecular orbitals

Strategy:

A. Calculate the number of valence electrons in NO_2^-. From the structure, predict the type of atomic orbital hybridization in the ion.

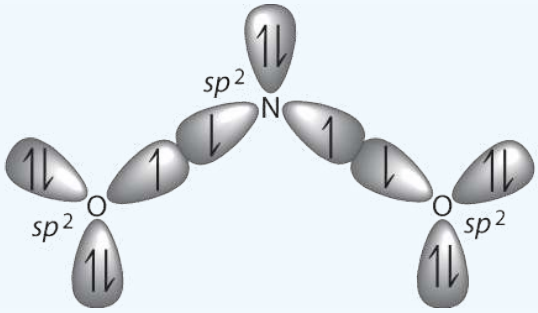
B. Predict the number and type of molecular orbitals that form during bonding. Use valence electrons to fill these orbitals and then calculate the number of electrons that remain.

C. If there are unhybridized orbitals, place the remaining electrons in these orbitals in order of increasing energy. Calculate the bond order and describe the bonding.

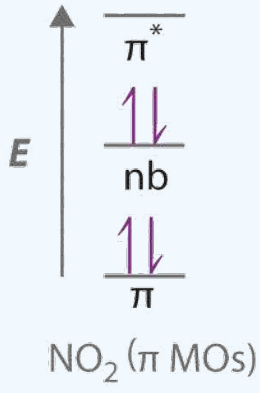
Solution:

A The lone pair of electrons on nitrogen and a bent structure suggest that the bonding in NO_2^- is similar to the bonding in ozone. This conclusion is supported by the fact that nitrite also contains 18 valence electrons (5 from N and 6 from each O, plus 1 for the −1 charge). The bent structure implies that the nitrogen is sp^2 hybridized.

B If we assume that the oxygen atoms are sp^2 hybridized as well, then we can use two sp^2 hybrid orbitals on each oxygen and one sp^2 hybrid orbital on nitrogen to accommodate the five lone pairs of electrons. Two sp^2 hybrid orbitals on nitrogen form σ bonds with the remaining sp^2 hybrid orbital on each oxygen. The σ bonds and lone pairs account for 14 electrons. We are left with three unhybridized $2p$ orbitals, one on each atom, perpendicular to the plane of the molecule, and 4 electrons. Just as with ozone, these three $2p$ orbitals interact to form bonding, nonbonding, and antibonding π molecular orbitals. The bonding molecular orbital is spread over the nitrogen and both oxygen atoms.



C Placing 4 electrons in the energy-level diagram fills both the bonding and nonbonding molecular orbitals and gives a π bond order of 1/2 per N–O bond. The overall N–O bond order is $1\frac{1}{2}$, consistent with a resonance structure.



NO_2 (π MOs)

EXERCISE 4.6.2

Describe the bonding in the formate ion (HCO_2^-), in terms of a combination of hybrid atomic orbitals and molecular orbitals.

Answer

Like nitrite, formate is a planar polyatomic ion with 18 valence electrons. The σ bonding framework can be described in terms of sp^2 hybridized carbon and oxygen, which account for 14 electrons. The three unhybridized $2p$ orbitals (on C and both O atoms) form three π molecular orbitals, and the remaining 4 electrons occupy both the bonding and nonbonding π molecular orbitals. The overall C–O bond order is therefore $\frac{3}{2}$

THE CHEMISTRY OF VISION

Hydrocarbons in which two or more carbon–carbon double bonds are directly linked by carbon–carbon single bonds (called *conjugated* structures) are generally more stable than expected because of resonance. Because the double bonds are close enough to interact electronically with one another, the π electrons are shared over all the carbon atoms, as illustrated for 1,3-butadiene in Figure 4.6.6. As the number of interacting atomic orbitals increases, the number of molecular orbitals increases, the energy spacing between molecular orbitals decreases, and the systems become more stable (Figure 4.6.7). Thus as a chain of alternating double and single bonds becomes longer, the energy required to excite an electron from the highest-energy occupied (bonding) orbital to the lowest-energy unoccupied (antibonding) orbital decreases. If the chain is long enough, the amount of energy required to excite an electron corresponds to the energy of visible light. For example, vitamin A is yellow because its chain of five alternating double bonds is able to absorb violet light. Many of the colors we associate with dyes result from this same phenomenon; most dyes are organic compounds with alternating double bonds.

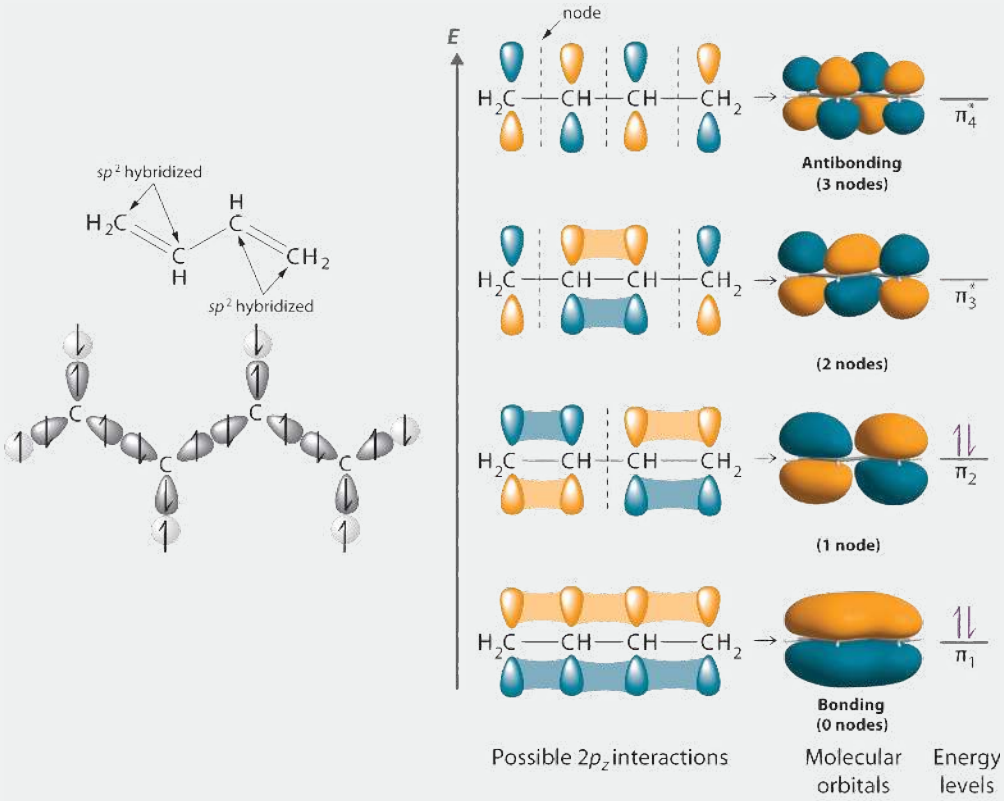


Figure 4.6.6: π Bonding in 1,3-Butadiene. (a) If each carbon atom is assumed to be sp^2 hybridized, we can construct a σ-bonded framework that accounts for the C–H and C–C single bonds, leaving *four* singly occupied $2p_z$ orbitals, one on each carbon atom. (b) As in ozone, these orbitals can interact, in this case to form *four* molecular orbitals. The molecular orbital at lowest energy is a bonding orbital with 0 nodes, the one at highest energy is antibonding with 3 nodes, and the two in the middle have 1 node and 2 nodes and are somewhere between bonding or antibonding and nonbonding, respectively. The energy of the molecular orbital increases with the number of nodes. With four electrons, only the two bonding orbitals are filled, consistent with the presence of two π bonds.

As the number of atomic orbitals increases, the difference in energy between the resulting molecular orbital energy levels decreases, which allows light of lower energy to be absorbed. As a result, organic compounds with long chains of carbon atoms and alternating single and double bonds tend to become more deeply colored as the number of double bonds increases.

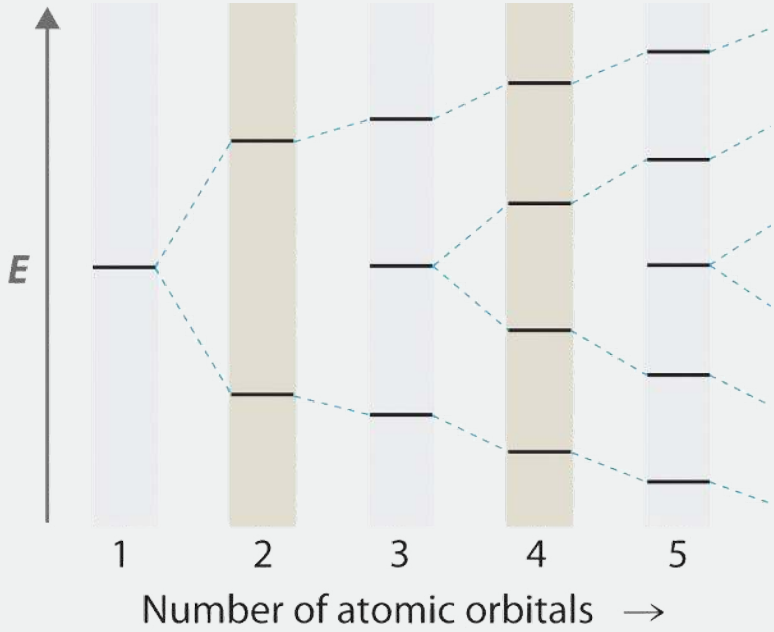


Figure **4.6.7**: Molecular Orbital Energy-Level Diagrams for a Chain of *n* Like Orbitals That Interact ($n \leq 5$).

> As the number of interacting atomic orbitals increases, the energy separation between the resulting molecular orbitals steadily decreases.

A derivative of vitamin A called *retinal* is used by the human eye to detect light and has a structure with alternating C=C double bonds. When visible light strikes retinal, the energy separation between the molecular orbitals is sufficiently close that the energy absorbed corresponds to the energy required to change one double bond in the molecule from *cis*, where like groups are on the same side of the double bond, to *trans*, where they are on opposite sides, initiating a process that causes a signal to be sent to the brain. If this mechanism is defective, we lose our vision in dim light. Once again, a molecular orbital approach to bonding explains a process that cannot be explained using any of the other approaches we have described.

4.6.3 SUMMARY

Polyatomic systems with multiple bonds can be described using hybrid atomic orbitals for σ bonding and molecular orbitals to describe π bonding. To describe the bonding in more complex molecules with multiple bonds, we can use an approach that uses hybrid atomic orbitals to describe the σ bonding and molecular orbitals to describe the π bonding. In this approach, unhybridized *np* orbitals on atoms bonded to one another are allowed to interact to produce bonding, antibonding, or nonbonding combinations. For π bonds between two atoms (as in ethylene or acetylene), the resulting molecular orbitals are virtually identical to the π molecular orbitals in diatomic molecules such as O_2 and N_2. Applying the same approach to π bonding between three or four atoms requires combining three or four unhybridized *np* orbitals on adjacent atoms to generate π bonding, antibonding, and nonbonding molecular orbitals extending over all of the atoms. Filling the resulting energy-level diagram with the appropriate number of electrons explains the bonding in molecules or ions that previously required the use of resonance structures in the Lewis electron-pair approach.

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4.7: MOLECULAR ORBITALS (SUPPLEMENTARY)

LEARNING OBJECTIVES

- To use molecular orbital theory to predict bond order

None of the approaches we have described so far can adequately explain why some compounds are colored and others are not, why some substances with unpaired electrons are stable, and why others are effective semiconductors. These approaches also cannot describe the nature of resonance. Such limitations led to the development of a new approach to bonding in which electrons are *not* viewed as being localized between the nuclei of bonded atoms but are instead delocalized throughout the entire molecule. Just as with the valence bond theory, the approach we are about to discuss is based on a quantum mechanical model.

Previously, we described the electrons in isolated atoms as having certain spatial distributions, called *orbitals*, each with a particular *orbital energy*. Just as the positions and energies of electrons in *atoms* can be described in terms of *atomic orbitals* (AOs), the positions and energies of electrons in *molecules* can be described in terms of molecular orbitals (MOs) A particular spatial distribution of electrons in a molecule that is associated with a particular orbital energy.—a spatial distribution of electrons *in a molecule* that is associated with a particular orbital energy. As the name suggests, molecular orbitals are not localized on a single atom but extend over the entire molecule. Consequently, the molecular orbital approach, called molecular orbital theory is a *delocalized* approach to bonding.

4.7.1 MOLECULAR ORBITAL THEORY: A DELOCALIZED BONDING APPROACH

Although the molecular orbital theory is computationally demanding, the principles on which it is based are similar to those we used to determine electron configurations for atoms. The key difference is that in molecular orbitals, the electrons are allowed to interact with more than one atomic nucleus at a time. Just as with atomic orbitals, we create an energy-level diagram by listing the molecular orbitals in order of increasing energy. We then fill the orbitals with the required number of valence electrons according to the Pauli principle. This means that each molecular orbital can accommodate a maximum of two electrons with opposite spins.

4.7.1.1 MOLECULAR ORBITALS INVOLVING ONLY *NS* ATOMIC ORBITALS

We begin our discussion of molecular orbitals with the simplest molecule, H_2, formed from two isolated hydrogen atoms, each with a $1s^1$ electron configuration. As we explained in Chapter 9, electrons can behave like waves. In the molecular orbital approach, the overlapping atomic orbitals are described by mathematical equations called *wave functions*. The 1*s* atomic orbitals on the two hydrogen atoms interact to form two new molecular orbitals, one produced by taking the *sum* of the two H 1*s* wave functions, and the other produced by taking their *difference*:

$$\begin{aligned} MO(1) = \ & AO(atom\ A) + AO(atom B) \\ MO(1) = \ & AO(atom\ A) - AO(atom B) \end{aligned} \tag{4.7.1}$$

The molecular orbitals created from Equation 4.7.1 are called linear combinations of atomic orbitals (LCAOs) Molecular orbitals created from the sum and the difference of two wave functions (atomic orbitals). A molecule must have as many molecular orbitals as there are atomic orbitals.

> *A molecule must have as many molecular orbitals as there are atomic orbitals.*

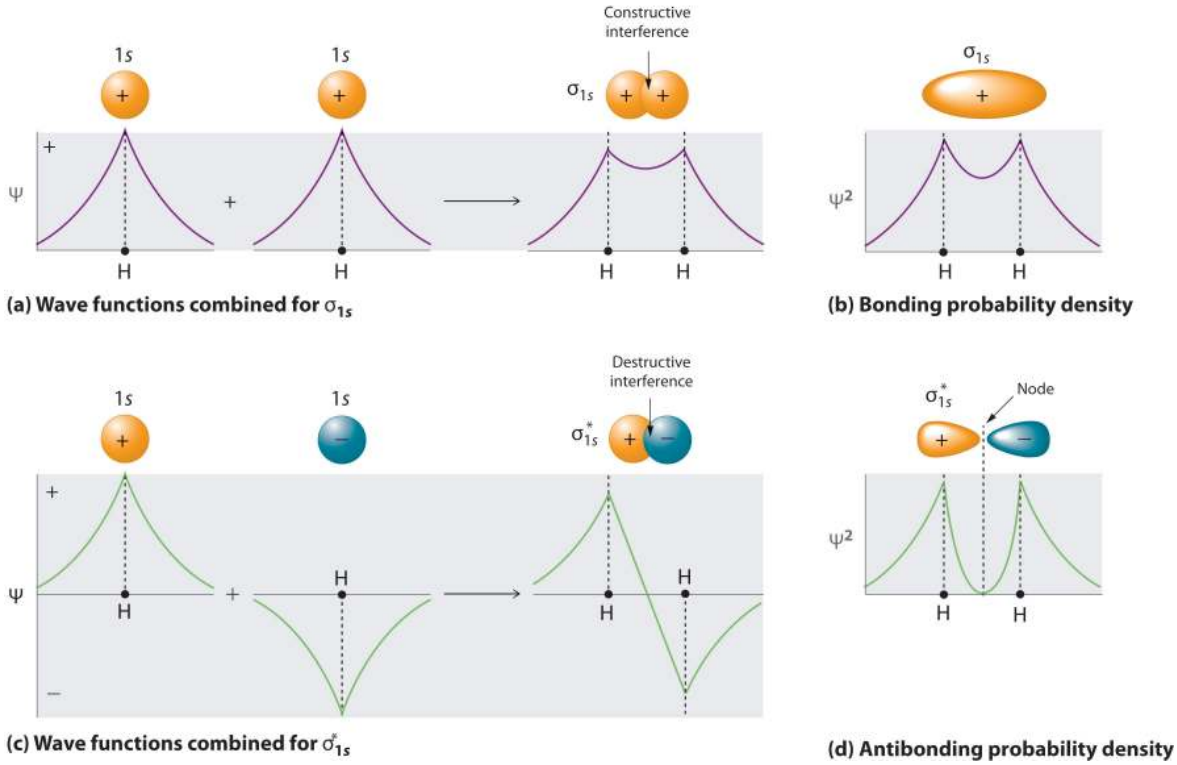


Figure 4.7.1: Molecular Orbitals for the H_2 Molecule. (a) This diagram shows the formation of a bonding σ_{1s} molecular orbital for H_2 as the sum of the wave functions (Ψ) of two H 1*s* atomic orbitals. (b) This plot of the square of the wave function (Ψ^2) for the bonding σ_{1s} molecular orbital illustrates the increased electron probability density between the two hydrogen nuclei. (Recall that the probability density is proportional to the *square* of the wave function.) (c) This diagram shows the formation of an antibonding σ^*_{1s} molecular orbital for H_2 as the difference of the wave functions (Ψ) of two H 1*s* atomic orbitals. (d) This plot of the square of the wave function (Ψ^2) for the σ^*_{1s} antibonding molecular orbital illustrates the node corresponding to zero electron probability density between the two hydrogen nuclei.

Adding two atomic orbitals corresponds to *constructive* interference between two waves, thus reinforcing their intensity; the internuclear electron probability density is *increased*. The molecular orbital corresponding to the sum of the two H 1*s* orbitals is called a σ_{1s} combination (pronounced "sigma one ess") (part (a) and part (b) in Figure 4.7.1). In a sigma (σ) orbital, (i.e., a bonding molecular orbital in which the electron density along the internuclear axis and between the nuclei has cylindrical symmetry), the electron density along the internuclear axis and between the nuclei has cylindrical symmetry; that is, all cross-sections perpendicular to the internuclear axis are circles. The subscript 1*s* denotes the atomic orbitals from which the molecular orbital was derived: The ≈ sign is used rather than an = sign because we are ignoring certain constants that are not important to our argument.

$$\sigma_{1s} \approx 1s\,(A) + 1s\,(B) \tag{4.7.2}$$

Conversely, subtracting one atomic orbital from another corresponds to *destructive* interference between two waves, which reduces their intensity and causes a *decrease* in the internuclear electron probability density (part (c) and part (d) in Figure 4.7.1). The resulting pattern contains a *node* where the electron density is zero. The molecular orbital corresponding to the difference is called σ^*_{1s} ("sigma one ess star"). In a sigma star (σ*) orbital An antibonding molecular orbital in which there is a region of zero electron probability (a nodal plane) perpendicular to the internuclear axis., there is a region of zero electron probability, a nodal plane, perpendicular to the internuclear axis:

$$\sigma^*_{1s} \approx 1s\,(A) - 1s\,(B) \tag{4.7.3}$$

The electron density in the σ_{1s} molecular orbital is greatest between the two positively charged nuclei, and the resulting electron–nucleus electrostatic attractions reduce repulsions between the nuclei. Thus the σ_{1s} orbital represents a bonding molecular orbital. A molecular orbital that forms when atomic orbitals or orbital lobes with the same sign interact to give increased electron probability between the nuclei due to constructive reinforcement of the wave functions. In contrast, electrons in the σ^*_{1s} orbital are generally found in the space outside the internuclear region. Because this allows the positively charged nuclei to repel one another, the σ^*_{1s} orbital is an antibonding molecular orbital (a molecular orbital that forms when atomic orbitals or orbital lobes of opposite sign interact to give decreased electron probability between the nuclei due to destructive reinforcement of the wave functions).

> *Antibonding orbitals contain a node perpendicular to the internuclear axis; bonding orbitals do not.*

4.7.1.2 ENERGY-LEVEL DIAGRAMS

Because electrons in the σ_{1s} orbital interact simultaneously with both nuclei, they have a lower energy than electrons that interact with only one nucleus. This means that the σ_{1s} molecular orbital has a *lower* energy than either of the hydrogen 1*s* atomic orbitals. Conversely, electrons in the σ^*_{1s} orbital interact with only one hydrogen nucleus at a time. In addition, they are farther away from the nucleus than they were in the parent hydrogen 1*s* atomic orbitals. Consequently, the σ^*_{1s} molecular orbital has a *higher* energy than either of the hydrogen 1*s* atomic orbitals. The σ_{1s} (bonding) molecular orbital is *stabilized* relative to the 1*s* atomic orbitals, and the σ^*_{1s} (antibonding) molecular orbital is *destabilized*. The relative energy levels of these orbitals are shown in the energy-level diagram (a schematic drawing that compares the energies of the molecular orbitals (bonding, antibonding, and nonbonding) with the energies of the parent atomic orbitals) in Figure **4.7.2**

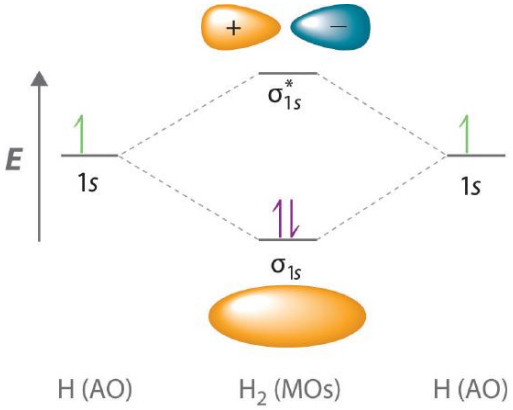


Figure **4.7.2**: Molecular Orbital Energy-Level Diagram for H_2. The two available electrons (one from each H atom) in this diagram fill the bonding σ_{1s} molecular orbital. Because the energy of the σ_{1s} molecular orbital is lower than that of the two H 1*s* atomic orbitals, the H_2 molecule is more stable (at a lower energy) than the two isolated H atoms.

> *A bonding molecular orbital is always lower in energy (more stable) than the component atomic orbitals, whereas an antibonding molecular orbital is always higher in energy (less stable).*

To describe the bonding in a homonuclear diatomic molecule (a molecule that consists of two atoms of the same element) such as H_2, we use molecular orbitals; that is, for a molecule in which two identical atoms interact, we insert the total number of valence electrons into the energy-level diagram (Figure **4.7.2**). We fill the orbitals according to the Pauli principle and Hund's rule: each orbital can accommodate a maximum of two electrons with opposite spins, and the orbitals are filled in order of increasing energy. Because each H atom contributes one valence electron, the resulting two electrons are exactly enough to fill the σ_{1s} bonding molecular orbital. The two electrons enter an orbital whose energy is lower than that of the parent atomic orbitals, so the H_2 molecule is more stable than the two isolated hydrogen atoms. Thus molecular orbital theory correctly predicts that H_2 is a stable molecule. Because bonds form when electrons are concentrated in the space between nuclei, this approach is also consistent with our earlier discussion of electron-pair bonds.

4.7.1.3 BOND ORDER IN MOLECULAR ORBITAL THEORY

In the Lewis electron structures, the number of electron pairs holding two atoms together was called the *bond order*. In the molecular orbital approach, bond order One-half the net number of bonding electrons in a molecule. is defined as one-half the *net* number of bonding electrons:

$$\textit{bond order} = \frac{\textit{number of bonding electrons} - \textit{number of antibonding electrons}}{2} \tag{4.7.4}$$

To calculate the bond order of H_2, we see from Figure **4.7.2** that the σ_{1s} (bonding) molecular orbital contains two electrons, while the σ^*_{1s} (antibonding) molecular orbital is empty. The bond order of H_2 is therefore

$$\frac{2-0}{2} = 1 \tag{4.7.5}$$

This result corresponds to the single covalent bond predicted by Lewis dot symbols. Thus molecular orbital theory and the Lewis electron-pair approach agree that a single bond containing two electrons has a bond order of 1. Double and triple bonds contain four or six electrons, respectively, and correspond to bond orders of 2 and 3. We can use energy-level diagrams such as the one in Figure **4.7.2** to describe the bonding in other pairs of atoms and ions where $n = 1$, such as the H_2^+ ion, the He_2^+ ion, and the He_2 molecule. Again, we fill the lowest-energy molecular orbitals first while being sure not to violate the Pauli principle or Hund's rule.

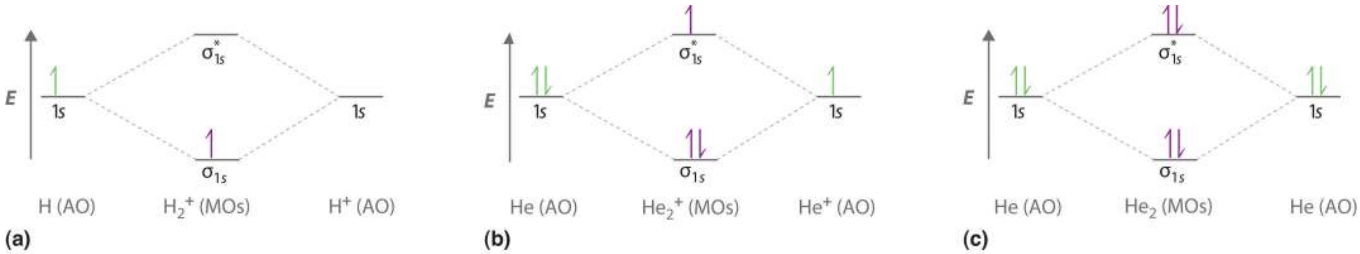


Figure **4.7.3**: Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1*s* Atomic Orbitals. (a) The H_2^+ ion, (b) the He_2^+ ion, and (c) the He_2 molecule are shown here.

for the H2+ ion the H has one unpaired electron in the 1s orbital so the H2+ has one unpaired electron in the sigmas 1 s orbital. for He2+ ion, He has a full 1 s orbital and He+ has one upaired electron in the 1 s orbital. This means that the sigmal 1s orbital is full and the sigmal*1s orbital has one upaired electron. For the He2 molecule, each He has a full 1 s orbital. This means that sigma 1s and sigma * 1s orbital are full.

Figure **4.7.3*a*** shows the energy-level diagram for the H_2^+ ion, which contains two protons and only one electron. The single electron occupies the σ_{1s} bonding molecular orbital, giving a $(\sigma_{1s})^1$ electron configuration. The number of electrons in an orbital is indicated by a superscript. In this case, the bond order is

$$\frac{1-0}{2} = 1/2$$

Because the bond order is greater than zero, the H_2^+ ion should be more stable than an isolated H atom and a proton. We can therefore use a molecular orbital energy-level diagram and the calculated bond order to predict the relative stability of species such as H_2^+. With a bond order of only 1/2 the bond in H_2^+ should be weaker than in the H_2 molecule, and the H–H bond should be longer. As shown in Table **4.7.1**, these predictions agree with the experimental data.

Figure **4.7.3*b*** is the molecular orbital energy-level diagram for He_2^+. This ion has a total of three valence electrons. Because the first two electrons completely fill the σ_{1s} molecular orbital, the Pauli principle states that the third electron must be in the σ^*_{1s} antibonding orbital, giving a $(\sigma_{1s})^2(\sigma^*_{1s})^1$ electron configuration. This electron configuration gives a bond order of

$$\frac{2-1}{2} = 1/2$$

As with H_2^+, the He_2^+ ion should be stable, but the He–He bond should be weaker and longer than in H_2. In fact, the He_2^+ ion can be prepared, and its properties are consistent with our predictions (Table **4.7.1**).

Table **4.7.1**: Molecular Orbital Electron Configurations, Bond Orders, Bond Lengths, and Bond Energies for some Simple Homonuclear Diatomic Molecules and Ions

Molecule or Ion	Electron Configuration	Bond Order	Bond Length (pm)	Bond Energy (kJ/mol)
H_2^+	$(\sigma_{1s})^1$	1/2	106	269
H_2	$(\sigma_{1s})^2$	1	74	436
He_2^+	$(\sigma_{1s})^2(\sigma^*_{1s})^1$	1/2	108	251
He_2	$(\sigma_{1s})^2(\sigma^*_{1s})^2$	0	not observed	not observed

Finally, we examine the He_2 molecule, formed from two He atoms with $1s^2$ electron configurations. Figure **4.7.3*c*** is the molecular orbital energy-level diagram for He_2. With a total of four valence electrons, both the σ_{1s} bonding and σ^*_{1s} antibonding orbitals must contain two electrons. This gives a $(\sigma_{1s})^2(\sigma^*_{1s})^2$ electron configuration, with a predicted bond order of (2 − 2) ÷ 2 = 0, which indicates that the He_2 molecule has no net bond and is not a stable species. Experiments show that the He_2 molecule is actually *less* stable than two isolated He atoms due to unfavorable electron–electron and nucleus–nucleus interactions.

In molecular orbital theory, *electrons in antibonding orbitals effectively cancel the stabilization resulting from electrons in bonding orbitals*. Consequently, any system that has equal numbers of bonding and antibonding electrons will have a bond order of 0, and it is predicted to be unstable and therefore not to exist in nature. In contrast to Lewis electron structures and the valence bond approach, molecular orbital theory is able to accommodate systems with an odd number of electrons, such as the H_2^+ ion.

> *In contrast to Lewis electron structures and the valence bond approach, molecular orbital theory can accommodate systems with an odd number of electrons.*



EXAMPLE 4.7.1

Use a molecular orbital energy-level diagram, such as those in Figure **4.7.2**, to predict the bond order in the He_2^{2+} ion. Is this a stable species?

Given: chemical species

Asked for: molecular orbital energy-level diagram, bond order, and stability

Strategy:

A. Combine the two He valence atomic orbitals to produce bonding and antibonding molecular orbital

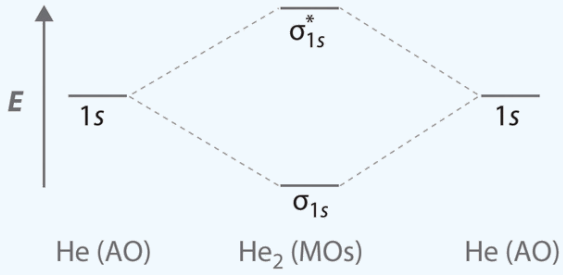
B. s. Draw the molecular orbital energy-level diagram for the system.

C. Determine the total number of valence electrons in the He_2^{2+} ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.

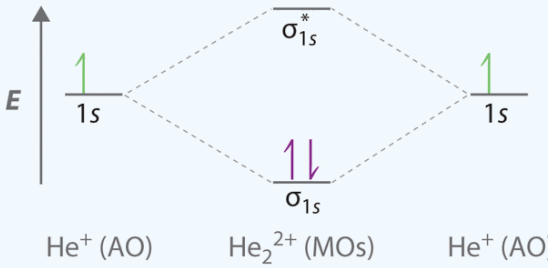
D. Calculate the bond order and predict whether the species is stable.

Solution:

A Two He 1*s* atomic orbitals combine to give two molecular orbitals: a σ_{1s} bonding orbital at lower energy than the atomic orbitals and a σ_{1s}^* antibonding orbital at higher energy. The bonding in any diatomic molecule with two He atoms can be described using the following molecular orbital diagram:



B The He_2^{2+} ion has only two valence electrons (two from each He atom minus two for the +2 charge). We can also view He_2^{2+} as being formed from two He^+ ions, each of which has a single valence electron in the 1*s* atomic orbital. We can now fill the molecular orbital diagram:



Each He+ has one unpaired electron in the 1 s orbital. This means that He2 2+ has a full sigma 1 s orbital.

The two electrons occupy the lowest-energy molecular orbital, which is the bonding (σ_{1s}) orbital, giving a $(\sigma_{1s})^2$ electron configuration. To avoid violating the Pauli principle, the electron spins must be paired. **C** So the bond order is

$$\frac{2-0}{2}=1$$

He_2^{2+} is therefore predicted to contain a single He–He bond. Thus it should be a stable species.

EXERCISE 4.7.1

Use a molecular orbital energy-level diagram to predict the valence-electron configuration and bond order of the H_2^{2-} ion. Is this a stable species?

Answer

H_2^{2-} has a valence electron configuration of $(\sigma_{1s})^2(\sigma_{1s}^*)^2$ with a bond order of 0. It is therefore predicted to be unstable.

So far, our discussion of molecular orbitals has been confined to the interaction of valence orbitals, which tend to lie farthest from the nucleus. When two atoms are close enough for their valence orbitals to overlap significantly, the filled inner electron shells are largely unperturbed; hence they do not need to be considered in a molecular orbital scheme. Also, when the inner orbitals are completely filled, they contain exactly enough electrons to completely fill both the bonding and antibonding molecular orbitals that arise from their interaction. Thus the interaction of filled shells always gives a bond order of 0, so filled shells are not a factor when predicting the stability of a species. This means that we can focus our attention on the molecular orbitals derived from valence atomic orbitals.

A molecular orbital diagram that can be applied to any **homonuclear diatomic molecule** with two identical alkali metal atoms (Li_2 and Cs_2, for example) is shown in part (a) in Figure **4.7.4**, where M represents the metal atom. Only two energy levels are important for describing the valence electron molecular orbitals of these species: a σ_{ns} bonding molecular orbital and a σ^*_{ns} antibonding molecular orbital. Because each alkali metal (M) has an ns^1 valence electron configuration, the M_2 molecule has two valence electrons that fill the σ_{ns} bonding orbital. As a result, a bond order of 1 is predicted for all homonuclear diatomic species formed from the alkali metals (Li_2, Na_2, K_2, Rb_2, and Cs_2). The general features of these M_2 diagrams are identical to the diagram for the H_2 molecule in Figure **4.7.4**. Experimentally, all are found to be stable in the gas phase, and some are even stable in solution.

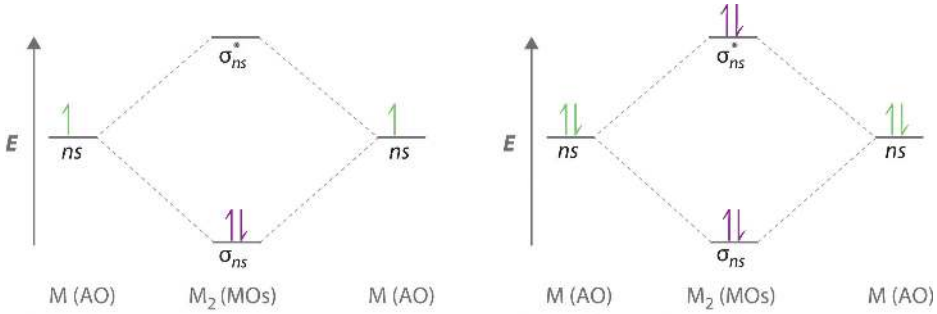


Figure **4.7.4** : Molecular Orbital Energy-Level Diagrams for Alkali Metal and Alkaline Earth Metal Diatomic (M_2) Molecules. (a) For alkali metal diatomic molecules, the two valence electrons are enough to fill the σ_{ns} (bonding) level, giving a bond order of 1. (b) For alkaline earth metal diatomic molecules, the four valence electrons fill both the σ_{ns} (bonding) and the σ_{ns}* (nonbonding) levels, leading to a predicted bond order of 0.

Similarly, the molecular orbital diagrams for homonuclear diatomic compounds of the alkaline earth metals (such as Be_2), in which each metal atom has an ns^2 valence electron configuration, resemble the diagram for the He_2 molecule in part (c) in Figure **4.7.2**. As shown in part (b) in Figure **4.7.4**, this is indeed the case. All the homonuclear alkaline earth diatomic molecules have four valence electrons, which fill both the σ_{ns} bonding orbital and the σ_{ns}* antibonding orbital and give a bond order of 0. Thus Be_2, Mg_2, Ca_2, Sr_2, and Ba_2 are all expected to be unstable, in agreement with experimental data.In the solid state, however, all the alkali metals and the alkaline earth metals exist as extended lattices held together by metallic bonding. At low temperatures, Be_2 is stable.

EXAMPLE 4.7.2

Use a qualitative molecular orbital energy-level diagram to predict the valence electron configuration, bond order, and likely existence of the Na_2^- ion.

Given: chemical species

Asked for: molecular orbital energy-level diagram, valence electron configuration, bond order, and stability

Strategy:

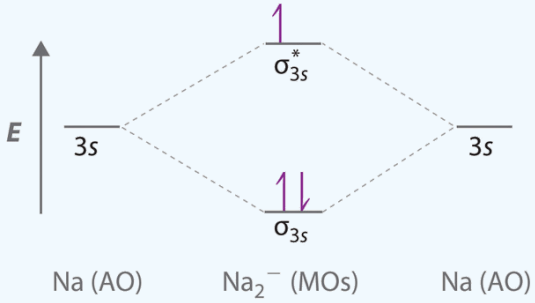
A. Combine the two sodium valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for this system.

B. Determine the total number of valence electrons in the Na_2^- ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.

C. Calculate the bond order and predict whether the species is stable.

Solution:

A Because sodium has a [Ne]$3s^1$ electron configuration, the molecular orbital energy-level diagram is qualitatively identical to the diagram for the interaction of two 1*s* atomic orbitals. **B** The Na_2^- ion has a total of three valence electrons (one from each Na atom and one for the negative charge), resulting in a filled σ_{3s} molecular orbital, a half-filled σ_{3s^*} and a $(\sigma_{3s})^2(\sigma^*_{3s})^1$ electron configuration.



C The bond order is (2-1)÷2=1/2 With a fractional bond order, we predict that the Na_2^- ion exists but is highly reactive.

EXERCISE 4.7.2

Use a qualitative molecular orbital energy-level diagram to predict the valence electron configuration, bond order, and likely existence of the Ca_2^+ ion.

Answer

Ca_2^+ has a $(\sigma_{4s})^2(\sigma^*_{4s})^1$ electron configurations and a bond order of 1/2 and should exist.

4.7.2 MOLECULAR ORBITALS FORMED FROM *NS* AND *NP* ATOMIC ORBITALS

Atomic orbitals other than *ns* orbitals can also interact to form molecular orbitals. Because individual *p*, *d*, and *f* orbitals are not spherically symmetrical, however, we need to define a coordinate system so we know which lobes are interacting in three-dimensional space. Recall that for each *np* subshell, for example, there are np_x, np_y, and np_z orbitals. All have the same energy and are therefore degenerate, but they have different spatial orientations.

$$\sigma_{np_z} = np_z(A) - np_z(B) \tag{4.7.6}$$

Just as with *ns* orbitals, we can form molecular orbitals from *np* orbitals by taking their mathematical sum and difference. When two positive lobes with the appropriate spatial orientation overlap, as illustrated for two np_z atomic orbitals in part (a) in Figure **4.7.5**, it is the mathematical *difference* of their wave functions that results in *constructive* interference, which in turn increases the electron probability density between the two atoms. The difference therefore corresponds to a molecular orbital called a σ_{np_z} *bonding molecular orbital* because, just as with the σ orbitals discussed previously, it is symmetrical about the internuclear axis (in this case, the *z*-axis):

$$\sigma_{np_z} = np_z(A) - np_z(B) \tag{4.7.7}$$

The other possible combination of the two np_z orbitals is the mathematical sum:

$$\sigma_{np_z} = np_z(A) + np_z(B) \tag{4.7.8}$$

In this combination, shown in part (b) in Figure **4.7.5**, the positive lobe of one np_z atomic orbital overlaps the negative lobe of the other, leading to *destructive* interference of the two waves and creating a node between the two atoms. Hence this is an antibonding molecular orbital. Because it, too, is symmetrical about the internuclear axis, this molecular orbital is called a $\sigma_{np_z} = np_z(A) - np_z(B)$ *antibonding molecular orbital*. Whenever orbitals combine, *the bonding combination is always lower in energy* (more stable) than the atomic orbitals from which it was derived, and *the antibonding combination is higher in energy* (less stable).

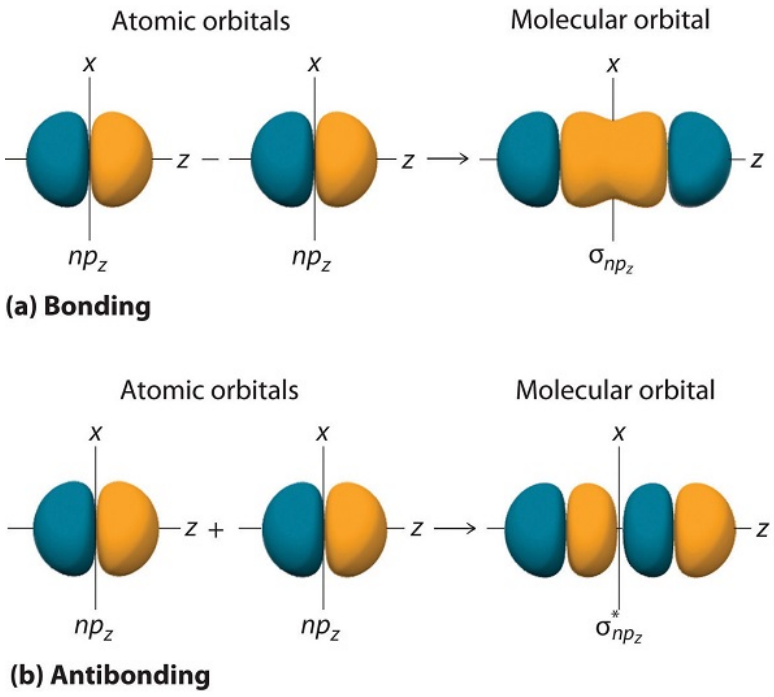


Figure **4.7.5** Formation of Molecular Orbitals from np_z Atomic Orbitals on Adjacent Atoms.(a) By convention, in a linear molecule or ion, the *z*-axis always corresponds to the internuclear axis, with +*z* to the right. As a result, the signs of the lobes of the np_z atomic orbitals on the two atoms alternate − + − +, from left to right. In this case, the σ (bonding) molecular orbital corresponds to the mathematical *difference*, in which the overlap of lobes with the same sign results in increased probability density between the nuclei. (b) In contrast, the σ* (antibonding) molecular orbital corresponds to the mathematical *sum*, in which the overlap of lobes with opposite signs results in a nodal plane of zero probability density perpendicular to the internuclear axis.

> Overlap of atomic orbital lobes with the *same sign* produces a bonding molecular orbital, regardless of whether it corresponds to the sum or the difference of the atomic orbitals.

The remaining *p* orbitals on each of the two atoms, np_x and np_y, do not point directly toward each other. Instead, they are perpendicular to the internuclear axis. If we arbitrarily label the axes as shown in Figure **4.7.6**, we see that we have two pairs of *np* orbitals: the two np_x orbitals lying in the plane of the page, and two np_y orbitals perpendicular to the plane. Although these two pairs are equivalent in energy, the np_x orbital on one atom can interact with only the np_x orbital on the other, and the np_y orbital on one atom can interact with only the np_y on the other. These interactions are side-to-side rather than the head-to-head interactions characteristic of σ orbitals. Each pair of overlapping atomic orbitals again forms two molecular orbitals: one corresponds to the arithmetic sum of the two atomic orbitals and one to the difference. The sum of these side-to-side interactions increases the electron probability in the region above and below a line connecting the nuclei, so it is a bonding molecular orbital that is called a pi (π) orbital (a bonding molecular orbital formed from the side-to-side interactions of two or more parallel np atomic orbitals). The difference results in the overlap of orbital lobes with opposite signs, which produces a nodal plane perpendicular to the internuclear axis; hence it is an antibonding molecular orbital, called a pi star (π*) orbital An antibonding molecular orbital formed from the difference of the side-to-side interactions of two or more parallel *np* atomic orbitals, creating a nodal plane perpendicular to the internuclear axis..

$$\pi_{np_z} = np_x\,(A) + np_x\,(B) \tag{4.7.9}$$

$$\pi^*_{np_z} = np_x\,(A) - np_x\,(B) \tag{4.7.10}$$

The two np_y orbitals can also combine using side-to-side interactions to produce a bonding π_{np_y} molecular orbital and an antibonding $\pi^*_{np_y}$ molecular orbital. Because the np_x and np_y atomic orbitals interact in the same way (side-to-side) and have the same energy, the π_{np_z} and π_{np_y}molecular orbitals are a degenerate pair, as are the $\pi^*_{np_z}$ and $\pi^*_{np_y}$ molecular orbitals.

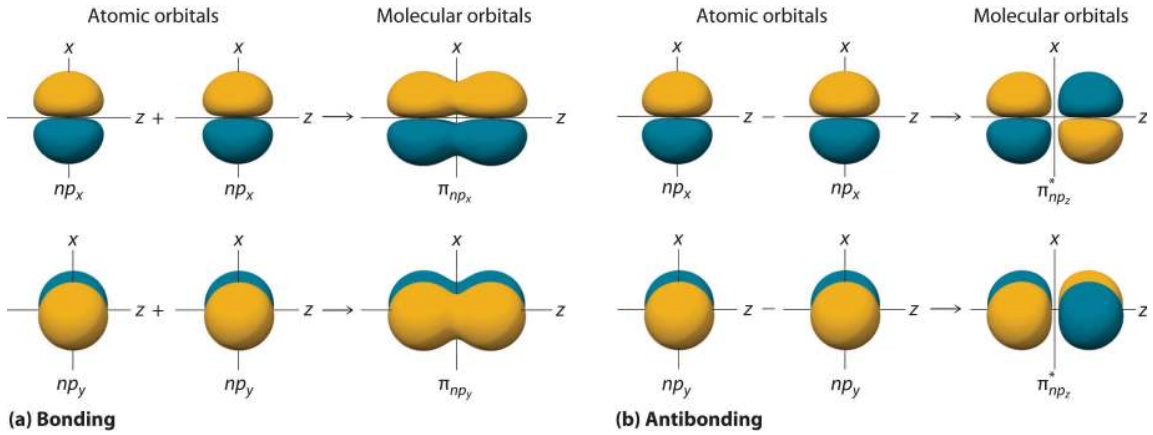


Figure **4.7.6**: Formation of π Molecular Orbitals from np_x and np_y Atomic Orbitals on Adjacent Atoms.(a) Because the signs of the lobes of both the np_x and the np_y atomic orbitals on adjacent atoms are the same, in both cases the mathematical sum corresponds to a π (bonding) molecular orbital. (b) In contrast, in both cases, the mathematical difference corresponds to a π* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis.

Figure **4.7.7** is an energy-level diagram that can be applied to two identical interacting atoms that have three *np* atomic orbitals each. There are six degenerate *p* atomic orbitals (three from each atom) that combine to form six molecular orbitals, three bonding and three antibonding. The bonding molecular orbitals are lower in energy than the atomic orbitals because of the increased stability associated with the formation of a bond. Conversely, the antibonding molecular orbitals are higher in energy, as shown. The energy difference between the σ and σ* molecular orbitals is significantly greater than the difference between the two π and π* sets. The reason for this is that the atomic orbital overlap and thus the strength of the interaction are greater for a σ bond than a π bond, which means that the σ molecular orbital is more stable (lower in energy) than the π molecular orbitals.

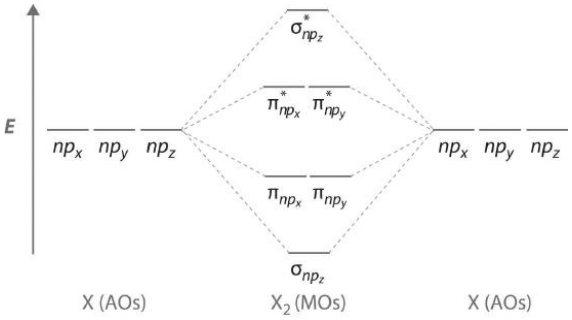


Figure **4.7.7** : The Relative Energies of the σ and π Molecular Orbitals Derived from np_x, np_y, and np_z Orbitals on Identical Adjacent Atoms. Because the two np_z orbitals point directly at each other, their orbital overlap is greater, so the difference in energy between the σ and σ* molecular orbitals is greater than the energy difference between the π and π* orbitals.

Although many combinations of atomic orbitals form molecular orbitals, we will discuss only one other interaction: an *ns* atomic orbital on one atom with an np_z atomic orbital on another. As shown in Figure **4.7.8**, the sum of the two atomic wave functions ($ns + np_z$) produces a σ bonding molecular orbital. Their difference ($ns - np_z$) produces a σ* antibonding molecular orbital, which has a nodal plane of zero probability density perpendicular to the internuclear axis.

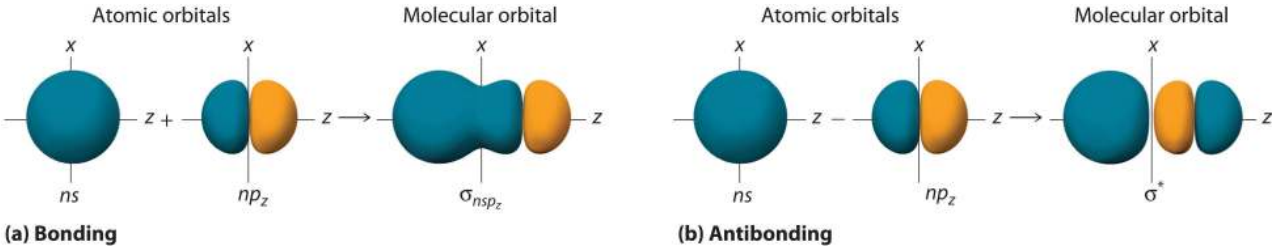


Figure **4.7.8** : Formation of Molecular Orbitals from an *ns* Atomic Orbital on One Atom and an np_z Atomic Orbital on an Adjacent Atom.(a) The mathematical sum results in a σ (bonding) molecular orbital, with increased probability density between the nuclei. (b) The mathematical difference results in a σ* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis.

4.7.3 SUMMARY

Molecular orbital theory, a delocalized approach to bonding, can often explain a compound's color, why a compound with unpaired electrons is stable, semiconductor behavior, and resonance, none of which can be explained using a localized approach. A **molecular orbital (MO)** is an allowed spatial distribution of electrons in a molecule that is associated with a particular orbital energy. Unlike an atomic orbital (AO), which is centered on a single atom, a molecular orbital extends over all the atoms in a molecule or ion. Hence the **molecular orbital theory** of bonding is a *delocalized* approach. Molecular orbitals are constructed using **linear combinations of atomic orbitals (LCAOs)**, which are usually the mathematical sums and differences of wave functions that describe overlapping atomic orbitals. Atomic orbitals interact to form three types of molecular orbitals.

A completely bonding molecular orbital contains no nodes (regions of zero electron probability) perpendicular to the internuclear axis, whereas a completely **antibonding molecular orbital** contains at least one node perpendicular to the internuclear axis. A **sigma (σ) orbital** (bonding) or a **sigma star (σ*) orbital** (antibonding) is symmetrical about the internuclear axis. Hence all cross-sections perpendicular to that axis are circular. Both a **pi (π) orbital** (bonding) and a **pi star (π*) orbital** (antibonding) possess a nodal plane that contains the nuclei, with electron density localized on both sides of the plane.

The energies of the molecular orbitals versus those of the parent atomic orbitals can be shown schematically in an **energy-level diagram**. The electron configuration of a molecule is shown by placing the correct number of electrons in the appropriate energy-level diagram, starting with the lowest-energy orbital and obeying the Pauli principle; that is, placing only two electrons with opposite spin in each orbital. From the completed energy-level diagram, we can calculate the **bond order**, defined as one-half the net number of bonding electrons. In bond orders, electrons in antibonding molecular orbitals cancel electrons in bonding molecular orbitals, while electrons in nonbonding orbitals have no effect and are not counted. Bond orders of 1, 2, and 3 correspond to single, double, and triple bonds, respectively. Molecules with predicted bond orders of 0 are generally less stable than the isolated atoms and do not normally exist.

4.7.4 CONTRIBUTORS AND ATTRIBUTIONS

Modified by Joshua Halpern (Howard University)

1. Orbitals or orbital lobes with the same sign interact to give increased electron probability along the plane of the internuclear axis because of *constructive* reinforcement of the wave functions. Consequently, electrons in such molecular orbitals help to hold the positively charged nuclei together. Such orbitals are **bonding molecular orbitals**, and they are always lower in energy than the parent atomic orbitals.
2. Orbitals or orbital lobes with opposite signs interact to give decreased electron probability density between the nuclei because of *destructive* interference of the wave functions. Consequently, electrons in such molecular orbitals are primarily located outside the internuclear region, leading to increased repulsions between the positively charged nuclei. These orbitals are called **antibonding molecular orbitals**, and they are always higher in energy than the parent atomic orbitals.
3. Some atomic orbitals interact only very weakly, and the resulting molecular orbitals give essentially no change in the electron probability density between the nuclei. Hence electrons in such orbitals have no effect on the bonding in a molecule or ion. These orbitals are **nonbonding molecular orbitals**, and they have approximately the same energy as the parent atomic orbitals.

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4.8: SECOND-ROW DIATOMIC MOLECULES (SUPPLEMENTARY)

LEARNING OBJECTIVES

- To apply Molecular Orbital Theory to the diatomic homonuclear molecule from the elements in the second period.

If we combine the splitting schemes for the 2s and 2p orbitals, we can predict bond order in all of the diatomic molecules and ions composed of elements in the first complete row of the periodic table. Remember that only the valence orbitals of the atoms need be considered; as we saw in the cases of lithium hydride and dilithium, the inner orbitals remain tightly bound and retain their localized atomic character. We now describe examples of systems involving period 2 homonuclear diatomic molecules, such as N_2, O_2, and F_2.

FOUR KEY POINTS TO REMEMBER WHEN DRAWING MOLECULAR ORBITAL DIAGRAMS:

1. The number of molecular orbitals produced is the same as the number of atomic orbitals used to create them (the *"law of conservation of orbitals"*).
2. As the overlap between two atomic orbitals increases, the difference in energy between the resulting bonding and antibonding molecular orbitals increases.
3. When two atomic orbitals combine to form a pair of molecular orbitals, the bonding molecular orbital is stabilized about as much as the antibonding molecular orbital is destabilized.
4. The interaction between atomic orbitals is greatest when they have the same energy.

We illustrate how to use these points by constructing a molecular orbital energy-level diagram for F_2. We use the diagram in part (a) in Figure 4.8.1; the $n = 1$ orbitals (σ_{1s} and σ_{1s}*) are located well below those of the $n = 2$ level and are not shown. As illustrated in the diagram, the σ_{2s} and σ_{2s}* molecular orbitals are much lower in energy than the molecular orbitals derived from the 2*p* atomic orbitals because of the large difference in energy between the 2*s* and 2*p* atomic orbitals of fluorine. The lowest-energy molecular orbital derived from the three 2*p* orbitals on each F is σ_{2p_z} and the next most stable are the two degenerate orbitals, π_{2p_x} and π_{2p_y}. For each bonding orbital in the diagram, there is an antibonding orbital, and the antibonding orbital is destabilized by about as much as the corresponding bonding orbital is stabilized. As a result, the $\sigma^*_{2p_z}$ orbital is higher in energy than either of the degenerate $\pi^*_{2p_x}$ and $\pi^*_{2p_y}$ orbitals. We can now fill the orbitals, beginning with the one that is lowest in energy.

Each fluorine has 7 valence electrons, so there are a total of 14 valence electrons in the F_2 molecule. Starting at the lowest energy level, the electrons are placed in the orbitals according to the Pauli principle and Hund's rule. Two electrons each fill the σ_{2s} and σ_{2s}* orbitals, 2 fill the σ_{2p_z} orbital, 4 fill the two degenerate π orbitals, and 4 fill the two degenerate π^* orbitals, for a total of 14 electrons. To determine what type of bonding the molecular orbital approach predicts F_2 to have, we must calculate the bond order. According to our diagram, there are 8 bonding electrons and 6 antibonding electrons, giving a bond order of $(8 - 6) \div 2 = 1$. Thus F_2 is predicted to have a stable F–F single bond, in agreement with experimental data.

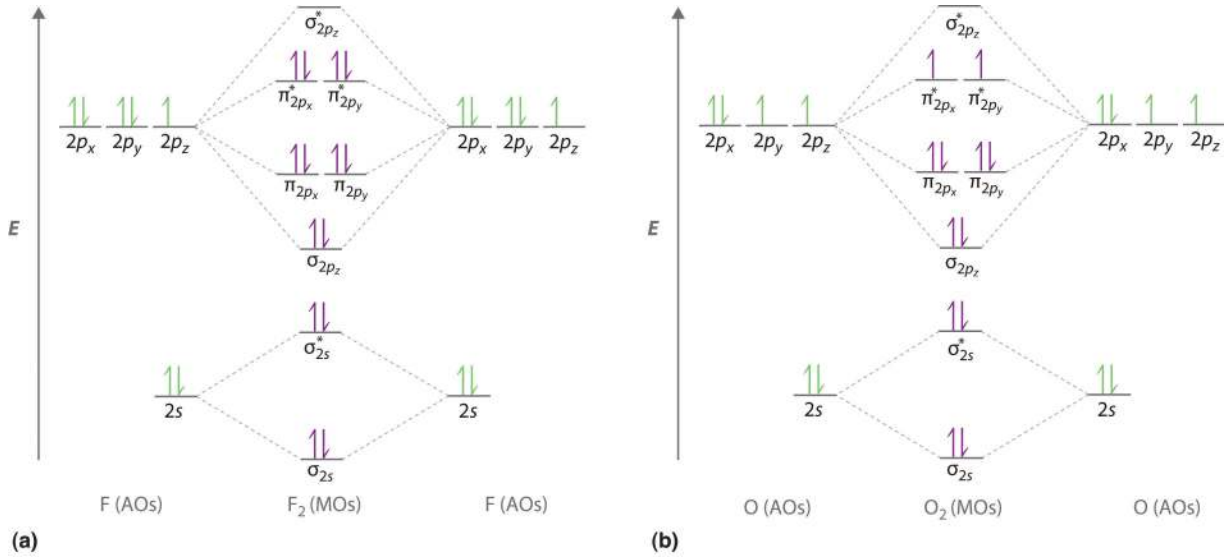


Figure 4.8.1: Molecular Orbital Energy-Level Diagrams for Homonuclear Diatomic Molecules.(a) For F_2, with 14 valence electrons (7 from each F atom), all of the energy levels except the highest, $\sigma^*_{2p_z}$ are filled. This diagram shows 8 electrons in bonding orbitals and 6 in antibonding orbitals, resulting in a bond order of 1. (b) For O_2, with 12 valence electrons (6 from each O atom), there are only 2 electrons to place in the $\left(\pi^*_{np_x}, \pi^*_{np_y}\right)$ pair of orbitals. Hund's rule dictates that one electron occupies each orbital, and their spins are parallel, giving the O_2 molecule two unpaired electrons. This diagram shows 8 electrons in bonding orbitals and 4 in antibonding orbitals, resulting in a predicted bond order of 2.

We now turn to a molecular orbital description of the bonding in O_2. It so happens that the molecular orbital description of this molecule provided an explanation for a long-standing puzzle that could not be explained using other bonding models. To obtain the molecular orbital energy-level diagram for O_2, we need to place 12 valence electrons (6 from each O atom) in the energy-level diagram shown in part (b) in Figure 4.8.1. We again fill the orbitals according to Hund's rule and the Pauli principle, beginning with the orbital that is lowest in energy. Two electrons each are needed to fill the σ_{2s} and σ_{2s}* orbitals, 2 more to fill the σ_{2p_z} orbital, and 4 to fill the degenerate $\pi^*_{2p_x}$ and $\pi^*_{2p_y}$ orbitals. According to Hund's rule, the last 2 electrons must be placed in separate π^* orbitals with their spins parallel, giving two unpaired electrons. This leads to a predicted bond order of $(8 - 4) \div 2 = 2$, which corresponds to a double bond, in agreement with experimental data (Table 4.5): the O–O bond length is 120.7 pm, and the bond energy is 498.4 kJ/mol at 298 K.

None of the other bonding models can predict the presence of two unpaired electrons in O_2. Chemists had long wondered why, unlike most other substances, liquid O_2 is attracted into a magnetic field. As shown in Figure 4.8.2, it actually remains suspended between the poles of a magnet until the liquid boils away. The only way to explain this behavior was for O_2 to have unpaired electrons, making it paramagnetic, exactly as predicted by molecular orbital theory. This result was one of the earliest triumphs of molecular orbital theory over the other bonding approaches we have discussed.



Figure 4.8.2: Liquid O_2 Suspended between the Poles of a Magnet.Because the O_2 molecule has two unpaired electrons, it is paramagnetic. Consequently, it is attracted into a magnetic field, which allows it to remain suspended between the poles of a powerful magnet until it evaporates. Full video can be found at www.youtube.com/watch?featur...&v=Lt4P6ctf06Q.

The magnetic properties of O_2 are not just a laboratory curiosity; they are absolutely crucial to the existence of life. Because Earth's atmosphere contains 20% oxygen, all organic compounds, including those that compose our body tissues, should react rapidly with air to

form H_2O, CO_2, and N_2 in an exothermic reaction. Fortunately for us, however, this reaction is very, very slow. The reason for the unexpected stability of organic compounds in an oxygen atmosphere is that virtually all organic compounds, as well as H_2O, CO_2, and N_2, have only paired electrons, whereas oxygen has two unpaired electrons. Thus the reaction of O_2 with organic compounds to give H_2O, CO_2, and N_2 would require that at least one of the electrons on O_2 change its spin during the reaction. This would require a large input of energy, an obstacle that chemists call a *spin barrier*. Consequently, reactions of this type are usually exceedingly slow. If they were not so slow, all organic substances, including this book and you, would disappear in a puff of smoke!

For period 2 diatomic molecules to the left of N_2 in the periodic table, a slightly different molecular orbital energy-level diagram is needed because the σ_{2p_z} molecular orbital is slightly *higher* in energy than the degenerate $\pi^*_{np_z}$ and $\pi^*_{np_y}$ orbitals. The difference in energy between the 2*s* and 2*p* atomic orbitals increases from Li_2 to F_2 due to increasing nuclear charge and poor screening of the 2*s* electrons by electrons in the 2*p* subshell. The bonding interaction between the 2*s* orbital on one atom and the 2*pz* orbital on the other is most important when the two orbitals have similar energies. This interaction decreases the energy of the σ_{2s} orbital and increases the energy of the σ_{2p_z} orbital. Thus for Li_2, Be_2, B_2, C_2, and N_2, the σ_{2p_z} orbital is higher in energy than the σ_{3p_z} orbitals, as shown in Figure **4.8.3** Experimentally, it is found that the energy gap between the *ns* and *np* atomic orbitals *increases* as the nuclear charge increases (Figure **4.8.3**). Thus for example, the σ_{2p_z} molecular orbital is at a lower energy than the $\pi_{2p_{x,y}}$ pair.

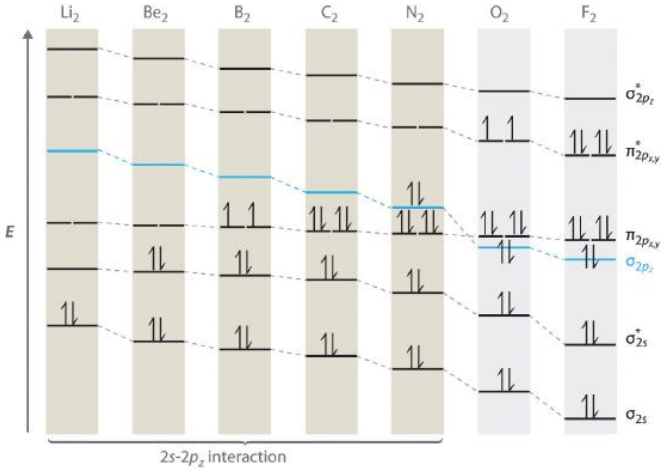


Figure **4.8.3**: Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements. Unlike earlier diagrams, only the molecular orbital energy levels for the molecules are shown here. For simplicity, the atomic orbital energy levels for the component *atoms* have been omitted. For Li_2 through N_2, the σ_{2p_z} orbital is higher in energy than the $\pi_{2p_{x,y}}$ orbitals. In contrast, the σ_{2p_z} orbital is *lower* in energy than the $\pi_{2p_{x,y}}$ orbitals for O_2 and F_2 due to the increase in the energy difference between the 2*s* and 2*p* atomic orbitals as the nuclear charge increases across the row.

Completing the diagram for N_2 in the same manner as demonstrated previously, we find that the 10 valence electrons result in 8 bonding electrons and 2 antibonding electrons, for a predicted bond order of 3, a triple bond. Experimental data show that the N–N bond is significantly shorter than the F–F bond (109.8 pm in N_2 versus 141.2 pm in F_2), and the bond energy is much greater for N_2 than for F_2 (945.3 kJ/mol versus 158.8 kJ/mol, respectively). Thus the N_2 bond is much shorter and stronger than the F_2 bond, consistent with what we would expect when comparing a triple bond with a single bond.

✔ EXAMPLE **4.8.3**: DIATOMIC SULFUR

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in S_2, a bright blue gas at high temperatures.

Given: chemical species

Asked for: molecular orbital energy-level diagram, bond order, and number of unpaired electrons

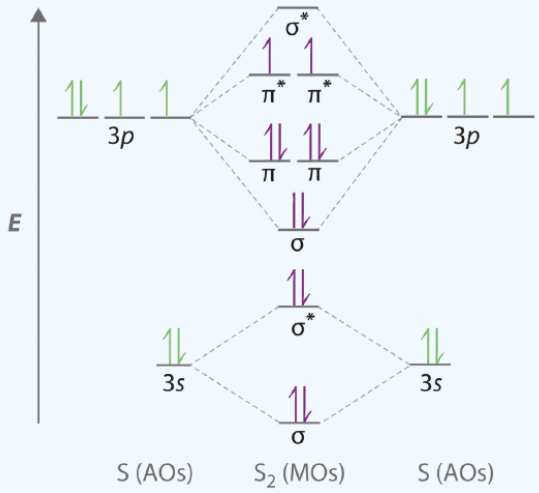
Strategy:

A. Write the valence electron configuration of sulfur and determine the type of molecular orbitals formed in S_2. Predict the relative energies of the molecular orbitals based on how close in energy the valence atomic orbitals are to one another.
B. Draw the molecular orbital energy-level diagram for this system and determine the total number of valence electrons in S_2.
C. Fill the molecular orbitals in order of increasing energy, being sure to obey the Pauli principle and Hund's rule.
D. Calculate the bond order and describe the bonding.

Solution:

A Sulfur has a [Ne]$3s^2 3p^4$ valence electron configuration. To create a molecular orbital energy-level diagram similar to those in Figure **4.8.1** and Figure **4.8.3**, we need to know how close in energy the 3*s* and 3*p* atomic orbitals are because their energy separation will determine whether the $\pi_{3p_{z,y}}$ or the σ_{3p_z}> molecular orbital is higher in energy. Because the *ns*–*np* energy gap *increases* as the nuclear charge increases (Figure **4.8.3**), the σ_{3p_z} molecular orbital will be lower in energy than the $\pi_{3p_{z,y}}$ pair.

B The molecular orbital energy-level diagram is as follows:



Two filled sigma orbitals, one filled sigma * orbital, two filled pi orbitals, and two pi * orbitals with one unpaired electron.

Each sulfur atom contributes 6 valence electrons, for a total of 12 valence electrons.

C Ten valence electrons are used to fill the orbitals through π_{3p_z} and π_{3p_y}, leaving 2 electrons to occupy the degenerate $\pi^*_{3p_z}$ and $\pi^*_{3p_y}$ pair. From Hund's rule, the remaining 2 electrons must occupy these orbitals separately with their spins aligned. With the numbers of electrons written as superscripts, the electron configuration of S_2 is $(\sigma_{3s})^2 (\sigma^*_{3s})^2 (\sigma_{3p_z})^2 (\pi_{3p_{z,y}})^4 (\pi_{3p^*_{z,y}})^2$ with 2 unpaired electrons. The bond order is (8 − 4) ÷ 2 = 2, so we predict an S=S double bond.

? EXERCISE 4.8.3: THE PEROXIDE ION

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in the peroxide ion (O_2^{2-}).

Answer

$(\sigma_{2s})^2 (\sigma^*_{2s})^2 (\sigma_{2p_z})^2 (\pi_{2p_{z,y}})^4 (\pi_{2p^*_{z,y}})^4$ bond order of 1; no unpaired electrons

4.8.1 MOLECULAR ORBITALS FOR HETERONUCLEAR DIATOMIC MOLECULES

Diatomic molecules with two different atoms are called heteronuclear diatomic molecules. When two nonidentical atoms interact to form a chemical bond, the interacting atomic orbitals do not have the same energy. If, for example, element B is more electronegative than element A ($\chi_B > \chi_A$), the net result is a "skewed" molecular orbital energy-level diagram, such as the one shown for a hypothetical A–B molecule in Figure **4.8.4**. The atomic orbitals of element B are uniformly lower in energy than the corresponding atomic orbitals of element A because of the enhanced stability of the electrons in element B. The molecular orbitals are no longer symmetrical, and the energies of the bonding molecular orbitals are more similar to those of the atomic orbitals of B. Hence the electron density of bonding electrons is likely to be closer to the more electronegative atom. In this way, molecular orbital theory can describe a polar covalent bond.

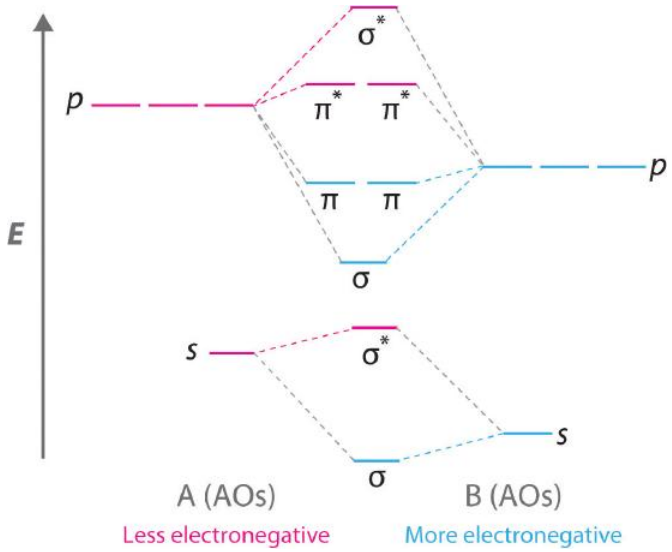


Figure **4.8.4**: Molecular Orbital Energy-Level Diagram for a Heteronuclear Diatomic Molecule AB, Where $\chi_B > \chi_A$. The bonding molecular orbitals are closer in energy to the atomic orbitals of the more electronegative B atom. Consequently, the electrons in the bonding orbitals are not shared equally between the two atoms. On average, they are closer to the B atom, resulting in a polar covalent bond.

> *A molecular orbital energy-level diagram is always skewed toward the more electronegative atom.*

AN ODD NUMBER OF VALENCE ELECTRONS: NO

Nitric oxide (NO) is an example of a heteronuclear diatomic molecule. The reaction of O_2 with N_2 at high temperatures in internal combustion engines forms nitric oxide, which undergoes a complex reaction with O_2 to produce NO_2, which in turn is responsible for the brown color we associate with air pollution. Recently, however, nitric oxide has also been recognized to be a vital biological messenger involved in regulating blood pressure and long-term memory in mammals.

Because NO has an odd number of valence electrons (5 from nitrogen and 6 from oxygen, for a total of 11), its bonding and properties cannot be successfully explained by either the Lewis electron-pair approach or valence bond theory. The molecular orbital energy-level diagram for NO (Figure **4.8.13**) shows that the general pattern is similar to that for the O_2 molecule (Figure **4.8.11**). Because 10 electrons are sufficient to fill all the bonding molecular orbitals derived from 2*p* atomic orbitals, the 11th electron must occupy one of the degenerate π^* orbitals. The predicted bond order for NO is therefore (8-3) ÷ 2 = 2 1/2 . Experimental data, showing an N–O bond length of 115 pm and N–O bond energy of 631 kJ/mol, are consistent with this description. These values lie between those of the N_2 and O_2 molecules, which have triple and double bonds, respectively. As we stated earlier, molecular orbital theory can therefore explain the bonding in molecules with an odd number of electrons, such as NO, whereas Lewis electron structures cannot.

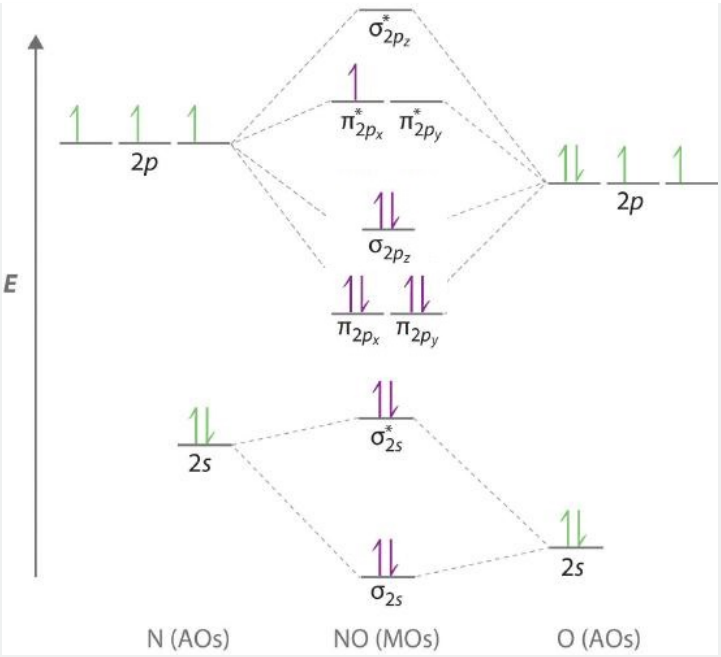


Figure **4.8.13**: Molecular Orbital Energy-Level Diagram for **NO**. Because **NO** has 11 valence electrons, it is paramagnetic, with a single electron occupying the $\left(\pi^*_{2p_x}, \pi^*_{2p_y}\right)$ pair of orbitals.

Note that electronic structure studies show the ground state configuration of **NO** to be $(\sigma_{2s})^2 (\sigma^*_{2s})^2 \left(\pi_{2p_{x,y}}\right)^4 (\sigma_{2p_z})^2 \left(\pi^*_{2p_{x,y}}\right)^1$ in order of increasing energy. Hence, the $\pi_{2p_{x,y}}$ orbitals are lower in energy than the σ_{2p_z} orbital. This is because the **NO** molecule is near the transition of flipping energies levels observed in homonuclear diatomics where the sigma bond drops below the pi bond (Figure **4.8.11**).

Molecular orbital theory can also tell us something about the *chemistry* of NO. As indicated in the energy-level diagram in Figure **4.8.13**, NO has a single electron in a relatively high-energy molecular orbital. We might therefore expect it to have similar reactivity as alkali metals such as Li and Na with their single valence electrons. In fact, NO is easily oxidized to the NO^+ cation, which is isoelectronic with N_2 and has a bond order of 3, corresponding to an N≡O triple bond.

4.8.2 NONBONDING MOLECULAR ORBITALS

Molecular orbital theory is also able to explain the presence of lone pairs of electrons. Consider, for example, the HCl molecule, whose Lewis electron structure has three lone pairs of electrons on the chlorine atom. Using the molecular orbital approach to describe the bonding in HCl, we can see from Figure **4.8.6** that the 1*s* orbital of atomic hydrogen is closest in energy to the 3*p* orbitals of chlorine. Consequently, the filled Cl 3*s* atomic orbital is not involved in bonding to any appreciable extent, and the only important interactions are those between the H 1*s* and Cl 3*p* orbitals. Of the three *p* orbitals, only one, designated as $3p_z$, can interact with the H 1*s* orbital. The $3p_x$ and $3p_y$ atomic orbitals have no net overlap with the 1*s* orbital on hydrogen, so they are not involved in bonding. Because the energies of the Cl 3*s*, $3p_x$, and $3p_y$ orbitals do not change when HCl forms, they are called **nonbonding molecular orbitals**. A nonbonding molecular orbital occupied by a pair of electrons is the molecular orbital equivalent of a lone pair of electrons. By definition, electrons in nonbonding orbitals have no effect on bond order, so they are not counted in the calculation of bond order. Thus the predicted bond order of HCl is (2 − 0) ÷ 2 = 1. Because the σ bonding molecular orbital is closer in energy to the Cl $3p_z$ than to the H 1*s* atomic orbital, the electrons in the σ orbital are concentrated closer to the chlorine atom than to hydrogen. A molecular orbital approach to bonding can therefore be used to describe the polarization of the H–Cl bond to give $H^{\delta+} - - Cl^{\delta-}$.

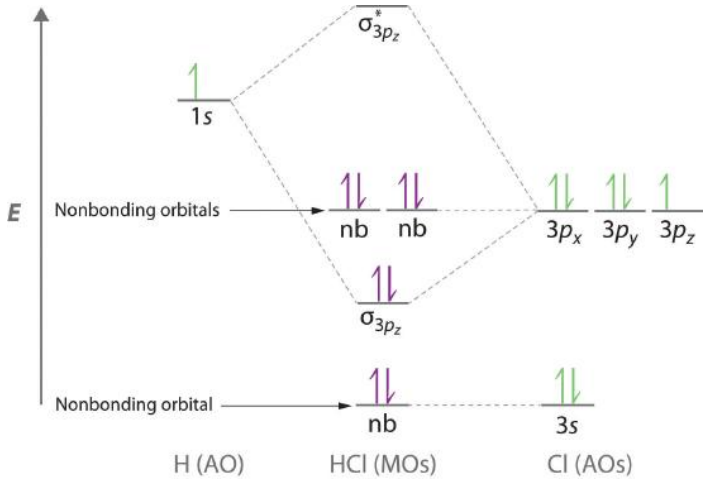


Figure **4.8.6**: Molecular Orbital Energy-Level Diagram for HCl. The hydrogen 1*s* atomic orbital interacts most strongly with the $3p_z$ orbital on chlorine, producing a bonding/antibonding pair of molecular orbitals. The other electrons on Cl are best viewed as nonbonding. As a result, only the bonding σ orbital is occupied by electrons, giving a bond order of 1.

> *Electrons in nonbonding molecular orbitals have no effect on bond order.*

EXAMPLE 4.8.4: THE CYANIDE ION

Use a "skewed" molecular orbital energy-level diagram like the one in Figure **4.8.4** to describe the bonding in the cyanide ion (CN^-). What is the bond order?

Given: chemical species

Asked for: "skewed" molecular orbital energy-level diagram, bonding description, and bond order

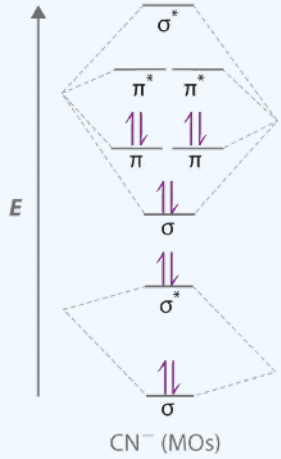
Strategy:

A. Calculate the total number of valence electrons in CN^-. Then place these electrons in a molecular orbital energy-level diagram like Figure **4.8.4** in order of increasing energy. Be sure to obey the Pauli principle and Hund's rule while doing so.

B. Calculate the bond order and describe the bonding in CN^-.

Solution:

A The CN^- ion has a total of 10 valence electrons: 4 from C, 5 from N, and 1 for the −1 charge. Placing these electrons in an energy-level diagram like Figure **4.8.4** fills the five lowest-energy orbitals, as shown here:



Because $\chi_N > \chi_C$, the atomic orbitals of N (on the right) are lower in energy than those of C.

B The resulting valence electron configuration gives a predicted bond order of (8 − 2) ÷ 2 = 3, indicating that the CN^- ion has a triple bond, analogous to that in N_2.

EXERCISE 4.8.4: THE HYPOCHLORITE ION

Use a qualitative molecular orbital energy-level diagram to describe the bonding in the hypochlorite ion (OCl^-). What is the bond order?

Answer

All molecular orbitals except the highest-energy σ* are filled, giving a bond order of 1.

Although the molecular orbital approach reveals a great deal about the bonding in a given molecule, the procedure quickly becomes computationally intensive for molecules of even moderate complexity. Furthermore, because the computed molecular orbitals extend over the entire molecule, they are often difficult to represent in a way that is easy to visualize. Therefore we do not use a pure molecular orbital approach to describe the bonding in molecules or ions with more than two atoms. Instead, we use a valence bond approach and a molecular orbital approach to explain, among other things, the concept of resonance, which cannot adequately be explained using other methods.



4.8.3 SUMMARY

Molecular orbital energy-level diagrams for diatomic molecules can be created if the electron configuration of the parent atoms is known, following a few simple rules. Most important, the number of molecular orbitals in a molecule is the same as the number of atomic orbitals that interact. The difference between bonding and antibonding molecular orbital combinations is proportional to the overlap of the parent orbitals and decreases as the energy difference between the parent atomic orbitals increases. With such an approach, the electronic structures of virtually all commonly encountered **homonuclear diatomic molecules**, molecules with two identical atoms, can be understood. The molecular orbital approach correctly predicts that the O_2 molecule has two unpaired electrons and hence is attracted into a magnetic field. In contrast, most substances have only paired electrons. A similar procedure can be applied to molecules with two dissimilar atoms, called **heteronuclear diatomic molecules**, using a molecular orbital energy-level diagram that is skewed or tilted toward the more electronegative element. Molecular orbital theory is able to describe the bonding in a molecule with an odd number of electrons such as NO and even to predict something about its chemistry.

4.8.4 CONTRIBUTORS AND ATTRIBUTIONS

- Modified by Joshua Halpern (Howard University)

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4.E: EXERCISES

4.E.1 THE VSEPR MODEL

4.E.1.1 CONCEPTUAL PROBLEMS

1. What is the main difference between the VSEPR model and Lewis electron structures?
2. What are the differences between molecular geometry and Lewis electron structures? Can two molecules with the same Lewis electron structures have different molecular geometries? Can two molecules with the same molecular geometry have different Lewis electron structures? In each case, support your answer with an example.
3. How does the VSEPR model deal with the presence of multiple bonds?
4. Three molecules have the following generic formulas: AX_2, AX_2E, and AX_2E_2. Predict the molecular geometry of each, and arrange them in order of increasing X–A–X angle.
5. Which has the smaller angles around the central atom—H_2S or SiH_4? Why? Do the Lewis electron structures of these molecules predict which has the smaller angle?
6. Discuss in your own words why lone pairs of electrons occupy more space than bonding pairs. How does the presence of lone pairs affect molecular geometry?
7. When using VSEPR to predict molecular geometry, the importance of repulsions between electron pairs decreases in the following order: LP–LP, LP–BP, BP–BP. Explain this order. Draw structures of real molecules that separately show each of these interactions.
8. How do multiple bonds affect molecular geometry? Does a multiple bond take up more or less space around an atom than a single bond? a lone pair?
9. Straight-chain alkanes do not have linear structures but are “kinked.” Using *n*-hexane as an example, explain why this is so. Compare the geometry of 1-hexene to that of *n*-hexane.
10. How is molecular geometry related to the presence or absence of a molecular dipole moment?
11. How are molecular geometry and dipole moments related to physical properties such as melting point and boiling point?
12. What two features of a molecule’s structure and bonding are required for a molecule to be considered polar? Is COF_2 likely to have a significant dipole moment? Explain your answer.
13. When a chemist says that a molecule is *polar*, what does this mean? What are the general physical properties of polar molecules?
14. Use the VSPER model and your knowledge of bonding and dipole moments to predict which molecules will be liquids or solids at room temperature and which will be gases. Explain your rationale for each choice. Justify your answers.
    1. CH_3Cl
    2. PCl_3
    3. CO
    4. SF_6
    5. IF_5
    6. CH_3OCH_3
    7. CCl_3H
    8. H_3COH
15. The idealized molecular geometry of BrF_5 is square pyramidal, with one lone pair. What effect does the lone pair have on the actual molecular geometry of BrF_5? If LP–BP repulsions were *weaker* than BP–BP repulsions, what would be the effect on the molecular geometry of BrF_5?
16. Which has the smallest bond angle around the central atom—H_2S, H_2Se, or H_2Te? the largest? Justify your answers.
17. Which of these molecular geometries *always* results in a molecule with a net dipole moment: linear, bent, trigonal planar, tetrahedral, seesaw, trigonal pyramidal, square pyramidal, and octahedral? For the geometries that do not always produce a net dipole moment, what factor(s) will result in a net dipole moment?

4.E.1.2 CONCEPTUAL ANSWERS

1.
2.
3. To a first approximation, the VSEPR model assumes that multiple bonds and single bonds have the same effect on electron pair geometry and molecular geometry; in other words, VSEPR treats multiple bonds like single bonds. Only when considering fine points of molecular structure does VSEPR recognize that multiple bonds occupy more space around the central atom than single bonds.
4.
5.
6.
7.
8.
9.
10.
11. Physical properties like boiling point and melting point depend upon the existence and magnitude of the dipole moment of a molecule. In general, molecules that have substantial dipole moments are likely to exhibit greater intermolecular interactions, resulting in higher melting points and boiling points.
12.
13. The term “polar” is generally used to mean that a molecule has an asymmetrical structure and contains polar bonds. The resulting dipole moment causes the substance to have a higher boiling or melting point than a nonpolar substance.

4.E.1.3 NUMERICAL PROBLEMS

18. Give the number of electron groups around the central atom and the molecular geometry for each molecule. Classify the electron groups in each species as bonding pairs or lone pairs.
    1. BF_3
    2. PCl_3
    3. XeF_2
    4. $AlCl_4^-$
    5. CH_2Cl_2
19. Give the number of electron groups around the central atom and the molecular geometry for each species. Classify the electron groups in each species as bonding pairs or lone pairs.
    1. ICl_3
    2. CCl_3^+
    3. H_2Te
    4. XeF_4
    5. NH_4^+
20. Give the number of electron groups around the central atom and the molecular geometry for each molecule. For structures that are not linear, draw three-dimensional representations, clearly showing the positions of the lone pairs of electrons.
    1. HCl
    2. NF_3
    3. ICl_2^+
    4. N_3^-
    5. H_3O^+
21. Give the number of electron groups around the central atom and the molecular geometry for each molecule. For structures that are not linear, draw three-dimensional representations, clearly showing the positions of the lone pairs of electrons.
    1. SO_3
    2. NH_2^-
    3. NO_3^-
    4. I_3^-
    5. OF_2

22. What is the molecular geometry of ClF_3? Draw a three-dimensional representation of its structure and explain the effect of any lone pairs on the idealized geometry.

23. Predict the molecular geometry of each of the following.

    1. ICl_3
    2. AsF_5
    3. NO_2^-
    4. $TeCl_4$

24. Predict whether each molecule has a net dipole moment. Justify your answers and indicate the direction of any bond dipoles.

    1. NO
    2. HF
    3. PCl_3
    4. CO_2
    5. SO_2
    6. SF_4

25. Predict whether each molecule has a net dipole moment. Justify your answers and indicate the direction of any bond dipoles.

    1. OF_2
    2. BCl_3
    3. CH_2Cl_2
    4. TeF_4
    5. CH_3OH
    6. XeO_4

26. Of the molecules $Cl_2C{=}Cl_2$, IF_3, and SF_6, which has a net dipole moment? Explain your reasoning.

27. Of the molecules SO_3, XeF_4, and $H_2C{=}Cl_2$, which has a net dipole moment? Explain your reasoning.

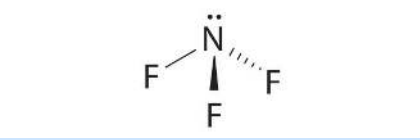
4.E.1.4 NUMERICAL ANSWERS

18. 1. trigonal planar (all electron groups are bonding pairs)
    2. tetrahedral (one lone pair on P)
    3. trigonal bipyramidal (three lone pairs on Xe)
    4. tetrahedral (all electron groups on Al are bonding pairs)
    5. tetrahedral (all electron groups on C are bonding pairs)

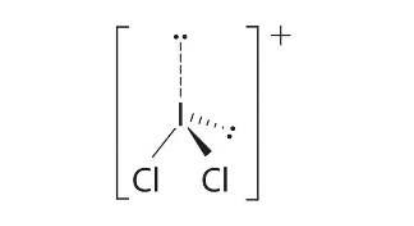
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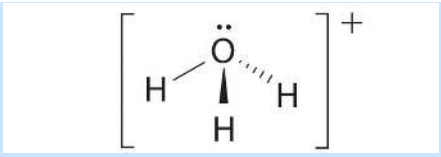
    1. four electron groups, linear molecular geometry
    2. four electron groups, pyramidal molecular geometry



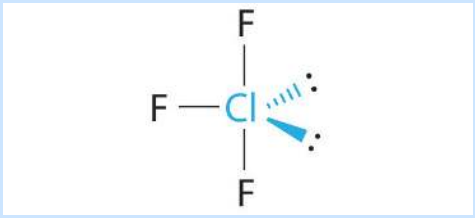
    3. four electron groups, bent molecular geometry



    4. two electron groups, linear molecular geometry
    5. four electron groups, pyramidal molecular geometry



21.

22. 

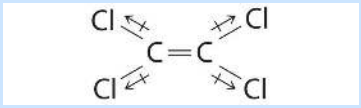
The idealized geometry is T shaped, but the two lone pairs of electrons on Cl will distort the structure, making the F–Cl–F angle *less* than 180°.

23.

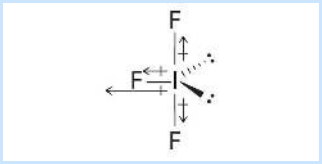
24.

25.

26. $Cl_2C=CCl_2$: Although the C–Cl bonds are rather polar, the individual bond dipoles cancel one another in this symmetrical structure, and $Cl_2C=CCl_2$ does not have a net dipole moment.



IF_3: In this structure, the individual I–F bond dipoles cannot cancel one another, giving IF_3 a net dipole moment.



SF_6: The S–F bonds are quite polar, but the individual bond dipoles cancel one another in an octahedral structure. Thus, SF_6 has no net dipole moment.



4.E.2 MOLECULAR SHAPE AND MOLECULAR POLARITY

4.E.2.1 CONCEPTUAL PROBLEMS

28. Why do ionic compounds such as KI exhibit substantially less than 100% ionic character in the gas phase?
29. Of the compounds LiI and LiF, which would you expect to behave more like a classical ionic compound? Which would have the greater dipole moment in the gas phase? Explain your answers.

4.E.2.2 NUMERICAL PROBLEMS

30. Predict whether each compound is purely covalent, purely ionic, or polar covalent.

    1. RbCl
    2. S_8
    3. $TiCl_2$
    4. $SbCl_3$
    5. LiI
    6. Br_2

31. Based on relative electronegativities, classify the bonding in each compound as ionic, covalent, or polar covalent. Indicate the direction of the bond dipole for each polar covalent bond.
    1. NO
    2. HF
    3. MgO
    4. $AlCl_3$
    5. SiO_2
    6. the C=O bond in acetone
    7. O_3
32. Based on relative electronegativities, classify the bonding in each compound as ionic, covalent, or polar covalent. Indicate the direction of the bond dipole for each polar covalent bond.
    1. NaBr
    2. OF_2
    3. BCl_3
    4. the S–S bond in $CH_3CH_2SSCH_2CH_3$
    5. the C–Cl bond in CH_2Cl_2
    6. the O–H bond in CH_3OH
    7. $PtCl_4^{2-}$
33. Classify each species as having 0%–40% ionic character, 40%–60% ionic character, or 60%–100% ionic character based on the type of bonding you would expect. Justify your reasoning.
    1. CaO
    2. S_8
    3. $AlBr_3$
    4. ICl
    5. Na_2S
    6. SiO_2
    7. LiBr
34. If the bond distance in HCl (dipole moment = 1.109 D) were double the actual value of 127.46 pm, what would be the effect on the charge localized on each atom? What would be the percent negative charge on Cl? At the actual bond distance, how would doubling the charge on each atom affect the dipole moment? Would this represent more ionic or covalent character?
35. Calculate the percent ionic character of HF (dipole moment = 1.826 D) if the H–F bond distance is 92 pm.
36. Calculate the percent ionic character of CO (dipole moment = 0.110 D) if the C–O distance is 113 pm.
37. Calculate the percent ionic character of PbS and PbO in the gas phase, given the following information: for PbS, r = 228.69 pm and μ = 3.59 D; for PbO, r = 192.18 pm and μ = 4.64 D. Would you classify these compounds as having covalent or polar covalent bonds in the solid state?

4.E.3 COVALENT BONDING AND ORBITAL OVERLAP

4.E.4 HYBRID ORBITALS

4.E.4.1 CONCEPTUAL PROBLEMS

38. Arrange sp, sp^3, and sp^2 in order of increasing strength of the bond formed to a hydrogen atom. Explain your reasoning.
39. What atomic orbitals are combined to form sp^3, sp, sp^3d^2, and sp^3d? What is the maximum number of electron-pair bonds that can be formed using each set of hybrid orbitals?
40. Why is it incorrect to say that an atom with sp^2 hybridization will form only three bonds? The carbon atom in the carbonate anion is sp^2 hybridized. How many bonds to carbon are present in the carbonate ion? Which orbitals on carbon are used to form each bond?
41. If hybridization did not occur, how many bonds would N, O, C, and B form in a neutral molecule, and what would be the approximate molecular geometry?
42. How are hybridization and molecular geometry related? Which has a stronger correlation—molecular geometry and hybridization or Lewis structures and hybridization?

43. In the valence bond approach to bonding in BeF_2, which step(s) require(s) an energy input, and which release(s) energy?
44. The energies of hybrid orbitals are intermediate between the energies of the atomic orbitals from which they are formed. Why?
45. How are lone pairs on the central atom treated using hybrid orbitals?
46. Because nitrogen bonds to only three hydrogen atoms in ammonia, why doesn't the nitrogen atom use sp^2 hybrid orbitals instead of sp^3 hybrids?
47. Using arguments based on orbital hybridization, explain why the CCl_6^{2-} ion does not exist.
48. Species such as NF_5^{2-} and OF_4^{2-} are unknown. If 3*d* atomic orbitals were much lower energy, low enough to be involved in hybrid orbital formation, what effect would this have on the stability of such species? Why? What molecular geometry, electron-pair geometry, and hybridization would be expected for each molecule?

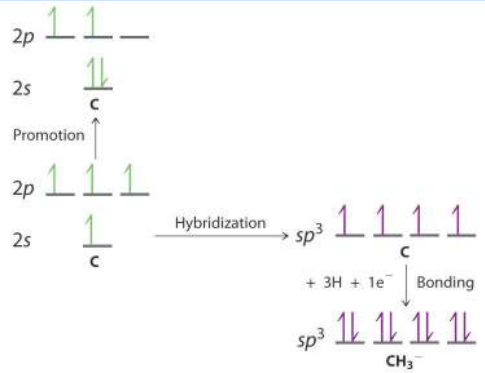
4.E.4.2 NUMERICAL PROBLEMS

49. Draw an energy-level diagram showing promotion and hybridization to describe the bonding in CH_3^-. How does your diagram compare with that for methane? What is the molecular geometry?
50. Draw an energy-level diagram showing promotion and hybridization to describe the bonding in CH_3^+. How does your diagram compare with that for methane? What is the molecular geometry?
51. Draw the molecular structure, including any lone pairs on the central atom, state the hybridization of the central atom, and determine the molecular geometry for each molecule.
    1. BBr_3
    2. PCl_3
    3. NO_3^-
52. Draw the molecular structure, including any lone pairs on the central atom, state the hybridization of the central atom, and determine the molecular geometry for each species.
    1. $AsBr_3$
    2. CF_3^+
    3. H_2O
53. What is the hybridization of the central atom in each of the following?
    1. CF_4
    2. CCl_2^{2-}
    3. IO_3^-
    4. SiH_4
54. What is the hybridization of the central atom in each of the following?
    1. CCl_3^+
    2. CBr_2O
    3. CO_3^{2-}
    4. IBr_2^-
55. What is the hybridization of the central atom in PF_6^-? Is this ion likely to exist? Why or why not? What would be the shape of the molecule?
56. What is the hybridization of the central atom in SF_5^-? Is this ion likely to exist? Why or why not? What would be the shape of the molecule?

4.E.4.3 NUMERICAL ANSWERS

49.

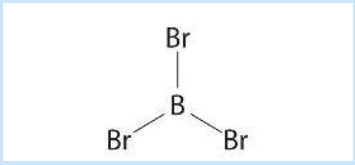
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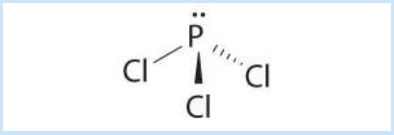
The promotion and hybridization process is exactly the same as shown for CH_4 in the chapter. The only difference is that the C atom uses the four singly occupied sp^3 hybrid orbitals to form electron-pair bonds with only *three* H atoms, and an electron is added to the fourth hybrid orbital to give a charge of 1–. The electron-pair geometry is tetrahedral, but the molecular geometry is pyramidal, as in NH_3.

50.

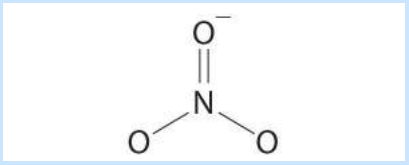
51.

1. 

   sp^2, trigonal planar

2. 

   sp^3, pyramidal

3. 

   sp^2, trigonal planar

52.

53. The central atoms in CF_4, CCl_2^{2-}, IO_3^-, and SiH_4 are all sp^3 hybridized.

54.

55. The phosphorus atom in the PF_6^- ion is sp^3d^2 hybridized, and the ion is octahedral. The PF_6^- ion is isoelectronic with SF_6 and has essentially the same structure. It should therefore be a stable species.

4.E.5 MULTIPLE BONDS

4.E.5.1 CONCEPTUAL PROBLEMS

57. What information is obtained by using the molecular orbital approach to bonding in O_3 that is not obtained using the VSEPR model? Can this information be obtained using a Lewis electron-pair approach?
58. How is resonance explained using the molecular orbital approach?
59. Indicate what information can be obtained by each method:

	Lewis Electron Structures	VSEPR Model	Valence Bond Theory	Molecular Orbital Theory
Geometry				
Resonance				
Orbital Hybridization				
Reactivity				
Expanded Valences				
Bond Order				

4.E.5.2 NUMERICAL PROBLEMS

60. Using both a hybrid atomic orbital and molecular orbital approaches, describe the bonding in BCl_3 and CS_3^{2-}.
61. Use both a hybrid atomic orbital and molecular orbital approaches to describe the bonding in CO_2 and N_3^-.

4.E.6 MOLECULAR ORBITALS

4.E.7 SECOND-ROW DIATOMIC MOLECULES

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4.S: MOLECULAR GEOMETRY AND BONDING THEORIES (SUMMARY)

4.S.1 9.1: MOLECULAR SHAPES

The Lewis electron-pair approach described previously can be used to predict the number and types of bonds between the atoms in a substance, and it indicates which atoms have lone pairs of electrons. This approach gives no information about the actual arrangement of atoms in space, however.

- **Bond angles**: angles made by the lines joining the nuclei of the atoms in a molecule
- Bond angles determine overall shape of molecule

4.S.2 VSEPR MODEL" DATA-CKE-SAVED-HREF="/BOOKSHELVES/GENERAL_CHEMISTRY/MAP:_CHEMISTRY_-_THE_CENTRAL_SCIENCE_(BROWN_ET_AL.)/09:_MOLECULAR_GEOMETRY_AND_BONDING_THEORIES/9.02:_THE_VSEPR_MODEL" HREF="/BOOKSHELVES/GENERAL_CHEMISTRY/MAP:_CHEMISTRY_-_THE_CENTRAL_SCIENCE_(BROWN_ET_AL.)/09:_MOLECULAR_GEOMETRY_AND_BONDING_THEORIES/9.02:_THE_VSEPR_MODEL" DATA-QUAIL-ID="12">9.2: THE VSEPR MODEL

The VSEPR model can predict the structure of nearly any molecule or polyatomic ion in which the central atom is a nonmetal, as well as the structures of many molecules and polyatomic ions with a central metal atom. The VSEPR model is not a theory; it does not attempt to explain observations. Instead, it is a counting procedure that accurately predicts the three-dimensional structures of a large number of compounds, which cannot be predicted using the Lewis electron-pair approach.

The Valence-Shell Electron Pair-Repulsion Model

- *Valence-shell electron-pair repulsion (VSEPR) model:* model that accounts for the geometric arrangements of shared and unshared electron pairs around a central atom in terms of the repulsions between electron pairs
- Electrons repel one another; hence, *the best arrangement of a given number of electron pairs is the one that minimizes the repulsions among them.*

Predicting Molecular Geometries

- Two types of valence-shell electron pairs; *bonding pairs* and *nonbonding pairs*.
- **Electron-pair geometry**: 3-D arrangement of electron pairs around an atom according to the VSEPR model
- **Molecular geometry**: the arrangement in space of the atoms of a molecule

When describing the shapes of molecules, we always give the *molecular* geometry rather than the *electron-pair* geometry. Molecular geometries only include BONDING pairs. For example, NH_3 is a tetrahedral according to electron-pair geometry because it has 3 bonds and an unshared pair of electron. However, according to molecular geometry it is a trigonal pyramidal because it has only 3 bonds.

How to predict molecular geometries using VSEPR model:

1. Sketch the Lewis dot structure of the molecule or ion
2. Count the total number of electron pairs around the central atom and arrange them in the way that minimizes electron-pair repulsions
3. Describe the molecular geometry in terms of the angular arrangement of the *bonding* pairs

Four or Fewer Valence-Shell Electron Pairs

A double or triple bond has essentially the same effect on bond angles as a single bond and is therefore counted as one bonding pair (that is, one electron region) when predicting geometry

The Effect of Nonbonding Electrons and Multiple Bonds on Bond Angles

Bond angles decrease as the number of nonbonding electron pairs increases. Bonding pairs are attracted by the two nuclei. By contrast, nonbonding electrons move under the attractive influence of only one nucleus and thus spread out more in space.

- *Nonbonding electron pairs exert greater repulsive forces on adjacent electron pairs and thus tend to compress the angles between the bonding pairs*
- *Electrons in multiple bonds, like nonbonding pairs, exert a greater repulsive force on adjacent electron pairs than do single bonds.*

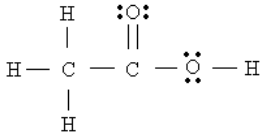
Geometries of Molecules with Expanded Valence Shells

- When the central atom of a molecule or ion is from the third period of the periodic table and beyond (has *d* subshell) that atom may have more than four electron pairs around it

- The most stable electron-pair geometry for five electron pairs is the Trigonal bipyramid.
- Trigonal bipyramid geometries have two distinct types of electron pairs. They are *axial pairs* and *equatorial pairs*. In axial position, an electron pair is situated 90° from the three equatorial pairs. In an equatorial position, an electron pairs is situated 120° from the other two equatorial pairs and 90° from the two axial pairs.
- Because nonbonding pairs exert larger repulsions than bonding pairs, they always occupy the equatorial positions
- The most stable electron-pair geometry for six electron pairs is the *octahedron*.
- In an octahedron, the angles are either 90° or 180°, and all six positions are equivalent

Molecules with No Single Central Atom

Consider acetic acid molecule



Carbon bonded to three hydrogens and one carbon. Second carbon is double bonded to one oxygen and single bonded to another oxygen. The single bonded oxygen is bonded to a hydrogen.

- Notice that the leftmost C has four bonded pairs around it. Hence, it must be a tetrahedral.
- The central C has 3 bonding pairs around it (counting the double bond as a single pair), hence, it is trigonal planar
- O has two bonding pairs, and two nonbonding ones. Hence, it is bent.

4.S.3 9.3: MOLECULAR SHAPE AND MOLECULAR POLARITY

Compounds with polar covalent bonds have electrons that are shared unequally between the bonded atoms. The polarity of such a bond is determined largely by the relative electronegativites of the bonded atoms. The asymmetrical charge distribution in a polar substance produces a dipole moment, which is the product of the partial charges on the bonded atoms and the distance between them.

Polar: in a molecule, if its centers of negative and positive charge don't coincide, aka **dipole**

- If there are no charges on the opposite ends of a molecule, or if the charges have the same sign, the molecule does not have a dipole moment and is therefore *nonpolar*. Any diatomic molecule with a polar bond is a polar molecule
- Polar molecules align themselves with respect to one another. The negative end of a polar molecule is attracted to a positive ion, the positive end is attracted to a negative ion
- **Dipole moment**: measures the degree of polarity of a given molecule. The dipole moment, μ, is the product of the charge at either end of the dipole, Q, times the distance, r, between the charges.

$$\mu = Qr$$

Therefore, the dipole moment increases as the quantity of charge that is separated increases and as the distance between the positive and negative centers increases. Dipole moments are generally reported in debyes (D), a unit equaling 3.33 X 10^{-30} C-m.

The Polarity of Polyatomic Molecules

- The polarity of a molecule containing more than two atoms depends on both the polarities of the bonds and the geometry of the molecule
- For each polar bond in a molecule, we can consider the *bond dipole*, that is, the dipole moment due only to the two atoms bonded together. We must then ask what the overall dipole moment results from adding up the individual bond dipoles. Let's use CO_2 (linear) as an example
- In CO_2, each C – O bond is polar, and because they are identical, the bond dipoles are equal in magnitude.
- The fact that both C – O bonds are polar doesn't necessarily mean the whole CO_2 molecule is
- Bond dipoles and dipole moments are vector quantities; they have both a magnitude and direction. When calculating the overall dipole moment, both the magnitude and direction of the bond dipoles must be considered in this sum of vectors
- The two bond dipoles in CO_2, although equal in magnitude, are opposite in direction, which makes them cancel each other out. Hence, CO_2 has an overall dipole moment of zero. Even though the oxygen atoms in CO_2 carry a partial negative charge, the geometry of the molecule dictates the overall dipole moment.
- Now, let's consider H_2O. Both of its bonds are identical once again, but the geometry is bent instead of linear. Hence, the bonds do not cancel each other out, and H_2O has a dipole moment
- Molecules in which the central is symmetrically surrounded by identical atoms (BF_3, CCl_4) are nonpolar.
- For AB_n molecules in which ALL of the B atoms are the same, certain symmetrical geometries – linear (AB_2), trigonal planar (AB_3), tetrahedral and square planar (AB_4), trigonal bipyramidal (AB_5), and octahedral (AB_6) – must lead to nonpolar molecules, regardless of

how polar the individual bonds are.

4.S.4 9.4: COVALENT BONDING AND ORBITAL OVERLAP

A more sophisticated treatment of bonding is needed for systems such as these. In this section, we present a quantum mechanical description of bonding, in which bonding electrons are viewed as being localized between the nuclei of the bonded atoms. The overlap of bonding orbitals is substantially increased through a process called hybridization, which results in the formation of stronger bonds.

Valence bond theory: model of chemical bonding in which an electron-pair bond is formed between two atoms by the overlap of orbitals on the two atoms

- Covalent bonding occurs when atoms share electrons. This increases the electron density between the two nuclei, and is visualized as occurring when a valence atomic orbital of one atom merges with that of another atom
- As the distance between the atoms decreases, their overlap increases. Because of the resultant increase in electron density between the nuclei, the potential energy of the system decreases, increasing the strength of the bond.
- The observed bond length is the distance at which the attractive forces between unlike charges (electrons and nuclei) are balanced by the repulsive forces between like charges (electron-electron and nucleus-nucleus)

4.S.5 9.5: HYBRID ORBITALS

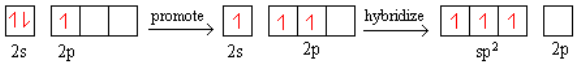
The localized valence bonding theory uses a process called hybridization, in which atomic orbitals that are similar in energy but not equivalent are combined mathematically to produce sets of equivalent orbitals that are properly oriented to form bonds. These new combinations are called hybrid atomic orbitals because they are produced by combining (hybridizing) two or more atomic orbitals from the same atom.

_sp_ Hybrid Orbitals

- Use the salt BeF_2 as an example. Its geometry is linear, however it is now hard to determine which orbitals on the Be atom overlap with those of the F atoms. The electron configuration of Be is $1s^2\ 2s^2$. Hence, Be in its ground state has no unpaired electrons and is unable to form bonds
- Be's only option is to "promote" one of its two electrons in the 2s shell to the 2p shell. It will then have a configuration of $1s^2\ 2s^1\ 2p^1$. Since the 2p orbital is at a higher energy level than the 2s orbital, this promotion requires energy
- The Be atom now has two unpaired electrons (2s and 2p) and would be able to form two bonds, which will not be similar. The two new orbitals are identical in shape (two lobes; one much larger than the other) but are oriented in different directions. Two hybrid orbitals have been created
- **Hybrid orbitals**: orbitals that result from the mixing of different kinds of atomic orbitals on the same atom. For example and sp^3 hybrid results from the mixing, or hybridizing, of one *s* orbital and three *p* orbitals
- **Hybridization**: mixing of different types of atomic orbitals to produce a set of equivalent hybrid orbitals
- In this case, we have hybridized one *s* and one *p* orbital, so we call each hybrid an *sp hybrid orbital*. For the Be atom of BeF_2, the orbital diagram is written as follows: $1s^2\ 2sp^2$
- Hybrid orbitals have one large lobe and can therefore be directed at surrounding atoms more effectively, forming stronger bonds. The energy released by such bonds enables the promotion of a 2s electron to the 2p level.

sp^2 and sp^3 Hybrid Orbitals

- Whenever we mix a certain number of atomic orbitals, we get the same number of hybrid orbitals. Each of these hybrid orbitals is equivalent to the others but points in a different direction.
- Consider BF_3. B has an electron configuration of $2s^2\ 2p^1$. It promotes one of its 2s electron to the 2p orbital to have a configuration of $2s^1\ 2p^2$. Then, it hybridizes into 3 sp^2 hybrid orbitals



The same process can apply to the creation of sp^3 hybrid orbitals

Hybridization Involving *d* Orbitals

Same process as sp^2 orbitals. For example, mixing one *s* orbital, three *p* orbitals, and two *d* orbitals gives six sp^3d^2 hybrid orbitals, which are directed at the vertices of an octahedron

Section Summary

The molecular geometry needs to be known first in order to use the concept of hybridization, then we can use the following rules:

1. Draw the Lewis structure for the molecule or ion
2. Determine the electron-pair geometry using the VSEPR model
3. Specify the hybrid orbitals needed to accommodate the electron pairs based on their geometrical arrangement

4.S.6 9.6: MULTIPLE BONDS

To describe the bonding in more complex molecules with multiple bonds, we can use an approach that uses hybrid atomic orbitals to describe the σσ bonding and molecular orbitals to describe the π bonding. In this approach, unhybridized np orbitals on atoms bonded to one another are allowed to interact to produce bonding, antibonding, or nonbonding combinations.

In each covalent bond we have considered so far, the electron density is concentrated symmetrically about the line that connects the two nuclei (*internuclear axis*). This axis passes through the middle of the overlap region

- **Sigma (σ) bond**: covalent bond in which electron density is concentrated along the internuclear axis
- **Pi (π) bond**: covalent bond in which electron density is concentrated above and below the internuclear axis. Pi bonds are generally weaker than sigma bonds (less overlap)

Usually, single bonds are σ bonds. A double bond has one σ bond and one π bond. A triple bond has one σ bond and two π bonds.

Consider C_2H_4 as an example. After hybridization, C has 3 sp^2 hybrid orbitals and one electron in the remaining unhybridized 2p orbital. The unhybridized 2p electron is directly perpendicular to the plane that contains the three sp^2 hybrid orbitals

- The C – H σ bond is formed by the overlap of a sp^2 hybrid orbital with the 1s orbital of hydrogen. Hence, the bond uses two electrons
- The C – C σ bond is formed by the overlap of two sp^2 hybrid orbitals, one on each carbon atom, and requires two more electrons. Overall, C_2H_4 has 12 valence electrons, 10 of which are used in the formation of the bonds
- The remaining two valence electrons reside in the unhybridized 2p orbitals, one electron on each of the atoms
- The 2p orbitals can overlap with one another in a sideways fashion. This will lead to the electron density being concentrated above and below the C – C bond axis, hence being a π bond

Because π bonds require that portions of a molecule be planar, they can introduce rigidity into molecules (strongly affects the properties of substances)

Although π bonds can be formed from *d* orbitals, we will only consider those formed by *p* orbitals. They can only form if unhybridized *p* orbitals are present on the bonded atoms. Only atoms having *sp* or sp^2 hybridization can be involved in π bonding. Double and triple bonds are more common in molecules with small atoms

Delocalized Bonding

- σ and π electrons are *localized* when they are associated totally with two atoms forming the bond.
- In some molecules, particularly those with more than one resonance form, we cannot accurately describe the bonding as localized. In order to deal with this, we "smear out" the bonds (*delocalize* them) so that it fits both resonance structures as best as possible

Delocalized electrons: electrons that are spread over a number of atoms in a molecule rather than localized between a pair of atoms

Section Summary

1. Every pair of bonded atoms shares one or more pairs of electrons. In every bond, at least one pair of electrons is localized in the space between the atoms, in a σ bond. The appropriate set of hybrid orbitals used to form the σ bonds between an atom and its neighbors is determined by the observed geometry of the molecule
2. The electrons in σ bonds are localized in the region between two bonded atoms and do not make a significant contributions to the bonding between any other two atoms
3. When atoms share more than one pair of electrons, the additional pairs are in π bonds. The centers of chare density in a π bond lie above an below the bond axis.
4. Molecules with two or more resonance forms can have π bonds that extend over more than two bonded atoms. Electrons in π bonds that extend over more than two bonded atoms are said to be delocalized

4.S.6.1 9.7: MOLECULAR ORBITALS

A molecular orbital is an allowed spatial distribution of electrons in a molecule that is associated with a particular orbital energy. Unlike an atomic orbital, which is centered on a single atom, a molecular orbital extends over all the atoms in a molecule or ion. Hence the molecular orbital theory of bonding is a delocalized approach. Molecular orbitals are constructed using linear combinations of atomic orbitals (LCAOs), which describe overlapping atomic orbitals.

- **Molecular orbital theory**: theory that predicts that electrons in molecules exist in allowed energy states.

- **Molecular orbitals**: allowed state for an electron in a molecule. Molecular orbitals are very similar to atomic orbitals. Both hold a maximum of two electrons (with opposite spins), have definite energies, and their electron-density distribution can be visualized by using contour representations. However, molecular orbitals are associated with the *entire* molecule

The Hydrogen Molecule

Consider H_2 as an example. Whenever two atomic orbitals overlap, two molecular orbitals form. Thus, the overlap of the 1s orbitals of two hydrogen atoms to form H_2 produces two molecular orbitals.

Bonding molecular orbital: molecular orbital in which the electron density is concentrated in the internuclear region. The energy of a bonding molecular orbital is lower than the energy of the separate atomic orbitals from which it forms.

The bonding molecular orbital results from summing the two atomic orbitals so that the atomic orbital wave functions enhance each other in the bond region. Because an electron in this molecular orbital is strongly attracted to both nuclei, the electron is more stable (lower energy) than it is in the 1s orbital of hydrogen. Because it concentrates electron density between both nuclei, the bonding molecular orbital holds the atoms together in a covalent bond.

Antibonding molecular orbital: molecular orbital in which electron density is concentrated outside the region between the two nuclei of bonded atoms. Such orbitals, designated as σ* or π*, are less stable (of higher energy) than bonding molecular orbitals

- An electron in the antibonding molecular orbital is repelled from the bonding region and is therefore less stable (higher energy) than it is in the 1s orbital of the hydrogen atom
- **Sigma (σ) molecular orbital**: molecular orbital that centers the electron density about an imaginary line passing through two nuclei
- **Energy level diagram**: aka **Molecular orbital diagram**; diagram that shows the energies of molecular orbitals relative to the atomic orbitals from which they are derived
- Electrons occupying a bonding molecular orbital are called *bonding* electrons

Bond Order

- **Bond order**: related to the stability of a covalent bond.

$$\text{Bond order} = \frac{1}{2}(\text{number of bonding electrons} - \text{number of antibonding electrons})$$

A bond order of 1 represents a single bond, a bond order of 2 represents a double bond, and a bond order of 3 represents a triple bond. A bond order of 0 means that no bonds exist

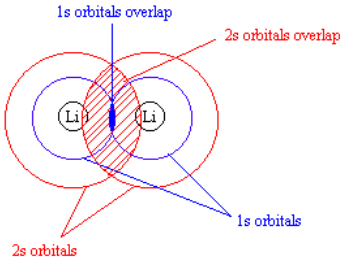
4.S.7 9.8: SECOND-ROW DIATOMIC MOLECULES

Molecular orbital energy-level diagrams for diatomic molecules can be created if the electron configuration of the parent atoms is known, following a few simple rules. Most important, the number of molecular orbitals in a molecule is the same as the number of atomic orbitals that interact. The difference between bonding and antibonding molecular orbital combinations is proportional to the overlap of the parent orbitals and decreases as the energy difference between the atomic orbitals increases.

Material here applies to *homonuclear* diatomic molecules (those composed of identical atoms)

1. The number of atomic orbitals formed equals the number of atomic orbitals combined
2. Atomic orbitals combine most effectively with other atomic orbitals of similar energy
3. The effectiveness with which two atomic orbitals combine is proportional to their overlap with one another; that is, as the overlap increases, the bonding orbital is lowered in energy, and the antibonding orbital is raised in energy
4. Each molecular orbital can accommodate at most two electrons, with their spins paired (Pauli exclusion principle)
5. When molecular orbitals have the same energy, one electron enters each orbital (with parallel spins) before spin pairing occurs (Hund's rule)

Molecular Orbitals for Li_2 and Be_2



The 2.s.orbitals are drawn in red whild the 1.s.orbitals are drawn in blue. There is an overlap between the two 1.s.orbitals and two 2.s.orbitals.

- Lithium has 1s and 2s orbitals, but both are extremely different. According to the Lewis structure of Li_2, there is a single Li – Li bond.
- Because the 1s and 2s orbitals are so different in energy, it is likely that the 1s orbitals interact with each other. (See rule 2)
- This would create a much larger overlap between the 2s orbitals (see figure)
- As a result, the energy seperation between the σ_{2s} and σ^*_{2s} is greater than that for the 1s-based orbitals.
- Each Li atom has 3 electrons; so six electrons must be placed in the molecular orbitals of Li_2
- The electrons occupy the σ_{1s} , σ^*_{1s} , and σ_{2s} orbitals (not the σ^*_{2s} orbital). There are 4 bonding orbitals and 2 nonbonding ones, so the bond order equals ½ (4 – 2) = 1. The molecule has a single bond, in accord with its Lewis structure.

Filled atomic subshells usually do not contribute significantly to bonding in molecule formation

In Be_2, each Be has 4 electrons, for a total of eight. When we place them in molecular orbitals, we fill the σ_{1s} , σ^*_{1s} , σ_{2s} , and σ^*_{2s} orbitals. There is an equal number of bonding and antibonding electrons, so the bond order is 0. Thus, Be_2 doesn't exist.

Molecular Orbitals from *2p* Atomic Orbitals

- *z* axis is internuclear axis (in this example). $2p_z$ orbitals face each other in a "head-to-head" fashion along the *z*-axis. They combine like the *s* orbitals, with one combination concentrating electron density between both nuclei, and the other excluding the electron density from the bonding region. In each of these combinations, the electron density lies along the internuclear axis. Hence, they are σ molecular orbitals: σ_{2p} and σ^*_{2p}
- The other 2p orbitals overlap in a sideways fashion and thus concentrate electron density on opposite sides of the internuclear axis. Molecular orbitals of this type are called **pi molecular orbitals** . We get two π_{2p} molecular orbitals by combining $2p_x$ and $2p_y$ molecular orbitals. The resulting π_{2p} molecular orbitals are degenerate (same energy). Likewise, two degenerate π^*_{2p} antibonding molecular orbitals are formed.
- The $2p_z$ orbitals on two atoms point directly at one another, hence, having a greater overlap than the $2p_x$ and $2p_y$ orbitals. From rule 3, we can expect the σ_{2p} molecular orbital to be lower in energy (more stable) tha n the π_{2p} molecular orbitals.

Electron Configurations for B_2 Through F_2

- The elements Boron through Fluorine all have 2s and 2p valence electrons
- In the energy diagram, the σ_{2p} molecular orbital is at higher energy than the π_{2p} molecular orbitals, contrary to what we would expect from rule 3.
- This is because of interaction between the σ_{2s} and σ_{2p} molecular orbitals. It results in the σ_{2p} molecular orbital being pushed upward in energy to the point where it is above the π_{2p} orbi tals, and the σ_{2s} molecular orbital is pushed down in energy. (The interaction between σ_{2p} and σ_{2s} molecular orbitals decreases as we move from left to right in the second period. As a result, the σ_{2p} is higher in energy than the π_{2p} orbitals for B_2, C_2, and N_2. For O_2, F_2, and Ne_2 , the σ_{2p} orbital is lower in energy than the π_{2p} orbitals)
- Boron has 3 valence electrons. Thus, for B_2, we must place 6 electrons in molecular orbitals. Four of these occupy the σ_{2s} and σ^*_{2s} molecular orbitals, leading to no net bonding. The last two electrons are put in the π_{2p} bonding molecular orbitals; one electron is put in each π_{2p} molecular orbital with the same spin (rule 5). Therefore, B_2 has a bond order of 1.

Electron Configurations and Molecular Properties

- Molecules with one or more unpaired electrons are attracted into a magnetic field. The more unpaired electrons, the stronger the force of the attraction
- **Paramagnetism**: property that a substance possesses if it contains one or more unpaired electrons. A paramagnetic substance is drawn into a magnetic field
- **Diamagnetism**: type of magnetism that causes a substance with no unpaired electrons to be weakly repelled from a magnetic field.
- Diamagnetism is a much weaker effect than paramagnetism
- As bond orders increase, bond distances decrease and bond-dissociation energies increase.

- Molecules with the same bond order do not have the same bond distances and bond-dissociation energies. There are other factors involved, such as nuclear charges and the extend of orbital overlap.

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CHAPTER OVERVIEW

6: GASES

A general chemistry Libretexts Textmap organized around the textbook

Chemistry: The Central Science

by Brown, LeMay, Bursten, Murphy, and Woodward

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Previously, we focused on the *microscopic* properties of matter—the properties of individual atoms, ions, and molecules—and how the electronic structures of atoms and ions determine the stoichiometry and three-dimensional geometry of the compounds they form. We will now focus on *macroscopic* properties—the behavior of aggregates with large numbers of atoms, ions, or molecules. An understanding of macroscopic properties is central to an understanding of chemistry. Why, for example, are many substances gases under normal pressures and temperatures (1.0 atm, 25°C), whereas others are liquids or solids? We will examine each form of matter—gases, liquids, and solids—as well as the nature of the forces, such as hydrogen bonding and electrostatic interactions, that hold molecular and ionic compounds together in these three states.

In this chapter, we explore the relationships among pressure, temperature, volume, and the amount of gases. You will learn how to use these relationships to describe the physical behavior of a sample of both a pure gaseous substance and mixtures of gases. By the end of this chapter, your understanding of the gas laws and the model used to explain the behavior of gases will allow you to explain how straws and hot-air balloons work, why hand pumps cannot be used in wells beyond a certain depth, why helium-filled balloons deflate so rapidly, and how a gas can be liquefied for use in preserving biological tissue.

6.1: Characteristics of Gases
6.2: Pressure
6.3: The Gas Laws
6.4: The Ideal Gas Equation
6.5: Further Applications of the Ideal-Gas Equations
6.6: Gas Mixtures and Partial Pressures
6.7: Kinetic-Molecular Theory
6.8: Molecular Effusion and Diffusion
6.9: Real Gases - Deviations from Ideal Behavior
6.E: Exercises
6.S: Gases (Summary)

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6.1: CHARACTERISTICS OF GASES

LEARNING OBJECTIVES

- To describe the characteristics of a gas.

The three common phases (or states) of matter are gases, liquids, and solids. Gases have the lowest density of the three, are highly compressible, and completely fill any container in which they are placed. Gases behave this way because their intermolecular forces are relatively weak, so their molecules are constantly moving independently of the other molecules present. Solids, in contrast, are relatively dense, rigid, and incompressible because their intermolecular forces are so strong that the molecules are essentially locked in place. Liquids are relatively dense and incompressible, like solids, but they flow readily to adapt to the shape of their containers, like gases. We can therefore conclude that the sum of the intermolecular forces in liquids are between those of gases and solids. Figure **6.1.1** compares the three states of matter and illustrates the differences at the molecular level.

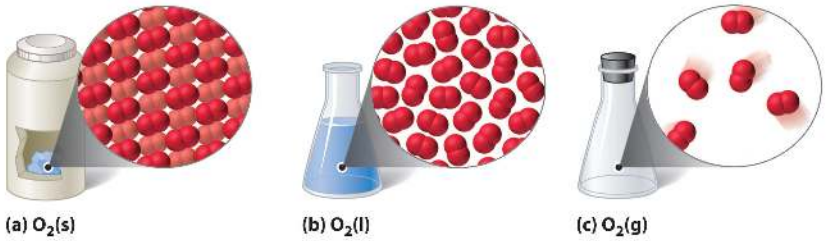


Figure **6.1.1**: A Diatomic Substance (O_2) in the Solid, Liquid, and Gaseous States: (a) Solid O_2 has a fixed volume and shape, and the molecules are packed tightly together. (b) Liquid O_2 conforms to the shape of its container but has a fixed volume; it contains relatively densely packed molecules. (c) Gaseous O_2 fills its container completely—regardless of the container's size or shape—and consists of widely separated molecules.

The state of a given substance depends strongly on conditions. For example, H_2O is commonly found in all three states: solid ice, liquid water, and water vapor (its gaseous form). Under most conditions, we encounter water as the liquid that is essential for life; we drink it, cook with it, and bathe in it. When the temperature is cold enough to transform the liquid to ice, we can ski or skate on it, pack it into a snowball or snow cone, and even build dwellings with it. Water vapor (the term *vapor* refers to the gaseous form of a substance that is a liquid or a solid under normal conditions so nitrogen (N_2) and oxygen (O_2) are referred to as gases, but gaseous water in the atmosphere is called water vapor) is a component of the air we breathe, and it is produced whenever we heat water for cooking food or making coffee or tea. Water vapor at temperatures greater than 100°C is called steam. Steam is used to drive large machinery, including turbines that generate electricity. The properties of the three states of water are summarized in Table 10.1.

Table **6.1.1**: Properties of Water at 1.0 atm

Temperature	State	Density (g/cm3)
≤0°C	solid (ice)	0.9167 (at 0.0°C)
0°C–100°C	liquid (water)	0.9997 (at 4.0°C)
≥100°C	vapor (steam)	0.005476 (at 127°C)

The geometric structure and the physical and chemical properties of atoms, ions, and molecules usually do *not* depend on their physical state; the individual water molecules in ice, liquid water, and steam, for example, are all identical. In contrast, the macroscopic properties of a substance depend strongly on its physical state, which is determined by intermolecular forces and conditions such as temperature and pressure.

Figure **6.1.2** shows the locations in the periodic table of those elements that are commonly found in the gaseous, liquid, and solid states. Except for hydrogen, the elements that occur naturally as gases are on the right side of the periodic table. Of these, all the noble gases (group 18) are monatomic gases, whereas the other gaseous elements are diatomic molecules (**H_2, N_2, O_2, F_2, and Cl_2**). Oxygen can also form a second allotrope, the highly reactive triatomic molecule ozone (**O_3**), which is also a gas. In contrast, bromine (as Br_2) and mercury (Hg) are liquids under normal conditions (25°C and 1.0 atm, commonly referred to as "room temperature and pressure"). Gallium (Ga), which melts at only 29.76°C, can be converted to a liquid simply by holding a container of it in your hand or keeping it in a non-air-conditioned room on a hot summer day. The rest of the elements are all solids under normal conditions.

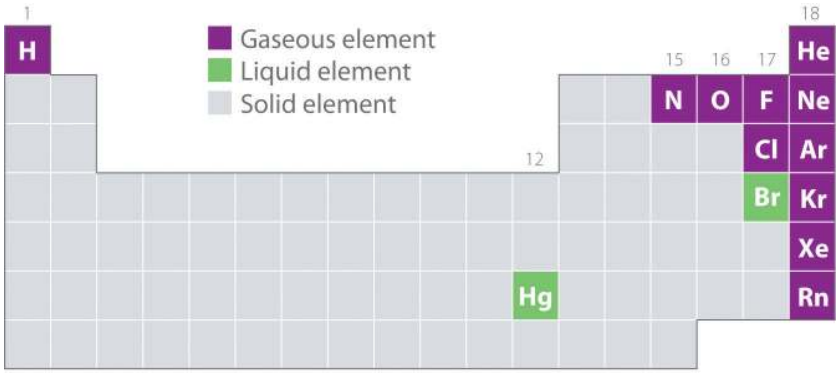


Figure **6.1.2**: Elements That Occur Naturally as Gases, Liquids, and Solids at 25°C and 1 atm. The noble gases and mercury occur as monatomic species, whereas all other gases and bromine are diatomic molecules.

Purple elements are gaseous elements, green are liquid, and gray and solid. H, N, O, F, Cl, He, Ne, Ar, Kr, Xe, and Rn are all purple. Br and Hg are green. The rest are gray.

All of the gaseous elements (other than the monatomic noble gases) are molecules. Within the same group (1, 15, 16 and 17), the lightest elements are gases. All gaseous substances are characterized by weak interactions between the constituent molecules or atoms.

6.1.1 SUMMARY

Bulk matter can exist in three states: gas, liquid, and solid. Gases have the lowest density of the three, are highly compressible, and fill their containers completely. Elements that exist as gases at room temperature and pressure are clustered on the right side of the periodic table; they occur as either monatomic gases (the noble gases) or diatomic molecules (some halogens, N_2, O_2).



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6.2: PRESSURE

LEARNING OBJECTIVES

- to describe and measure the pressure of a gas.

At the macroscopic level, a complete physical description of a sample of a gas requires four quantities:

- ***temperature*** (expressed in kelvins),
- ***volume*** (expressed in liters),
- ***amount*** (expressed in moles), and
- ***pressure*** (in atmospheres).

As we demonstrated below, these variables are *not* independent (i.e., they cannot be arbitrarily be varied). If we know the values of any *three* of these quantities, we can calculate the fourth and thereby obtain a full physical description of the gas. Temperature, volume, and amount have been discussed in previous chapters. We now discuss pressure and its units of measurement.

6.2.1 UNITS OF PRESSURE

Any object, whether it is your computer, a person, or a sample of gas, exerts a force on any surface with which it comes in contact. The air in a balloon, for example, exerts a force against the interior surface of the balloon, and a liquid injected into a mold exerts a force against the interior surface of the mold, just as a chair exerts a force against the floor because of its mass and the effects of gravity. If the air in a balloon is heated, the increased kinetic energy of the gas eventually causes the balloon to burst because of the increased pressure (P) of the gas, the force (F) per unit area (A) of surface:

$$P = \frac{\text{Force}}{\text{Area}} = \frac{F}{A} \tag{6.2.1}$$

Pressure is dependent on *both* the force exerted *and* the size of the area to which the force is applied. We know from Equation 6.2.1 that applying the same force to a smaller area produces a higher pressure. When we use a hose to wash a car, for example, we can increase the pressure of the water by reducing the size of the opening of the hose with a thumb.

The units of pressure are derived from the units used to measure force and area. The SI unit for pressure, derived from the SI units for force (newtons) and area (square meters), is the newton per square meter (N/m^2), which is called the **Pascal (Pa)**, after the French mathematician Blaise Pascal (1623–1662):

$$1\ \text{Pa} = 1\ \text{N/m}^2 \tag{6.2.2}$$

EXAMPLE 6.2.1

Assuming a paperback book has a mass of 2.00 kg, a length of 27.0 cm, a width of 21.0 cm, and a thickness of 4.5 cm, what pressure does it exert on a surface if it is

a. lying flat?
b. standing on edge in a bookcase?

Given: mass and dimensions of object

Asked for: pressure

Strategy:

A. Calculate the force exerted by the book and then compute the area that is in contact with a surface.
B. Substitute these two values into Equation 6.2.1 to find the pressure exerted on the surface in each orientation.

Solution:

The force exerted by the book does *not* depend on its orientation. Recall that the force exerted by an object is $F = ma$, where m is its mass and a is its acceleration. In Earth's gravitational field, the acceleration is due to gravity (9.8067 m/s^2 at Earth's surface). In SI units, the force exerted by the book is therefore

$$F = ma = 2.00\ \text{kg} \times 9.8067 \frac{\text{m}}{\text{s}^2} = 19.6 \frac{\text{kg} \cdot \text{m}}{\text{s}^2} = 19.6\ \text{N}$$

A We calculated the force as 19.6 N. When the book is lying flat, the area is

$$A = 0.270\ \text{m} \times 0.210\ \text{m} = 0.0567\ \text{m}^2.$$

B The pressure exerted by the text lying flat is thus

$$P = \frac{F}{A} = \frac{19.6\ \text{N}}{0.0567\ \text{m}^2} = 3.46 \times 10^2 \text{Pa}$$

A If the book is standing on its end, the force remains the same, but the area decreases:

$$\text{A} = 21.0\ \text{cm} \times 4.5\ \text{cm} = 0.210\ \text{m} \times 0.045\ \text{m} = 9.5 \times 10^{-3}\ \text{m}^2$$

B The pressure exerted by the text lying flat is thus

$$P = \frac{19.6\ \text{N}}{9.5 \times 10^{-3}\ \text{m}^2} = 2.06 \times 10^3\ \text{Pa}$$

? EXERCISE 6.2.1

What pressure does a 60.0 kg student exert on the floor

a. when standing flat-footed in the laboratory in a pair of tennis shoes (the surface area of the soles is approximately 180 cm^2)?
b. as she steps heel-first onto a dance floor wearing high-heeled shoes (the area of the heel = 1.0 cm^2)?

Answer a

3.27×10^4 Pa

Answer b

5.9×10^6 Pa

6.2.2 BAROMETRIC PRESSURE

Just as we exert pressure on a surface because of gravity, so does our atmosphere. We live at the bottom of an ocean of gases that becomes progressively less dense with increasing altitude. Approximately 99% of the mass of the atmosphere lies within 30 km of Earth's surface (Figure **6.2.1**). Every point on Earth's surface experiences a net pressure called ***barometric pressure***. The pressure exerted by the atmosphere is considerable: a 1 m^2 column, measured from sea level to the top of the atmosphere, has a mass of about 10,000 kg, which gives a pressure of about 101 kPa:

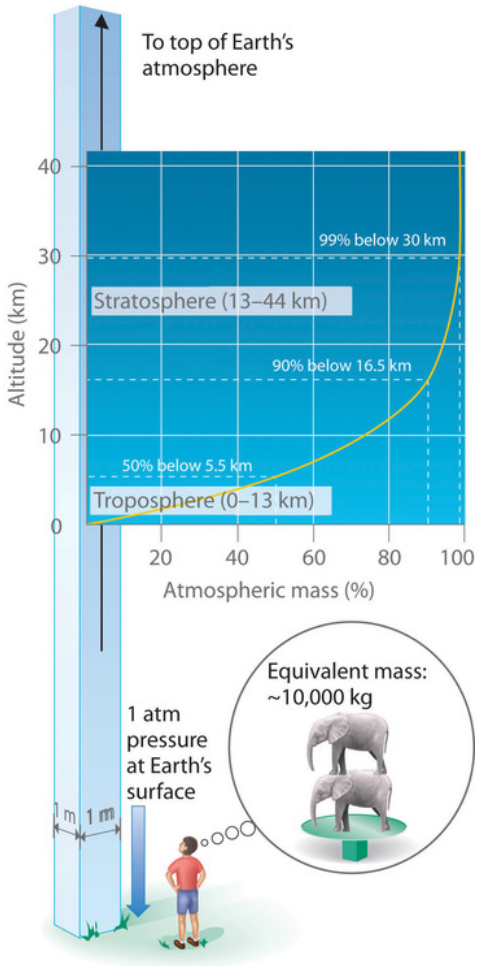


Figure **6.2.1**: Barometric Pressure. Each square meter of Earth's surface supports a column of air that is more than 200 km high and weighs about 10,000 kg at Earth's surface.

Barometric pressure can be measured using a barometer, a device invented in 1643 by one of Galileo's students, Evangelista Torricelli (1608–1647). A barometer may be constructed from a long glass tube that is closed at one end. It is filled with mercury and placed upside down in a dish of mercury without allowing any air to enter the tube. Some of the mercury will run out of the tube, but a relatively tall column remains inside (Figure **6.2.2**). Why doesn't all the mercury run out? Gravity is certainly exerting a downward force on the mercury in the tube, but it is opposed by the pressure of the atmosphere pushing down on the surface of the mercury in the dish, which has the net effect of pushing the mercury up into the tube. Because there is no air above the mercury inside the tube in a properly filled barometer (it contains a vacuum), there is no pressure pushing down on the column. Thus the mercury runs out of the tube until the pressure exerted by the mercury column itself exactly balances the pressure of the atmosphere. The pressure exerted by the mercury column can be expressed as:

$$P = \frac{F}{A} \tag{6.2.3}$$

$$= \frac{mg}{A} \tag{6.2.4}$$

$$= \frac{\rho V \cdot g}{A} \tag{6.2.5}$$

$$= \frac{\rho \cdot Ah \cdot g}{A} \tag{6.2.6}$$

$$= \rho gh \tag{6.2.7}$$

with

- g is the gravitational acceleration,
- m is the mass,
- ρ is the density,

- V is the volume,
- A is the bottom area, and
- h is height of the mercury column.

Under normal weather conditions at sea level, the two forces are balanced when the top of the mercury column is approximately 760 mm above the level of the mercury in the dish, as shown in Figure **6.2.2**. This value varies with meteorological conditions and altitude. In Denver, Colorado, for example, at an elevation of about 1 mile, or 1609 m (5280 ft), the height of the mercury column is 630 mm rather than 760 mm.

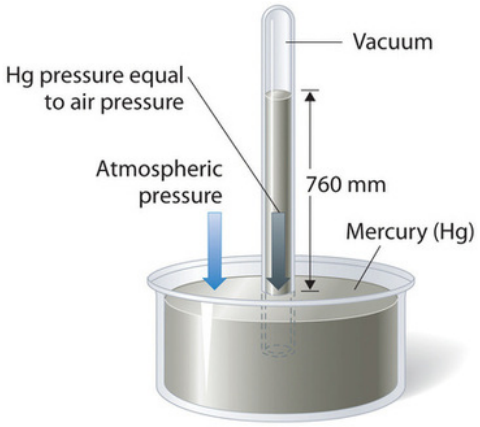


Figure **6.2.2**: A Mercury Barometer. The pressure exerted by the atmosphere on the surface of the pool of mercury supports a column of mercury in the tube that is about 760 mm tall. Because the boiling point of mercury is quite high (356.73°C), there is very little mercury vapor in the space above the mercury column.

Mercury barometers have been used to measure barometric pressure for so long that they have their own unit for pressure: the millimeter of mercury (mmHg), often called the torr, after Torricelli. Standard barometric pressure is the barometric pressure required to support a column of mercury exactly 760 mm tall; this pressure is also referred to as 1 atmosphere (atm). These units are also related to the pascal:

$$1 \text{ atm} = 760\ mmHg \tag{6.2.8}$$
$$= 760\ torr \tag{6.2.9}$$
$$= 1.01325 \times 10^5\ Pa \tag{6.2.10}$$
$$= 101.325\ kPa \tag{6.2.11}$$

Thus a pressure of 1 atm equals 760 mmHg exactly.

We are so accustomed to living under this pressure that we never notice it. Instead, what we notice are *changes* in the pressure, such as when our ears pop in fast elevators in skyscrapers or in airplanes during rapid changes in altitude. We make use of barometric pressure in many ways. We can use a drinking straw because sucking on it removes air and thereby reduces the pressure inside the straw. The barometric pressure pushing down on the liquid in the glass then forces the liquid up the straw.

✔ EXAMPLE 6.2.2: BAROMETRIC PRESSURE

One of the authors visited Rocky Mountain National Park several years ago. After departing from an airport at sea level in the eastern United States, he arrived in Denver (altitude 5280 ft), rented a car, and drove to the top of the highway outside Estes Park (elevation 14,000 ft). He noticed that even slight exertion was very difficult at this altitude, where the barometric pressure is only 454 mmHg. Convert this pressure to

a. atmospheres (atm).
b. bar.

Given: pressure in millimeters of mercury

Asked for: pressure in atmospheres and bar

Strategy:

Use the conversion factors in Equation 6.2.11 to convert from millimeters of mercury to atmospheres and kilopascals.

Solution:

From Equation 6.2.11, we have 1 atm = 760 mmHg = 101.325 kPa. The pressure at 14,000 ft in atm is thus

$$P = 454 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} \tag{6.2.12}$$
$$= 0.597 \ atm$$

The pressure in bar is given by

$$P = 0.597 \text{ atm} \times \frac{1.01325 \text{ bar}}{1 \text{ atm}} \tag{6.2.13}$$
$$= 0.605 \ bar$$

? EXERCISE 6.2.2: BAROMETRIC PRESSURE

Mt. Everest, at 29,028 ft above sea level, is the world's tallest mountain. The normal barometric pressure at this altitude is about 0.308 atm. Convert this pressure to

a. millimeters of mercury.
b. bar.

Answer a

234 mmHg;

Answer b

0.312 bar

6.2.3 MANOMETERS

Barometers measure barometric pressure, but manometers measure the pressures of samples of gases contained in an apparatus. The key feature of a manometer is a U-shaped tube containing mercury (or occasionally another nonvolatile liquid). A closed-end manometer is shown schematically in part (a) in Figure **6.2.3**. When the bulb contains no gas (i.e., when its interior is a near vacuum), the heights of the two columns of mercury are the same because the space above the mercury on the left is a near vacuum (it contains only traces of mercury vapor). If a gas is released into the bulb on the right, it will exert a pressure on the mercury in the right column, and the two columns of mercury will no longer be the same height. The *difference* between the heights of the two columns is equal to the pressure of the gas.

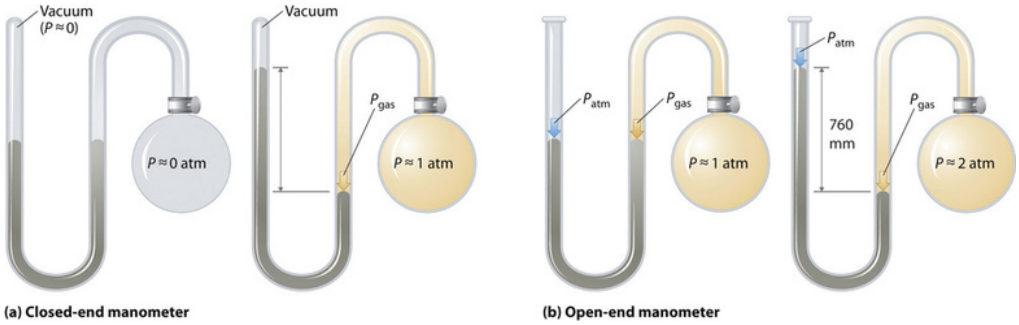


Figure **6.2.3**: The Two Types of Manometer. (a) In a closed-end manometer, the space above the mercury column on the left (the reference arm) is essentially a vacuum ($P \approx 0$), and the difference in the heights of the two columns gives the pressure of the gas contained in the bulb directly. (b) In an open-end manometer, the left (reference) arm is open to the atmosphere ($P \approx 1$ atm), and the difference in the heights of the two columns gives the *difference* between barometric pressure and the pressure of the gas in the bulb.

If the tube is open to the atmosphere instead of closed, as in the open-end manometer shown in part (b) in Figure **6.2.3**, then the two columns of mercury have the same height only if the gas in the bulb has a pressure equal to the barometric pressure. If the gas in the bulb has a *higher* pressure, the mercury in the open tube will be forced up by the gas pushing down on the mercury in the other arm of the U-shaped tube. The pressure of the gas in the bulb is therefore the sum of the barometric pressure (measured with a barometer) and the difference in the heights of the two columns. If the gas in the bulb has a pressure *less* than that of the atmosphere, then the height of the mercury will be greater in the arm attached to the bulb. In this case, the pressure of the gas in the bulb is the barometric pressure minus the difference in the heights of the two columns.

EXAMPLE 6.2.3

Suppose you want to construct a closed-end manometer to measure gas pressures in the range 0.000–0.200 atm. Because of the toxicity of mercury, you decide to use water rather than mercury. How tall a column of water do you need? (The density of water is 1.00 g/cm^3; the density of mercury is 13.53 g/cm^3.)

Given: pressure range and densities of water and mercury

Asked for: column height

Strategy:

A. Calculate the height of a column of mercury corresponding to 0.200 atm in millimeters of mercury. This is the height needed for a mercury-filled column.
B. From the given densities, use a proportion to compute the height needed for a water-filled column.

Solution:

A In millimeters of mercury, a gas pressure of 0.200 atm is

$$P = 0.200\ \text{atm} \times \frac{760\ \text{mmHg}}{1\ \text{atm}} = 152\ \text{mmHg}$$

Using a mercury manometer, you would need a mercury column at least 152 mm high.

B Because water is less dense than mercury, you need a *taller* column of water to achieve the same pressure as a given column of mercury. The height needed for a water-filled column corresponding to a pressure of 0.200 atm is proportional to the ratio of the density of mercury to the density of water

$$P = d_{\text{wat}} g h_{\text{wat}} = d_{\text{Hg}} g h_{\text{Hg}}$$

$$h_{\text{wat}} = h_{\text{Hg}} \times \frac{d_{\text{Hg}}}{g_{\text{wat}}} = 152\ \text{mm} \times \frac{13.53\ \text{g/cm}^3}{1.00\ \text{g/cm}^3} = 2070\ \text{mm}$$

The answer makes sense: it takes a taller column of a less dense liquid to achieve the same pressure.

EXERCISE 6.2.3

Suppose you want to design a barometer to measure barometric pressure in an environment that is always hotter than 30°C. To avoid using mercury, you decide to use gallium, which melts at 29.76°C; the density of liquid gallium at 25°C is 6.114 g/cm^3. How tall a column of gallium do you need if P = 1.00 atm?

Answer

1.68 m

The answer to Example **6.2.3** also tells us the maximum depth of a farmer's well if a simple suction pump will be used to get the water out. The 1.00 atm corresponds to a column height of

$$\begin{aligned} h_{\text{wat}} &= h_{\text{Hg}} \times \frac{d_{\text{Hg}}}{g_{\text{wat}}} \\ &= 760\ \text{mm} \times \frac{13.53\ \text{g/cm}^3}{1.00\ \text{g/cm}^3} \\ &= 1.03 \times 10^4\ mm \\ &= 10.3\ m \end{aligned}$$

A suction pump is just a more sophisticated version of a straw: it creates a vacuum above a liquid and relies on barometric pressure to force the liquid up a tube. If 1 atm pressure corresponds to a 10.3 m (33.8 ft) column of water, then it is physically impossible for barometric pressure to raise the water in a well higher than this. Until electric pumps were invented to push water mechanically from greater depths, this factor greatly limited where people could live because obtaining water from wells deeper than about 33 ft was difficult.

6.2.4 SUMMARY

Pressure is defined as the force exerted per unit area; it can be measured using a barometer or manometer. Four quantities must be known for a complete physical description of a sample of a gas: *temperature*, *volume*, *amount*, and *pressure*. **Pressure** is force per unit area of

surface; the SI unit for pressure is the **pascal (Pa)**, defined as 1 newton per square meter (N/m^2). The pressure exerted by an object is proportional to the force it exerts and inversely proportional to the area on which the force is exerted. The pressure exerted by Earth's atmosphere, called *barometric pressure*, is about 101 kPa or 14.7 $lb/in.^2$ at sea level. barometric pressure can be measured with a **barometer**, a closed, inverted tube filled with mercury. The height of the mercury column is proportional to barometric pressure, which is often reported in units of **millimeters of mercury (mmHg)**, also called **torr**. **Standard barometric pressure**, the pressure required to support a column of mercury 760 mm tall, is yet another unit of pressure: 1 **atmosphere (atm)**. A **manometer** is an apparatus used to measure the pressure of a sample of a gas.



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6.3: THE GAS LAWS

LEARNING OBJECTIVES

- To understand the relationships among pressure, temperature, volume, and the amount of a gas.

Early scientists explored the relationships among the pressure of a gas (P) and its temperature (T), volume (V), and amount (n) by holding two of the four variables constant (amount and temperature, for example), varying a third (such as pressure), and measuring the effect of the change on the fourth (in this case, volume). The history of their discoveries provides several excellent examples of the scientific method.

6.3.1 THE RELATIONSHIP BETWEEN PRESSURE AND VOLUME: BOYLE'S LAW

As the pressure on a gas increases, the volume of the gas decreases because the gas particles are forced closer together. Conversely, as the pressure on a gas decreases, the gas volume increases because the gas particles can now move farther apart. Weather balloons get larger as they rise through the atmosphere to regions of lower pressure because the volume of the gas has increased; that is, the atmospheric gas exerts less pressure on the surface of the balloon, so the interior gas expands until the internal and external pressures are equal.

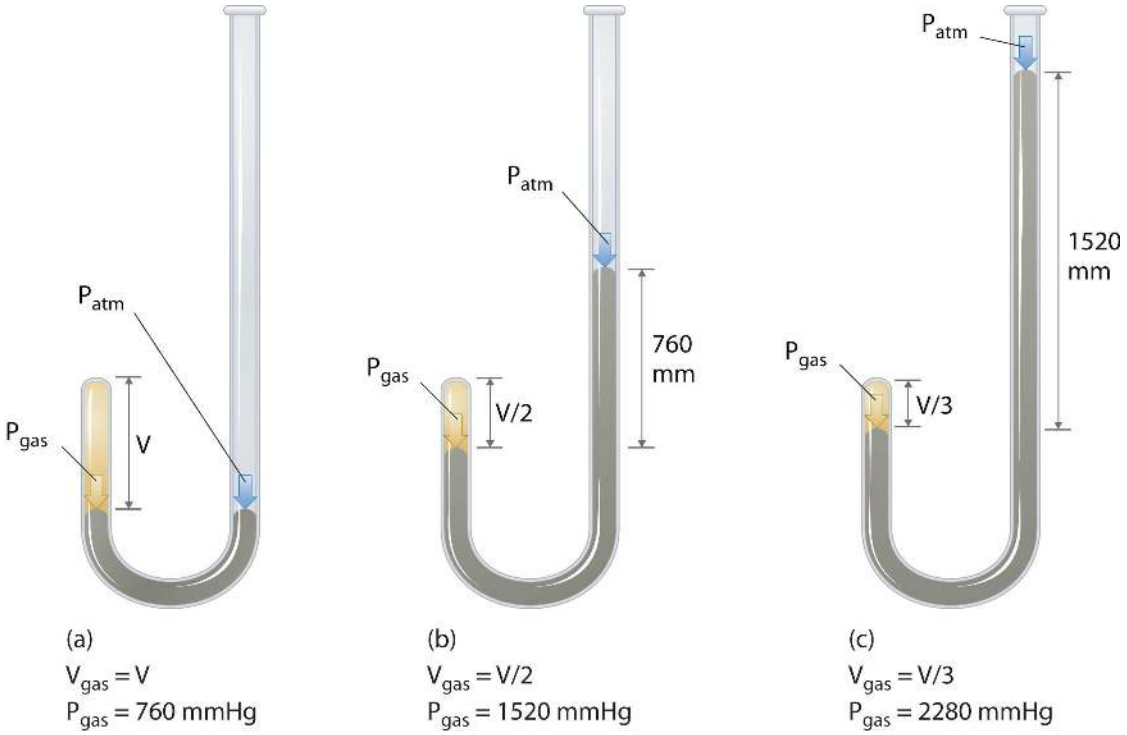


Figure **6.3.1**: Boyle's Experiment Using a J-Shaped Tube to Determine the Relationship between Gas Pressure and Volume. (a) Initially the gas is at a pressure of 1 atm = 760 mmHg (the mercury is at the same height in both the arm containing the sample and the arm open to the atmosphere); its volume is V. (b) If enough mercury is added to the right side to give a difference in height of 760 mmHg between the two arms, the pressure of the gas is 760 mmHg (atmospheric pressure) + 760 mmHg = 1520 mmHg and the volume is $V/2$. (c) If an additional 760 mmHg is added to the column on the right, the total pressure on the gas increases to 2280 mmHg, and the volume of the gas decreases to $V/3$ (CC BY-SA-NC; anonymous).

The Irish chemist Robert Boyle (1627–1691) carried out some of the earliest experiments that determined the quantitative relationship between the pressure and the volume of a gas. Boyle used a J-shaped tube partially filled with mercury, as shown in Figure **6.3.1**. In these experiments, a small amount of a gas or air is trapped above the mercury column, and its volume is measured at atmospheric pressure and constant temperature. More mercury is then poured into the open arm to increase the pressure on the gas sample. The pressure on the gas is atmospheric pressure plus the difference in the heights of the mercury columns, and the resulting volume is measured. This process is repeated until either there is no more room in the open arm or the volume of the gas is too small to be measured accurately. Data such as those from one of Boyle's own experiments may be plotted in several ways (Figure **6.3.2**). A simple plot of $\boldsymbol{V}$ versus $\boldsymbol{P}$ gives a curve called a hyperbola and reveals an inverse relationship between pressure and volume: as the pressure is doubled, the volume decreases by a factor of two. This relationship between the two quantities is described as follows:

$$PV = \text{constant} \tag{6.3.1}$$

Dividing both sides by P gives an equation illustrating the inverse relationship between P and V:

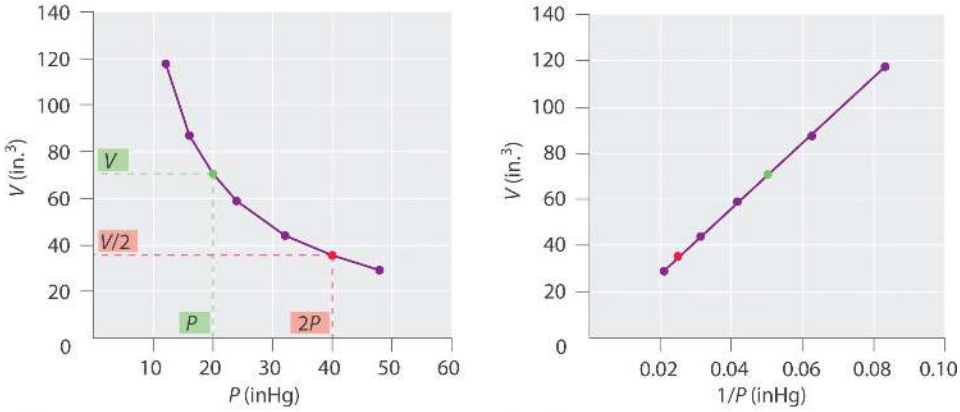
$$V = \frac{\text{const.}}{P} = \text{const.}\left(\frac{1}{P}\right) \tag{6.3.2}$$

or

$$V \propto \frac{1}{P} \tag{6.3.3}$$

where the ∝ symbol is read "is proportional to." A plot of V versus $1/P$ is thus a straight line whose slope is equal to the constant in Equations 6.3.1 and 6.3.3. Dividing both sides of Equation 6.3.1 by V instead of P gives a similar relationship between P and $1/V$. The numerical value of the constant depends on the amount of gas used in the experiment and on the temperature at which the experiments are carried out. This relationship between pressure and volume is known as Boyle's law, after its discoverer, and can be stated as follows: *At constant temperature, the volume of a fixed amount of a gas is inversely proportional to its pressure.* This law in practice is shown in Figure 6.3.2.

P (inHg)	V (in.^{3})	PV
12.0	117.5	1410
16.0	87.2	1400
20.0	70.7	1410
24.0	58.8	1410
32.0	44.2	1410
40.0	35.3	1410
48.0	29.1	1400



(a) Data from Boyle's experiment **(b) Volume vs. pressure** **(c) Volume vs. 1/pressure**

Figure 6.3.2: Plots of Boyle's Data. (a) Here are actual data from a typical experiment conducted by Boyle. Boyle used non-SI units to measure the volume (in.^{3} rather than cm^3) and the pressure (in. Hg rather than mmHg). (b) This plot of pressure versus volume is a hyperbola. Because PV is a constant, decreasing the pressure by a factor of two results in a twofold increase in volume and vice versa. (c) A plot of volume versus 1/pressure for the same data shows the inverse linear relationship between the two quantities, as expressed by the equation V = constant/P (CC BY-SA-NC; anonymous).

> *At constant temperature, the volume of a fixed amount of a gas is inversely proportional to its pressure*



6.3.2 THE RELATIONSHIP BETWEEN TEMPERATURE AND VOLUME: CHARLES'S LAW

Hot air rises, which is why hot-air balloons ascend through the atmosphere and why warm air collects near the ceiling and cooler air collects at ground level. Because of this behavior, heating registers are placed on or near the floor, and vents for air-conditioning are placed on or near the ceiling. The fundamental reason for this behavior is that gases expand when they are heated. Because the same amount of substance

now occupies a greater volume, hot air is less dense than cold air. The substance with the lower density—in this case hot air—rises through the substance with the higher density, the cooler air.

The first experiments to quantify the relationship between the temperature and the volume of a gas were carried out in 1783 by an avid balloonist, the French chemist Jacques Alexandre César Charles (1746–1823). Charles's initial experiments showed that a plot of the volume of a given sample of gas versus temperature (in degrees Celsius) at constant pressure is a straight line. Similar but more precise studies were carried out by another balloon enthusiast, the Frenchman Joseph-Louis Gay-Lussac (1778–1850), who showed that a plot of V versus T was a straight line that could be extrapolated to a point at zero volume, a theoretical condition now known to correspond to −273.15°C (Figure **6.3.3**).A sample of gas cannot really have a volume of zero because any sample of matter must have some volume. Furthermore, at 1 atm pressure all gases liquefy at temperatures well above −273.15°C. Note from part (a) in Figure **6.3.3** that the slope of the plot of V versus T varies for the same gas at different pressures but that the intercept remains constant at −273.15°C. Similarly, as shown in part (b) in Figure **6.3.3**, plots of V versus T for different amounts of varied gases are straight lines with different slopes but the same intercept on the T axis.

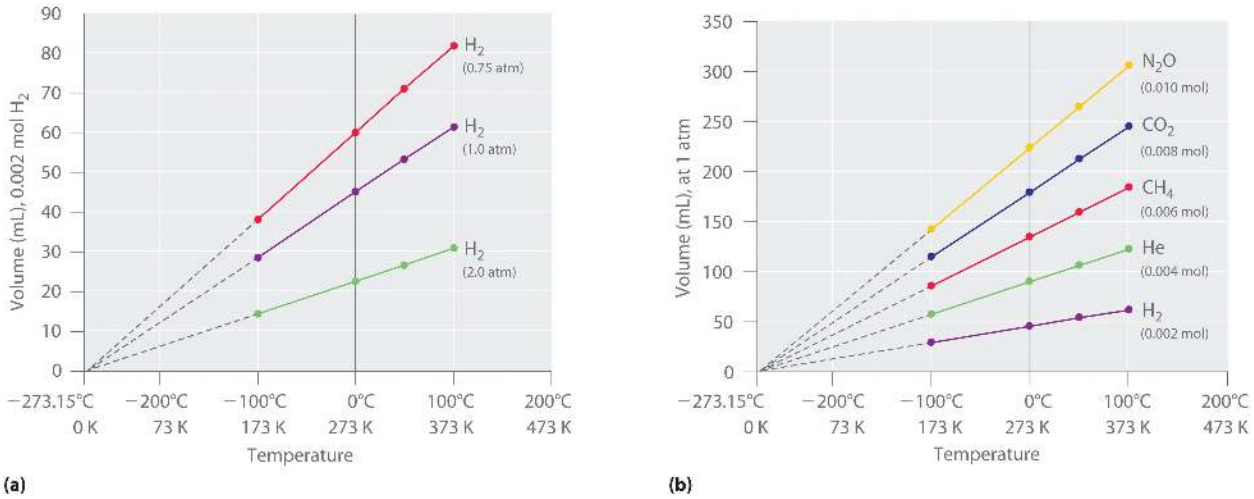


Figure **6.3.3**: The Relationship between Volume and Temperature. (a) In these plots of volume versus temperature for equal-sized samples of H_2 at three different pressures, the solid lines show the experimentally measured data down to −100°C, and the broken lines show the extrapolation of the data to $V = 0$. The temperature scale is given in both degrees Celsius and kelvins. Although the slopes of the lines decrease with increasing pressure, all of the lines extrapolate to the same temperature at $V = 0$ (−273.15°C = 0 K). (b) In these plots of volume versus temperature for different amounts of selected gases at 1 atm pressure, all the plots extrapolate to a value of $V = 0$ at −273.15°C, regardless of the identity or the amount of the gas (CC BY-SA-NC; anonymous).

The significance of the invariant T intercept in plots of V versus T was recognized in 1848 by the British physicist William Thomson (1824–1907), later named Lord Kelvin. He postulated that −273.15°C was the lowest possible temperature that could theoretically be achieved, for which he coined the term absolute zero (0 K).

We can state Charles's and Gay-Lussac's findings in simple terms: At constant pressure, the volume of a fixed amount of gas is directly proportional to its absolute temperature (in kelvins). This relationship, illustrated in part (b) in Figure **6.3.3** is often referred to as Charles's law and is stated mathematically as

$$V = \text{const.}\, T \tag{6.3.4}$$

or

$$V \propto T \tag{6.3.5}$$

with *temperature expressed in kelvins*, not *in degrees Celsius.* Charles's law is valid for virtually all gases at temperatures well above their boiling points.



6.3.3 THE RELATIONSHIP BETWEEN AMOUNT AND VOLUME: AVOGADRO'S LAW

We can demonstrate the relationship between the volume and the amount of a gas by filling a balloon; as we add more gas, the balloon gets larger. The specific quantitative relationship was discovered by the Italian chemist Amedeo Avogadro, who recognized the importance of Gay-Lussac's work on combining volumes of gases. In 1811, Avogadro postulated that, at the same temperature and pressure, equal volumes of gases contain the same number of gaseous particles (Figure **6.3.4**). This is the historic "Avogadro's hypothesis."

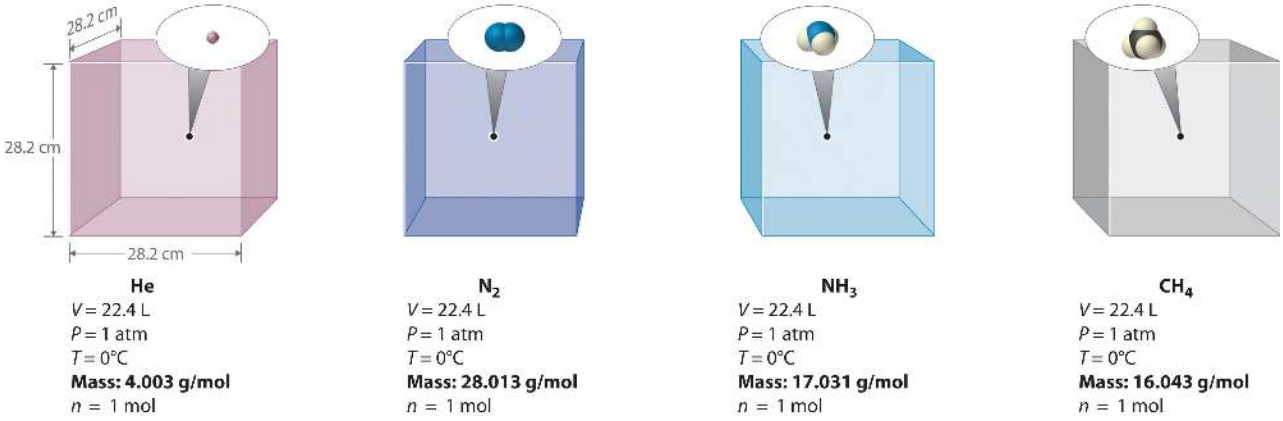


Figure **6.3.4**: Avogadro's Hypothesis. Equal volumes of four different gases at the same temperature and pressure contain the same number of gaseous particles. Because the molar mass of each gas is different, the *mass* of each gas sample is different even though all contain 1 mol of gas (CC BY-SA-NC; anonymous).

A logical corollary to Avogadro's hypothesis (sometimes called Avogadro's law) describes the relationship between the volume and the amount of a gas: *At constant temperature and pressure, the volume of a sample of gas is directly proportional to the number of moles of gas in the sample.* Stated mathematically,

$$V = \text{const.}\ (n) \tag{6.3.6}$$

or

$$V \propto .n@\ \text{constant T and P} \tag{6.3.7}$$

This relationship is valid for most gases at relatively low pressures, but deviations from strict linearity are observed at elevated pressures.



For a sample of gas,

- V increases as P decreases (and vice versa)
- V increases as T increases (and vice versa)
- V increases as n increases (and vice versa)

The relationships among the volume of a gas and its pressure, temperature, and amount are summarized in Figure **6.3.5**. Volume *increases* with increasing temperature or amount, but *decreases* with increasing pressure.

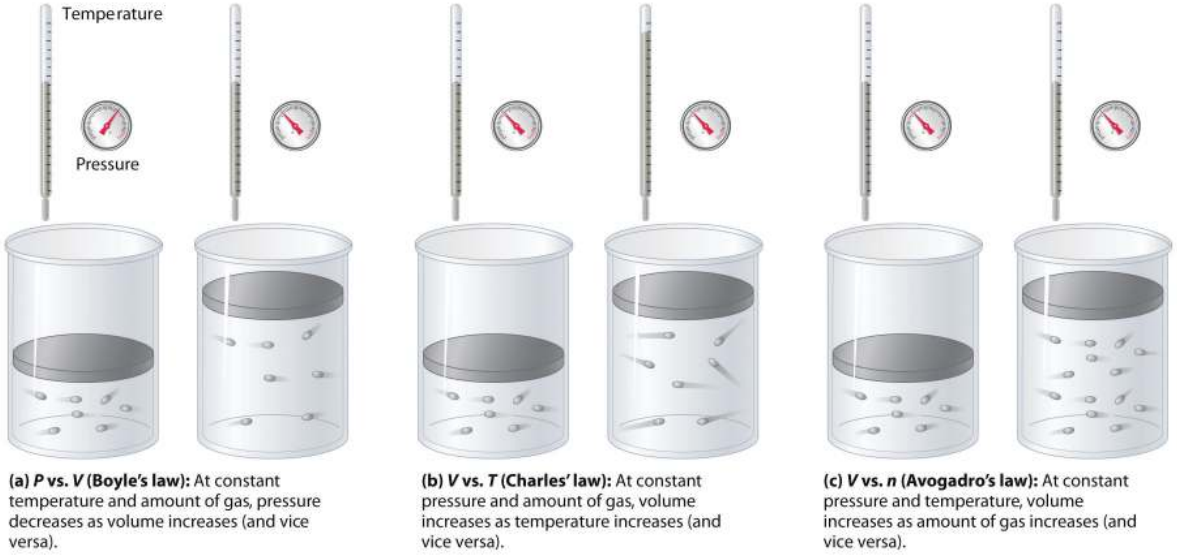


Figure **6.3.5**: The Empirically Determined Relationships among Pressure, Volume, Temperature, and Amount of a Gas. The thermometer and pressure gauge indicate the temperature and the pressure qualitatively, the level in the flask indicates the volume, and the number of particles in each flask indicates relative amounts (CC BY-SA-NC; anonymous).

6.3.4 SUMMARY

The volume of a gas is inversely proportional to its pressure and directly proportional to its temperature and the amount of gas. Boyle showed that the volume of a sample of a gas is inversely proportional to its pressure (**Boyle's law**), Charles and Gay-Lussac demonstrated that the volume of a gas is directly proportional to its temperature (in kelvins) at constant pressure (**Charles's law**), and Avogadro postulated that the volume of a gas is directly proportional to the number of moles of gas present (**Avogadro's law**). Plots of the volume of gases versus temperature extrapolate to zero volume at −273.15°C, which is **absolute zero (0 K)**, the lowest temperature possible. Charles's law implies that the volume of a gas is directly proportional to its absolute temperature.

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6.4: THE IDEAL GAS EQUATION

LEARNING OBJECTIVES

- Derive the ideal gas law from the constituent gas laws
- To use the ideal gas law to describe the behavior of a gas.

In this module, the relationship between pressure, temperature, volume, and amount of a gas are described and how these relationships can be combined to give a general expression that describes the behavior of a gas.

6.4.1 DERIVING THE IDEAL GAS LAW

Any set of relationships between a single quantity (such as V) and several other variables (P, T, and n) can be combined into a single expression that describes all the relationships simultaneously. The three individual expressions were derived previously:

- **Boyle's law**

$$V \propto \frac{1}{P} \text{ at constant n and T}$$

- **Charles's law**

$$V \propto T \text{ at constant n and P}$$

- **Avogadro's law**

$$V \propto n \text{ at constant T and P}$$

Combining these three expressions gives

$$V \propto \frac{nT}{P} \tag{6.4.1}$$

which shows that the volume of a gas is proportional to the number of moles and the temperature and inversely proportional to the pressure. This expression can also be written as

$$V = \text{Cons.}\left(\frac{nT}{P}\right) \tag{6.4.2}$$

By convention, the proportionality constant in Equation 6.4.1 is called the gas constant, which is represented by the letter R. Inserting R into Equation 6.4.2 gives

$$V = \frac{RnT}{P} = \frac{nRT}{P} \tag{6.4.3}$$

Clearing the fractions by multiplying both sides of Equation 6.4.4 by P gives

$$PV = nRT \tag{6.4.4}$$

This equation is known as the **ideal gas law**.

An ideal gas is defined as a hypothetical gaseous substance whose behavior is independent of attractive and repulsive forces and can be completely described by the ideal gas law. In reality, there is no such thing as an ideal gas, but an ideal gas is a useful conceptual model that allows us to understand how gases respond to changing conditions. As we shall see, under many conditions, most real gases exhibit behavior that closely approximates that of an ideal gas. The ideal gas law can therefore be used to predict the behavior of real gases under most conditions. The ideal gas law does not work well at very low temperatures or very high pressures, where deviations from ideal behavior are most commonly observed.

> *Significant deviations from ideal gas behavior commonly occur at low temperatures and very high pressures.*

Before we can use the ideal gas law, however, we need to know the value of the gas constant R. Its form depends on the units used for the other quantities in the expression. If V is expressed in liters (L), P in atmospheres (atm), T in kelvins (K), and n in moles (mol), then

$$R = 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \tag{6.4.5}$$

Because the product PV has the units of energy, R can also have units of J/(K•mol):

$$R = 8.3145 \frac{\text{J}}{\text{K} \cdot \text{mol}} \tag{6.4.6}$$

6.4.2 STANDARD CONDITIONS OF TEMPERATURE AND PRESSURE

Scientists have chosen a particular set of conditions to use as a reference: 0°C (273.15 K) and **1 atm** pressure, referred to as standard temperature and pressure (**STP**).

$$\text{STP:} \qquad T = 273.15 \text{ K and } P = 1 \text{ atm} \tag{6.4.7}$$

We can calculate the volume of 1.000 mol of an ideal gas under standard conditions using the variant of the ideal gas law given in Equation 6.4.4:

$$V = \frac{nRT}{P} \tag{6.4.8}$$

Thus the volume of 1 mol of an ideal gas is **22.41 L at STP**, approximately equivalent to the volume of three basketballs. The molar volumes of several real gases at 0°C and 1 atm are given in Table 10.3, which shows that the deviations from ideal gas behavior are quite small. Thus the ideal gas law does a good job of approximating the behavior of real gases at 0°C and 1 atm. The relationships described in Section 10.3 as Boyle's, Charles's, and Avogadro's laws are simply special cases of the ideal gas law in which two of the four parameters (P, V, T, and n) are held fixed.

Table **6.4.1**: Molar Volumes of Selected Gases at 0°C and 1 atm

Gas	Molar Volume (L)
He	22.434
Ar	22.397
H_2	22.433
N_2	22.402
O_2	22.397
CO_2	22.260
NH_3	22.079

6.4.3 APPLYING THE IDEAL GAS LAW

The ideal gas law allows us to calculate the value of the fourth variable for a gaseous sample if we know the values of any three of the four variables (*P*, *V*, *T*, and *n*). It also allows us to predict the *final state* of a sample of a gas (i.e., its final temperature, pressure, volume, and amount) following any changes in conditions if the parameters (*P*, *V*, *T*, and *n*) are specified for an *initial state*. Some applications are illustrated in the following examples. The approach used throughout is always to start with the same equation—the ideal gas law—and then determine which quantities are given and which need to be calculated. Let's begin with simple cases in which we are given three of the four parameters needed for a complete physical description of a gaseous sample.

✔ EXAMPLE 6.4.1

The balloon that Charles used for his initial flight in 1783 was destroyed, but we can estimate that its volume was 31,150 L (1100 ft^3), given the dimensions recorded at the time. If the temperature at ground level was 86°F (30°C) and the atmospheric pressure was 745 mmHg, how many moles of hydrogen gas were needed to fill the balloon?

Given: volume, temperature, and pressure

Asked for: amount of gas

Strategy:

A. Solve the ideal gas law for the unknown quantity, in this case *n*.

B. Make sure that all quantities are given in units that are compatible with the units of the gas constant. If necessary, convert them to the appropriate units, insert them into the equation you have derived, and then calculate the number of moles of hydrogen gas needed.

Solution:

A We are given values for *P*, *T*, and *V* and asked to calculate *n*. If we solve the ideal gas law (Equation 6.4.4) for n, we obtain

$$745 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 0.980 \text{ atm}$$

B *P* and *T* are given in units that are not compatible with the units of the gas constant [*R* = 0.08206 (L•atm)/(K•mol)]. We must therefore convert the temperature to kelvins and the pressure to atmospheres:

$$T = 273 + 30 = 303\text{K}$$

Substituting these values into the expression we derived for *n*, we obtain

$$\begin{aligned} n &= \frac{PV}{RT} \\ &= \frac{0.980 \text{ atm} \times 31150 \text{ L}}{0.08206 \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 303 \text{ K}} \\ &= 1.23 \times 10^3 \; mol \end{aligned}$$

? EXERCISE 6.4.1

Suppose that an “empty” aerosol spray-paint can has a volume of 0.406 L and contains 0.025 mol of a propellant gas such as CO_2. What is the pressure of the gas at 25°C?

Answer

1.5 atm

In Example 6.4.1, we were given three of the four parameters needed to describe a gas under a particular set of conditions, and we were asked to calculate the fourth. We can also use the ideal gas law to calculate the effect of *changes* in any of the specified conditions on any of the other parameters, as shown in Example 6.4.5.

6.4.4 GENERAL GAS EQUATION

When a gas is described under two different conditions, the ideal gas equation must be applied twice - to an initial condition and a final condition. This is:

$$\begin{array}{ll} \textbf{Initial condition } (i) & \textbf{Final condition} (f) \\ P_iV_i = n_iRT_i & P_fV_f = n_fRT_f \end{array}$$

Both equations can be rearranged to give:

$$R = \frac{P_iV_i}{n_iT_i} \qquad R = \frac{P_fV_f}{n_fT_f}$$

The two equations are equal to each other since each is equal to the same constant R. Therefore, we have:

$$\frac{P_iV_i}{n_iT_i} = \frac{P_fV_f}{n_fT_f} \tag{6.4.9}$$

The equation is called the **general gas equation**. The equation is particularly useful when one or two of the gas properties are held constant between the two conditions. In such cases, the equation can be simplified by eliminating these constant gas properties.



EXAMPLE 6.4.2

Suppose that Charles had changed his plans and carried out his initial flight not in August but on a cold day in January, when the temperature at ground level was −10°C (14°F). How large a balloon would he have needed to contain the same amount of hydrogen gas at the same pressure as in Example **6.4.1**?

Given: temperature, pressure, amount, and volume in August; temperature in January

Asked for: volume in January

Strategy:

A. Use the results from Example **6.4.1** for August as the initial conditions and then calculate the *change in volume* due to the change in temperature from 30°C to −10°C. Begin by constructing a table showing the initial and final conditions.

B. Simplify the general gas equation by eliminating the quantities that are held constant between the initial and final conditions, in this case P and n.

C. Solve for the unknown parameter.

Solution:

A To see exactly which parameters have changed and which are constant, prepare a table of the initial and final conditions:

Solution to Example 10.4.2

Initial (August)	Final (January)
$T_i = 30\,°C = 303\,K$	$T_f = -10\,°C = 263\,K$
$P_i = 0.980\,atm$	$P_f = 0.980\,atm$
$n_i = 1.23 \times 10^3\,mol$	$n_f = 1.23 \times 10^3\,mol$
$V_i = 31150\,L$	$V_f = ?$

B Both n and P are the same in both cases ($n_i = n_f, P_i = P_f$). Therefore, Equation 6.4.9 can be simplified to:

$$\frac{V_i}{T_i} = \frac{V_f}{T_f}$$

This is the relationship first noted by Charles.

C Solving the equation for V_f, we get:

$$\begin{aligned} V_f &= V_i \times \frac{T_f}{T_i} \\ &= 31150\ \text{L} \times \frac{263\ \text{K}}{303\ \text{K}} \\ &= 2.70 \times 10^4\ L \end{aligned}$$

It is important to check your answer to be sure that it makes sense, just in case you have accidentally inverted a quantity or multiplied rather than divided. In this case, the temperature of the gas decreases. Because we know that gas volume decreases with decreasing temperature, the final volume must be less than the initial volume, so the answer makes sense. We could have calculated the new

volume by plugging all the given numbers into the ideal gas law, but it is generally much easier and faster to focus on only the quantities that change.

? EXERCISE 6.4.2

At a laboratory party, a helium-filled balloon with a volume of 2.00 L at 22°C is dropped into a large container of liquid nitrogen (T = −196°C). What is the final volume of the gas in the balloon?

Answer

0.52 L

Example **6.4.1** illustrates the relationship originally observed by Charles. We could work through similar examples illustrating the inverse relationship between pressure and volume noted by Boyle (*PV* = constant) and the relationship between volume and amount observed by Avogadro (*V*/*n* = constant). We will not do so, however, because it is more important to note that the historically important gas laws are only special cases of the ideal gas law in which two quantities are varied while the other two remain fixed. The method used in Example **6.4.1** can be applied in *any* such case, as we demonstrate in Example **6.4.2** (which also shows why heating a closed container of a gas, such as a butane lighter cartridge or an aerosol can, may cause an explosion).

✓ EXAMPLE 6.4.3

Aerosol cans are prominently labeled with a warning such as “Do not incinerate this container when empty.” Assume that you did not notice this warning and tossed the “empty” aerosol can in Exercise **6.4.1** (0.025 mol in 0.406 L, initially at 25°C and 1.5 atm internal pressure) into a fire at 750°C. What would be the pressure inside the can (if it did not explode)?

Given: initial volume, amount, temperature, and pressure; final temperature

Asked for: final pressure

Strategy:

Follow the strategy outlined in Example **6.4.2**.

Solution:

Prepare a table to determine which parameters change and which are held constant:

Solution to Example 10.4.3

Initial	Final
$V_i = 0.406\ \text{L}$	$V_f = 0.406\ \text{L}$
$n_i = 0.025\ \text{mol}$	$n_f = 0.025\ \text{mol}$
$T_i = 25\ ^\circ\text{C} = 298\ \text{K}$	$T_i = 750\ ^\circ\text{C} = 1023\ \text{K}$
$P_i = 1.5\ \text{atm}$	$P_f = ?$

Both V and n are the same in both cases ($V_i = V_f, n_i = n_f$). Therefore, Equation can be simplified to:

$$\frac{P_i}{T_i} = \frac{P_f}{T_f}$$

By solving the equation for P_f, we get:

$$\begin{aligned} P_f &= P_i \times \frac{T_f}{T_i} \\ &= 1.5\ \text{atm} \times \frac{1023\ \text{K}}{298\ \text{K}} \\ &= 5.1\ atm \end{aligned}$$

This pressure is more than enough to rupture a thin sheet metal container and cause an explosion!

EXERCISE 6.4.3

Suppose that a fire extinguisher, filled with CO_2 to a pressure of 20.0 atm at 21°C at the factory, is accidentally left in the sun in a closed automobile in Tucson, Arizona, in July. The interior temperature of the car rises to 160°F (71.1°C). What is the internal pressure in the fire extinguisher?

Answer

23.4 atm

In Examples **6.4.1** and **6.4.2**, two of the four parameters (*P*, *V*, *T*, and *n*) were fixed while one was allowed to vary, and we were interested in the effect on the value of the fourth. In fact, we often encounter cases where two of the variables *P*, *V*, and *T* are allowed to vary for a given sample of gas (hence *n* is constant), and we are interested in the change in the value of the third under the new conditions.



EXAMPLE 6.4.4

We saw in Example **6.4.1** that Charles used a balloon with a volume of 31,150 L for his initial ascent and that the balloon contained 1.23 × 10^3 mol of H_2 gas initially at 30°C and 745 mmHg. Suppose that Gay-Lussac had also used this balloon for his record-breaking ascent to 23,000 ft and that the pressure and temperature at that altitude were 312 mmHg and −30°C, respectively. To what volume would the balloon have had to expand to hold the same amount of hydrogen gas at the higher altitude?

Given: initial pressure, temperature, amount, and volume; final pressure and temperature

Asked for: final volume

Strategy:

Follow the strategy outlined in Example **6.4.3**.

Solution:

Begin by setting up a table of the two sets of conditions:

Solution to Example 10.4.4

Initial	Final
$P_i = 745\ \text{mmHg} = 0.980\ \text{atm}$	$P_f = 312\ \text{mmHg} = 0.411\ \text{atm}$
$T_i = 30\ ^\circ\text{C} = 303\ \text{K}$	$T_f = 750 - 30\ ^\circ\text{C} = 243\ \text{K}$
$n_i = 1.2 \times 10^3\ \text{mol}$	$n_i = 1.2 \times 10^3\ \text{mol}$
$V_i = 31150\ \text{L}$	$V_f = ?$

By eliminating the constant property (n) of the gas, Equation 6.4.9 is simplified to:

$$\frac{P_iV_i}{T_i} = \frac{P_fV_f}{T_f}$$

By solving the equation for V_f, we get:

$$V_f = V_i \times \frac{P_i}{P_f}\frac{T_f}{T_i}$$

$$= 3.115 \times 10^4\ \text{L} \times \frac{0.980\ \text{atm}}{0.411\ \text{atm}}\frac{243\ \text{K}}{303\ \text{K}}$$

$$= 5.96 \times 10^4\ L$$

Does this answer make sense? Two opposing factors are at work in this problem: decreasing the pressure tends to *increase* the volume of the gas, while decreasing the temperature tends to *decrease* the volume of the gas. Which do we expect to predominate? The pressure drops by more than a factor of two, while the absolute temperature drops by only about 20%. Because the volume of a gas sample is directly proportional to both T and $1/P$, the variable that changes the most will have the greatest effect on V. In this case, the effect of decreasing pressure predominates, and we expect the volume of the gas to increase, as we found in our calculation.

We could also have solved this problem by solving the ideal gas law for V and then substituting the relevant parameters for an altitude of 23,000 ft:

Except for a difference caused by rounding to the last significant figure, this is the same result we obtained previously. *There is often more than one "right" way to solve chemical problems.*

? EXERCISE 6.4.4

A steel cylinder of compressed argon with a volume of 0.400 L was filled to a pressure of 145 atm at 10°C. At 1.00 atm pressure and 25°C, how many 15.0 mL incandescent light bulbs could be filled from this cylinder? (Hint: find the number of moles of argon in each container.)

Answer

4.07×10^3

6.4.5 USING THE IDEAL GAS LAW TO CALCULATE GAS DENSITIES AND MOLAR MASSES

The ideal gas law can also be used to calculate molar masses of gases from experimentally measured gas densities. To see how this is possible, we first rearrange the ideal gas law to obtain

$$\frac{n}{V} = \frac{P}{RT} \tag{6.4.10}$$

The left side has the units of moles per unit volume (mol/L). The number of moles of a substance equals its mass (m, in grams) divided by its molar mass (M, in grams per mole):

$$n = \frac{m}{M} \tag{6.4.11}$$

Substituting this expression for n into Equation 6.4.10 gives

$$\frac{m}{MV} = \frac{P}{RT} \tag{6.4.12}$$

Because m/V is the density d of a substance, we can replace m/V by d and rearrange to give

$$\rho = \frac{m}{V} = \frac{MP}{RT} \tag{6.4.13}$$

The distance between particles in gases is large compared to the size of the particles, so their densities are much lower than the densities of liquids and solids. Consequently, gas density is usually measured in grams per liter (g/L) rather than grams per milliliter (g/mL).



EXAMPLE 6.4.5

Calculate the density of butane at 25°C and a pressure of 750 mmHg.

Given: compound, temperature, and pressure

Asked for: density

Strategy:

A. Calculate the molar mass of butane and convert all quantities to appropriate units for the value of the gas constant.
B. Substitute these values into Equation 6.4.13 to obtain the density.

Solution:

A The molar mass of butane (C_4H_{10}) is

$$M = (4)(12.011) + (10)(1.0079) = 58.123 \text{g/mol}$$

Using 0.08206 (L•atm)/(K•mol) for R means that we need to convert the temperature from degrees Celsius to kelvins (T = 25 + 273 = 298 K) and the pressure from millimeters of mercury to atmospheres:

$$P = 750 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 0.987 \text{ atm}$$

B Substituting these values into Equation 6.4.13 gives

$$\rho = \frac{58.123 \text{ g/mol} \times 0.987 \text{ atm}}{0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \times 298 \text{ K}} = 2.35 \text{ g/L}$$

EXERCISE 6.4.5: DENSITY OF RADON

Radon (Rn) is a radioactive gas formed by the decay of naturally occurring uranium in rocks such as granite. It tends to collect in the basements of houses and poses a significant health risk if present in indoor air. Many states now require that houses be tested for radon before they are sold. Calculate the density of radon at 1.00 atm pressure and 20°C and compare it with the density of nitrogen gas, which constitutes 80% of the atmosphere, under the same conditions to see why radon is found in basements rather than in attics.

Answer

radon, 9.23 g/L; N_2, 1.17 g/L

A common use of Equation 6.4.13 is to determine the molar mass of an unknown gas by measuring its density at a known temperature and pressure. This method is particularly useful in identifying a gas that has been produced in a reaction, and it is not difficult to carry out. A flask or glass bulb of known volume is carefully dried, evacuated, sealed, and weighed empty. It is then filled with a sample of a gas at a known temperature and pressure and reweighed. The difference in mass between the two readings is the mass of the gas. The volume of the flask is usually determined by weighing the flask when empty and when filled with a liquid of known density such as water. The use of density measurements to calculate molar masses is illustrated in Example **6.4.6**.

EXAMPLE 6.4.6

The reaction of a copper penny with nitric acid results in the formation of a red-brown gaseous compound containing nitrogen and oxygen. A sample of the gas at a pressure of 727 mmHg and a temperature of 18°C weighs 0.289 g in a flask with a volume of 157.0 mL. Calculate the molar mass of the gas and suggest a reasonable chemical formula for the compound.

Given: pressure, temperature, mass, and volume

Asked for: molar mass and chemical formula

Strategy:

A. Solve Equation 6.4.13 for the molar mass of the gas and then calculate the density of the gas from the information given.

B. Convert all known quantities to the appropriate units for the gas constant being used. Substitute the known values into your equation and solve for the molar mass.

C. Propose a reasonable empirical formula using the atomic masses of nitrogen and oxygen and the calculated molar mass of the gas.

Solution:

A Solving Equation 6.4.13 for the molar mass gives

$$M = \frac{mRT}{PV} = \frac{dRT}{P}$$

Density is the mass of the gas divided by its volume:

$$\rho = \frac{m}{V} = \frac{0.289\text{g}}{0.157\text{L}} = 1.84\text{g/L}$$

B We must convert the other quantities to the appropriate units before inserting them into the equation:

$$T = 18 + 273 = 291K$$

$$P = 727\,mmHg \times \frac{1\text{atm}}{760\text{mmHg}} = 0.957\text{atm}$$

The molar mass of the unknown gas is thus

$$M = \frac{1.84\ \text{g/L} \times 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \times 291\ \text{K}}{0.957\ \text{atm}} = 45.9\text{g/mol}$$

C The atomic masses of N and O are approximately 14 and 16, respectively, so we can construct a list showing the masses of possible combinations:

$$M(\text{NO}) = 14 + 16 = 30\ \text{g/mol}$$

$$M(\text{N}_2\text{O}) = (2)(14) + 16 = 44\ \text{g/mol}$$

$$M(\text{NO}_2) = 14 + (2)(16) = 46\ \text{g/mol}$$

The most likely choice is NO_2 which is in agreement with the data. The red-brown color of smog also results from the presence of NO_2 gas.

EXERCISE 6.4.6

You are in charge of interpreting the data from an unmanned space probe that has just landed on Venus and sent back a report on its atmosphere. The data are as follows: pressure, 90 atm; temperature, 557°C; density, 58 g/L. The major constituent of the atmosphere (>95%) is carbon. Calculate the molar mass of the major gas present and identify it.

Answer

44 g/mol; CO_2

6.4.6 SUMMARY

The ideal gas law is derived from empirical relationships among the pressure, the volume, the temperature, and the number of moles of a gas; it can be used to calculate any of the four properties if the other three are known.

Ideal gas equation: $PV = nRT$,

where $R = 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} = 8.3145 \frac{\text{J}}{\text{K} \cdot \text{mol}}$

General gas equation: $\frac{P_i V_i}{n_i T_i} = \frac{P_f V_f}{n_f T_f}$

Density of a gas: $\rho = \frac{MP}{RT}$

The empirical relationships among the volume, the temperature, the pressure, and the amount of a gas can be combined into the **ideal gas law**, $PV = nRT$. The proportionality constant, R, is called the **gas constant** and has the value 0.08206 (L•atm)/(K•mol), 8.3145 J/(K•mol), or 1.9872 cal/(K•mol), depending on the units used. The ideal gas law describes the behavior of an **ideal gas**, a hypothetical substance whose behavior can be explained quantitatively by the ideal gas law and the kinetic molecular theory of gases. **Standard temperature and pressure (STP)** is 0°C and 1 atm. The volume of 1 mol of an ideal gas at STP is 22.41 L, the **standard molar volume**. All of the empirical gas relationships are special cases of the ideal gas law in which two of the four parameters are held constant. The ideal gas law allows us to calculate the value of the fourth quantity (P, V, T, or n) needed to describe a gaseous sample when the others are known and also predict the value of these quantities following a change in conditions if the original conditions (values of P, V, T, and n) are known. The ideal gas law can also be used to calculate the density of a gas if its molar mass is known or, conversely, the molar mass of an unknown gas sample if its density is measured.

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6.5: FURTHER APPLICATIONS OF THE IDEAL-GAS EQUATIONS

LEARNING OBJECTIVES

- To relate the amount of gas consumed or released in a chemical reaction to the stoichiometry of the reaction.
- To understand how the ideal gas equation and the stoichiometry of a reaction can be used to calculate the volume of gas produced or consumed in a reaction.

With the ideal gas law, we can use the relationship between the amounts of gases (in moles) and their volumes (in liters) to calculate the stoichiometry of reactions involving gases, if the pressure and temperature are known. This is important for several reasons. Many reactions that are carried out in the laboratory involve the formation or reaction of a gas, so chemists must be able to quantitatively treat gaseous products and reactants as readily as they quantitatively treat solids or solutions. Furthermore, many, if not most, industrially important reactions are carried out in the gas phase for practical reasons. Gases mix readily, are easily heated or cooled, and can be transferred from one place to another in a manufacturing facility via simple pumps and plumbing.

6.5.1 GAS DENSITIES AND MOLAR MASS

The ideal-gas equation can be manipulated to solve a variety of different types of problems. For example, the density, ρ, of a gas, depends on the number of gas molecules in a constant volume. To determine this value, we rearrange the ideal gas equation to

$$\frac{n}{V} = \frac{P}{RT} \tag{6.5.1}$$

Density of a gas is generally expressed in g/L (mass over volume). Multiplication of the left and right sides of Equation 6.5.1 by the molar mass in g/mol (M) of the gas gives

$$\rho = \frac{g}{L} = \frac{PM}{RT} \tag{6.5.2}$$

This allows us to determine the density of a gas when we know the molar mass, or vice versa.

> *The density of a gas INCREASES with increasing pressure and DECREASES with increasing temperature*



EXAMPLE 6.5.1

What is the density of nitrogen gas (N_2) at 248.0 Torr and 18° C?

Solution

Step 1: Write down your given information

- P = 248.0 Torr
- V = ?

- n = ?
- R = 0.0820574 L•atm•mol^{-1} K^{-1}
- T = 18° C

Step 2: Convert as necessary.

$$(248 \text{ Torr}) \times \frac{1 \text{ atm}}{760 \text{ Torr}} = 0.3263 \text{ atm}$$

$$18\,^{\circ}C + 273 = 291K$$

Step 3: This one is tricky. We need to manipulate the Ideal Gas Equation to incorporate density into the equation.

Write down all known equations:

$$PV = nRT$$

$$\rho = \frac{m}{V}$$

where ρ is density, m is mass, and V is volume.

$$m = M \times n$$

where M is molar mass and n is the number of moles.

Now take the definition of density (Equation 6.5.1)

$$\rho = \frac{m}{V}$$

Keeping in mind $m = M \times n$...replace $(M \times n)$ for $mass$ within the density formula.

$$\rho = \frac{M \times n}{V}$$

$$\frac{\rho}{M} = \frac{n}{V}$$

Now manipulate the Ideal Gas Equation

\[\begin{align*} PV &= nRT \[4pt] \dfrac{n}{V} &= \dfrac{P}{RT} \end{align*} \nonumber \]

(n/V) is in both equations.

$$\frac{n}{V} = \frac{\rho}{M}$$

$$= \frac{P}{RT}$$

Now combine them please.

$$\frac{\rho}{M} = \frac{P}{RT}$$

Isolate density.

$$\rho = \frac{PM}{RT}$$

Step 4: Now plug in the information you have.

$$\rho = \frac{PM}{RT}$$

$$= \frac{(0.3263 \text{ atm})(2 * 14.01 \text{ g/mol})}{(0.08206\, L\, atm/K mol)(291 \text{ K})}$$

$$= 0.3828\ g/L$$

An example of varying density for a useful purpose is the hot air balloon, which consists of a bag (called the envelope) that is capable of containing heated air. As the air in the envelope is heated, it becomes less dense than the surrounding cooler air (Equation 6.5.2), which is has enough lifting power (due to buoyancy) to cause the balloon to float and rise into the air. Constant heating of the air is required to keep

the balloon aloft. As the air in the balloon cools, it contracts, allowing outside cool air to enter, and the density increases. When this is carefully controlled by the pilot, the balloon can land as gently as it rose.



Figure **6.5.1**: A hot air balloon is inflated partially with cold air from a gas-powered fan, before the propane burners are used for final inflation.

6.5.2 DETERMINING GAS VOLUMES IN CHEMICAL REACTIONS

The ideal gas law can be used to calculate volume of gases consumed or produced. The ideal-gas equation frequently is used to interconvert between volumes and molar amounts in chemical equations.



EXAMPLE 6.5.2A

What volume of carbon dioxide gas is produced at STP by the decomposition of 0.150 g $\mathbf{CaCO_3}$ via the equation:

$$\mathbf{CaCO_3\,(s)\ \rightarrow CaO\,(s) + CO_2\,(g)}$$

Solution

Begin by converting the mass of calcium carbonate to moles.

$$\frac{0.150\ g}{100.1\ g/mol} = 0.00150\ mol$$

The stoichiometry of the reaction dictates that the number of moles $\mathbf{CaCO_3}$ decomposed equals the number of moles $\mathbf{CO_2}$ produced. Use the ideal-gas equation to convert moles of $\mathbf{CO_2}$ to a volume.

$$\begin{aligned} V &= \frac{nRT}{PR} \\ &= \frac{(0.00150\ mol)\left(0.08206\ \frac{L \cdot atm}{mol \cdot K}\right)(273.15\ K)}{1\ atm} \\ &= 0.0336\ L\ or\ 33.6\ mL \end{aligned}$$

EXAMPLE 6.5.2B

A 3.00 L container is filled with $\mathbf{Ne(g)}$ at 770 mmHg at 27°C. A $\mathbf{0.633\ g}$ sample of $\mathbf{CO_2}$ vapor is then added.

- What is the partial pressure of $\mathbf{CO_2}$ and $\mathbf{Ne}$ in atm?
- What is the total pressure in the container in atm?

Solution

Step 1: Write down all given information, and convert as necessary.

Before:

- \(P = 770\,mmHg \rigtharrow 1.01 \,atm \nonumber \]
- $V = 3.00\,L$
- $n_{Ne} = ?$
- $T = 27°C \rightarrow 300\ K$

Other Unknowns: n_{CO_2}= ?

$$n_{CO_2} = 0.633\text{ g } CO_2 \times \frac{1\text{ mol}}{44\text{ g}} = 0.0144\text{ mol } CO_2$$

***Step 2: After writing down all your given information, find the unknown moles of* Ne.**

$$\begin{aligned} n_{Ne} &= \frac{PV}{RT} \\ &= \frac{(1.01\text{ atm})(3.00\text{ L})}{(0.08206\ atm\ L/mol\ K)(300\text{ K})} \\ &= 0.123\text{ mol} \end{aligned}$$

Because the pressure of the container before the $\mathbf{CO_2}$ was added contained only **Ne**, that is your partial pressure of Ne. After converting it to atm, you have already answered part of the question!

$$P_{Ne} = 1.01\text{ atm}$$

Step 3: Now that have pressure for **Ne**, you must find the partial pressure for CO_2. Use the ideal gas equation.

$$\frac{P_{Ne}\cancel{V}}{n_{Ne}\cancel{RT}} = \frac{P_{CO_2}\cancel{V}}{n_{CO_2}\cancel{RT}}$$

but because both gases share the same Volume (V) and Temperature (T) and since the Gas Constant (R) is constants, all three terms cancel.

$$\begin{aligned} \frac{P}{n_{Ne}} &= \frac{P}{n_{CO_2}} \\ \frac{1.01\text{ atm}}{0.123\text{ mol Ne}} &= \frac{P_{CO_2}}{0.0144\text{ mol } CO_2} \\ P_{CO_2} &= 0.118\text{ atm} \end{aligned}$$

This is the partial pressure $\mathbf{CO_2}$.

Step 4: Now find total pressure.

$$\begin{aligned} P_{total} &= P_{Ne} + P_{CO_2} \\ &= 1.01\text{ atm} + 0.118\text{ atm} \\ &= 1.128\text{ atm} \\ &\approx 1.13\text{ atm (with appropriate significant figures)} \end{aligned}$$

EXAMPLE 6.5.2C: SULFURIC ACID

Sulfuric acid, the industrial chemical produced in greatest quantity (almost 45 million tons per year in the United States alone), is prepared by the combustion of sulfur in air to give $\mathbf{SO_2}$, followed by the reaction of $\mathbf{SO_2}$ with $\mathbf{O_2}$ in the presence of a catalyst to give $\mathbf{SO_3}$, which reacts with water to give $\mathbf{H_2SO_4}$. The overall chemical equation is as follows:

$$\mathbf{2\,S\,(s) + 3\,O_2\,(g) + 2\,H_2O\,(l) \rightarrow 2\,H_2SO_4\,(aq)}$$

What volume of O_2 (in liters) at 22°C and 745 mmHg pressure is required to produce 1.00 ton (907.18 kg) of H_2SO_4?

Given: reaction, temperature, pressure, and mass of one product

Asked for: volume of gaseous reactant

Strategy:

A Calculate the number of moles of H_2SO_4 in 1.00 ton. From the stoichiometric coefficients in the balanced chemical equation, calculate the number of moles of $\mathbf{O_2}$ required.

B Use the ideal gas law to determine the volume of $\mathbf{O_2}$ required under the given conditions. Be sure that all quantities are expressed in the appropriate units.

Solution:

$$\text{mass of } \mathbf{H_2SO_4} \rightarrow \text{moles } \mathbf{H_2SO_4} \rightarrow \text{moles } \mathbf{O_2} \rightarrow \text{liters } \mathbf{O_2}$$

A We begin by calculating the number of moles of H_2SO_4 in 1.00 ton:

$$\frac{907.18 \times 10^3 \text{ g } \mathbf{H_2SO_4}}{(2 \times 1.008 + 32.06 + 4 \times 16.00) \text{ g/mol}} = 9250 \text{ mol } \mathbf{H_2SO_4}$$

We next calculate the number of moles of $\mathbf{O_2}$ required:

$$9250 \text{ mol } \mathbf{H_2SO_4} \times \frac{3 \text{mol } \mathbf{O_2}}{2 \text{mol } \mathbf{H_2SO_4}} = 1.389 \times 10^4 \text{ mol } \mathbf{O_2}$$

B After converting all quantities to the appropriate units, we can use the ideal gas law to calculate the volume of O_2:

$$\begin{aligned} V &= \frac{nRT}{P} \\ &= \frac{1.389 \times 10^4 \text{ mol} \times 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times (273 + 22) \text{ K}}{745 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}} \\ &= 3.43 \times 10^5 \text{ L} \end{aligned}$$

The answer means that more than 300,000 L of oxygen gas are needed to produce 1 ton of sulfuric acid. These numbers may give you some appreciation for the magnitude of the engineering and plumbing problems faced in industrial chemistry.

EXERCISE 6.5.2

Charles used a balloon containing approximately 31,150 L of $\mathbf{H_2}$ for his initial flight in 1783. The hydrogen gas was produced by the reaction of metallic iron with dilute hydrochloric acid according to the following balanced chemical equation:

$$\mathbf{Fe(s) + 2\,HCl(aq) \rightarrow H_2(g) + FeCl_2(aq)}$$

How much iron (in kilograms) was needed to produce this volume of $\mathbf{H_2}$ if the temperature were 30°C and the atmospheric pressure was 745 mmHg?

Answer

68.6 kg of Fe (approximately 150 lb)

EXAMPLE 6.5.3: EMERGENCY AIR BAGS

Sodium azide ($\mathbf{NaN_3}$) decomposes to form sodium metal and nitrogen gas according to the following balanced chemical equation:

$$\mathbf{2\,NaN_3 \rightarrow 2\,Na(s) + 3\,N_2(g)}$$

This reaction is used to inflate the air bags that cushion passengers during automobile collisions. The reaction is initiated in air bags by an electrical impulse and results in the rapid evolution of gas. If the $\mathbf{N_2}$ gas that results from the decomposition of a 5.00 g sample of $\mathbf{NaN_3}$ could be collected by displacing water from an inverted flask, what volume of gas would be produced at 21°C and 762 mmHg?

Given: reaction, mass of compound, temperature, and pressure

Asked for: volume of nitrogen gas produced

Strategy:

A Calculate the number of moles of $\mathbf{N_2}$ gas produced. From the data in Table S3, determine the partial pressure of $\mathbf{N_2}$ gas in the flask.

B Use the ideal gas law to find the volume of $\mathbf{N_2}$ gas produced.

Solution:

A Because we know the mass of the reactant and the stoichiometry of the reaction, our first step is to calculate the number of moles of $\mathbf{N_2}$ gas produced:

$$\frac{5.00\ \text{g NaN}_3}{(22.99 + 3 \times 14.01)\ \text{g/mol}} \times \frac{3\text{mol N}_2}{2\text{mol NaN}_3} = 0.115\ \text{mol N}_2$$

The pressure given (762 mmHg) is the *total* pressure in the flask, which is the sum of the pressures due to the N_2 gas and the water vapor present. Table S3 tells us that the vapor pressure of water is 18.65 mmHg at 21°C (294 K), so the partial pressure of the $\mathbf{N_2}$ gas in the flask is only

$$(762 - 18.65)\ \text{mmHg} \times \frac{1\ \text{atm}}{760\ \text{mmHg}} = 743.4\ \cancel{mmHg} \times \frac{1\ atm}{760\ \cancel{mmHg}}$$

$$= 0.978\ atm.$$

B Solving the ideal gas law for V and substituting the other quantities (in the appropriate units), we get

$$V = \frac{nRT}{P} = \frac{0.115\ \text{mol} \times 0.08206 \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 294\ \text{K}}{0.978\ \text{atm}} = 2.84\ \text{L}$$

? EXERCISE 6.5.3

A 1.00 g sample of zinc metal is added to a solution of dilute hydrochloric acid. It dissolves to produce $\mathbf{H_2}$ gas according to the equation

$$\mathbf{Zn\,(s) + 2\,HCl\,(aq) \longrightarrow H_2\,(g) + ZnCl_2\,(aq).}$$

The resulting H_2 gas is collected in a water-filled bottle at 30°C and an atmospheric pressure of 760 mmHg. What volume does it occupy?

Answer

0.397 L

6.5.3 SUMMARY

The relationship between the amounts of products and reactants in a chemical reaction can be expressed in units of moles or masses of pure substances, of volumes of solutions, or of volumes of gaseous substances. The ideal gas law can be used to calculate the volume of gaseous products or reactants as needed. In the laboratory, gases produced in a reaction are often collected by the displacement of water from filled vessels; the amount of gas can then be calculated from the volume of water displaced and the atmospheric pressure. A gas collected in such a way is not pure, however, but contains a significant amount of water vapor. The measured pressure must therefore be corrected for the vapor pressure of water, which depends strongly on the temperature.

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6.6: GAS MIXTURES AND PARTIAL PRESSURES

LEARNING OBJECTIVES

- To determine the contribution of each component gas to the total pressure of a mixture of gases

In our use of the ideal gas law thus far, we have focused entirely on the properties of pure gases with only a single chemical species. But what happens when two or more gases are mixed? In this section, we describe how to determine the contribution of each gas present to the total pressure of the mixture.

6.6.1 PARTIAL PRESSURES

The ideal gas law *assumes* that all gases behave identically and that their behavior is independent of attractive and repulsive forces. If volume and temperature are held constant, the ideal gas equation can be rearranged to show that the pressure of a sample of gas is directly proportional to the number of moles of gas present:

$$P = n\left(\frac{RT}{V}\right) = n \times \text{const.} \tag{6.6.1}$$

Nothing in the equation depends on the *nature* of the gas—only the amount.

With this assumption, let's suppose we have a mixture of two ideal gases that are present in equal amounts. What is the total pressure of the mixture? Because the pressure depends on only the total number of particles of gas present, the total pressure of the mixture will simply be twice the pressure of either component. More generally, the total pressure exerted by a mixture of gases at a given temperature and volume is the sum of the pressures exerted by each gas alone. Furthermore, if we know the volume, the temperature, and the number of moles of each gas in a mixture, then we can calculate the pressure exerted by each gas individually, which is its partial pressure, the pressure the gas would exert if it were the only one present (at the same temperature and volume).

To summarize, ***the total pressure exerted by a mixture of gases is the sum of the partial pressures of component gases***. This law was first discovered by John Dalton, the father of the atomic theory of matter. It is now known as *Dalton's law of partial pressures*. We can write it mathematically as

$$P_{tot} = P_1 + P_2 + P_3 + P_4 \ldots \tag{6.6.2}$$

$$= \sum_{i=1}^{n} P_i \tag{6.6.3}$$

where P_{tot} is the total pressure and the other terms are the partial pressures of the individual gases (up to n component gases).

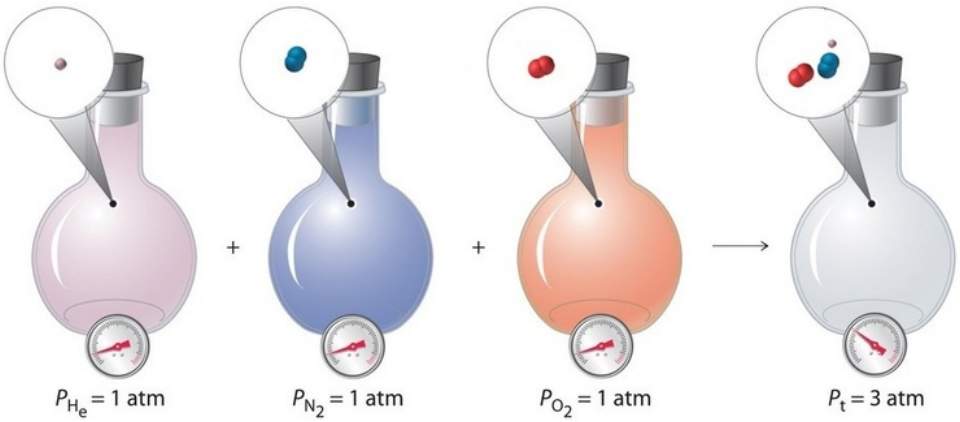


Figure **6.6.1**: Dalton's Law. The total pressure of a mixture of gases is the sum of the partial pressures of the individual gases.

For a mixture of two ideal gases, A and B, we can write an expression for the total pressure:

$$P_{tot} = P_A + P_B \tag{6.6.4}$$

$$= n_A\left(\frac{RT}{V}\right) + n_B\left(\frac{RT}{V}\right) \tag{6.6.5}$$

$$= (n_A + n_B)\left(\frac{RT}{V}\right) \tag{6.6.6}$$

More generally, for a mixture of n component gases, the total pressure is given by

$$P_{tot} = (n_1 + n_2 + n_3 + \cdots + n_n)\left(\frac{RT}{V}\right) \tag{6.6.7}$$

$$= \sum_{i=1}^{n} n_i \left(\frac{RT}{V}\right) \tag{6.6.8}$$

Equation 6.6.8 restates Equation 6.6.6 in a more general form and makes it explicitly clear that, at constant temperature and volume, the pressure exerted by a gas depends on only the total number of moles of gas present, whether the gas is a single chemical species or a mixture of dozens or even hundreds of gaseous species. For Equation 6.6.8 to be valid, the identity of the particles present cannot have an effect. Thus an ideal gas must be one whose properties are not affected by either the size of the particles or their intermolecular interactions because both will vary from one gas to another. The calculation of total and partial pressures for mixtures of gases is illustrated in Example 6.6.1.

EXAMPLE 6.6.1: THE BENDS

Deep-sea divers must use special gas mixtures in their tanks, rather than compressed air, to avoid serious problems, most notably a condition called "the bends." At depths of about 350 ft, divers are subject to a pressure of approximately 10 atm. A typical gas cylinder used for such depths contains 51.2 g of O_2 and 326.4 g of He and has a volume of 10.0 L. What is the partial pressure of each gas at 20.00°C, and what is the total pressure in the cylinder at this temperature?

Given: masses of components, total volume, and temperature

Asked for: partial pressures and total pressure

Strategy:

A. Calculate the number of moles of $\mathbf{He}$ and $\mathbf{O_2}$ present.

B. Use the ideal gas law to calculate the partial pressure of each gas. Then add together the partial pressures to obtain the total pressure of the gaseous mixture.

Solution:

A The number of moles of $\mathbf{He}$ is

$$n_{\mathrm{He}} = \frac{326.4\ \mathrm{g}}{4.003\ \mathrm{g/mol}} = 81.54\ \mathrm{mol}$$

The number of moles of $\mathbf{O_2}$ is

$$n_{\mathrm{O_2}} = \frac{51.2\ \mathrm{g}}{32.00\ \mathrm{g/mol}} = 1.60\ \mathrm{mol}$$

B We can now use the ideal gas law to calculate the partial pressure of each:

$$P_{\mathrm{He}} = \frac{n_{\mathrm{He}}RT}{V} = \frac{81.54\ \mathrm{mol} \times 0.08206\ \frac{\mathrm{atm \cdot L}}{\mathrm{mol \cdot K}} \times 293.15\ \mathrm{K}}{10.0\ \mathrm{L}} = 196.2\ \mathrm{atm}$$

$$P_{\mathrm{O_2}} = \frac{n_{\mathrm{O_2}}RT}{V} = \frac{1.60\ \mathrm{mol} \times 0.08206\ \frac{\mathrm{atm \cdot L}}{\mathrm{mol \cdot K}} \times 293.15\ \mathrm{K}}{10.0\ \mathrm{L}} = 3.85\ \mathrm{atm}$$

The total pressure is the sum of the two partial pressures:

$$P_{\mathrm{tot}} = P_{\mathrm{He}} + P_{\mathrm{O_2}} = (196.2 + 3.85)\ \mathrm{atm} = 200.1\ \mathrm{atm}$$

EXERCISE 6.6.1

A cylinder of compressed natural gas has a volume of 20.0 L and contains 1813 g of methane and 336 g of ethane. Calculate the partial pressure of each gas at 22.0°C and the total pressure in the cylinder.

Answer

$P_{CH_4} = 137\ atm;\ P_{C_2H_6} = 13.4\ atm;\ P_{tot} = 151\ atm$

6.6.2 MOLE FRACTIONS OF GAS MIXTURES

The composition of a gas mixture can be described by the mole fractions of the gases present. The mole fraction (χ) of any component of a mixture is the ratio of the number of moles of that component to the total number of moles of all the species present in the mixture (n_{tot}):

$$\chi_A = \frac{\text{moles of A}}{\text{total moles}} = \frac{n_A}{n_{tot}} = \frac{n_A}{n_A + n_B + \cdots} \tag{6.6.9}$$

The mole fraction is a dimensionless quantity between 0 and 1. If $\chi_A = 1.0$, then the sample is pure A, not a mixture. If $\chi_A = 0$, then no A is present in the mixture. The sum of the mole fractions of all the components present must equal 1.

To see how mole fractions can help us understand the properties of gas mixtures, let's evaluate the ratio of the pressure of a gas A to the total pressure of a gas mixture that contains A. We can use the ideal gas law to describe the pressures of both gas A and the mixture: $P_A = n_A RT/V$ and $P_{tot} = n_t RT/V$. The ratio of the two is thus

$$\frac{P_A}{P_{tot}} = \frac{n_A RT/V}{n_{tot} RT/V} = \frac{n_A}{n_{tot}} = \chi_A \tag{6.6.10}$$

Rearranging this equation gives

$$P_A = \chi_A P_{tot} \tag{6.6.11}$$

That is, the partial pressure of any gas in a mixture is the total pressure multiplied by the mole fraction of that gas. This conclusion is a direct result of the ideal gas law, which assumes that all gas particles behave ideally. Consequently, the pressure of a gas in a mixture depends on only the percentage of particles in the mixture that are of that type, not their specific physical or chemical properties. By volume, Earth's atmosphere is about 78% N_2, 21% O_2, and 0.9% Ar, with trace amounts of gases such as CO_2, H_2O, and others. This means that 78% of the particles present in the atmosphere are N_2; hence the mole fraction of N_2 is 78%/100% = 0.78. Similarly, the mole fractions of O_2 and Ar are 0.21 and 0.009, respectively. Using Equation 6.6.11, we therefore know that the partial pressure of N_2 is 0.78 atm (assuming an atmospheric pressure of exactly 760 mmHg) and, similarly, the partial pressures of O_2 and Ar are 0.21 and 0.009 atm, respectively.



EXAMPLE 6.6.2: EXHALING COMPOSITION

We have just calculated the partial pressures of the major gases in the air we inhale. Experiments that measure the composition of the air we *exhale* yield different results, however. The following table gives the measured pressures of the major gases in both inhaled and exhaled air. Calculate the mole fractions of the gases in exhaled air.

the mole fractions of the gases

	Inhaled Air / mmHg	Exhaled Air / mmHg
P_{N_2}	597	568
P_{O_2}	158	116
P_{H_2O}	0.3	28
P_{CO_2}	5	48
P_{Ar}	8	8
P_{tot}	767	767

Given: pressures of gases in inhaled and exhaled air

Asked for: mole fractions of gases in exhaled air

Strategy:

Calculate the mole fraction of each gas using Equation 6.6.11.

Solution:

The mole fraction of any gas A is given by

$$\chi_A = \frac{P_A}{P_{tot}}$$

where P_A is the partial pressure of A and P_{tot} is the total pressure. For example, the mole fraction of CO_2 is given as:

$$\chi_{CO_2} = \frac{48 \text{ mmHg}}{767 \text{ mmHg}} = 0.063$$

The following table gives the values of χ_A for the gases in the exhaled air.

Solutions to Example 10.6.2

Gas	Mole Fraction
N_2	0.741
O_2	0.151
H_2O	0.037
CO_2	0.063
Ar	0.010

? EXERCISE 6.6.2

Venus is an inhospitable place, with a surface temperature of 560°C and a surface pressure of 90 atm. The atmosphere consists of about 96% CO_2 and 3% N_2, with trace amounts of other gases, including water, sulfur dioxide, and sulfuric acid. Calculate the partial pressures of CO_2 and N_2.

Answer

$$P_{CO_2} = 86 \text{ atm}$$

$$P_{N_2} = 2.7 \text{ atm}$$

6.6.3 SUMMARY

The partial pressure of each gas in a mixture is proportional to its mole fraction. The pressure exerted by each gas in a gas mixture (its **partial pressure**) is independent of the pressure exerted by all other gases present. Consequently, the total pressure exerted by a mixture of gases is the sum of the partial pressures of the components (**Dalton's law of partial pressures**). The amount of gas present in a mixture may be described by its partial pressure or its mole fraction. The **mole fraction** of any component of a mixture is the ratio of the number of moles of that substance to the total number of moles of all substances present. In a mixture of gases, the partial pressure of each gas is the product of the total pressure and the mole fraction of that gas.

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6.7: KINETIC-MOLECULAR THEORY

LEARNING OBJECTIVES

- To understand the significance of the kinetic molecular theory of gases.

The laws that describe the behavior of gases were well established long before anyone had developed a coherent model of the properties of gases. In this section, we introduce a theory that describes why gases behave the way they do. The theory we introduce can also be used to derive laws such as the ideal gas law from fundamental principles and the properties of individual particles.

6.7.1 A MOLECULAR DESCRIPTION

The kinetic molecular theory of gases explains the laws that describe the behavior of gases. Developed during the mid-19th century by several physicists, including the Austrian Ludwig Boltzmann (1844–1906), the German Rudolf Clausius (1822–1888), and the Englishman James Clerk Maxwell (1831–1879), who is also known for his contributions to electricity and magnetism, this theory is based on the properties of individual particles as defined for an ideal gas and the fundamental concepts of physics. Thus the kinetic molecular theory of gases provides a molecular explanation for observations that led to the development of the ideal gas law. The kinetic molecular theory of gases is based on the following five postulates:

FIVE POSTULATES OF KINETIC MOLECULAR THEORY

1. A gas is composed of a large number of particles called molecules (whether monatomic or polyatomic) that are in constant random motion.
2. Because the distance between gas molecules is much greater than the size of the molecules, the volume of the molecules is negligible.
3. Intermolecular interactions, whether repulsive or attractive, are so weak that they are also negligible.
4. Gas molecules collide with one another and with the walls of the container, but these collisions are perfectly elastic; that is, they do not change the average kinetic energy of the molecules.
5. The average kinetic energy of the molecules of any gas depends on only the temperature, and at a given temperature, all gaseous molecules have exactly the same average kinetic energy.

Although the molecules of real gases have nonzero volumes and exert both attractive and repulsive forces on one another, for the moment we will focus on how the kinetic molecular theory of gases relates to the properties of gases we have been discussing. In the following sections, we explain how this theory must be modified to account for the behavior of real gases.

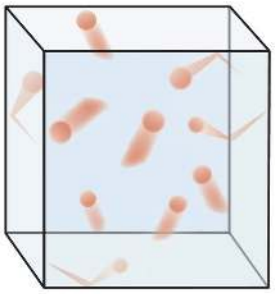


Figure 6.7.1: Visualizing molecular motion. Molecules of a gas are in constant motion and collide with one another and with the container wall.

Postulates 1 and 4 state that gas molecules are in constant motion and collide frequently with the walls of their containers. The collision of molecules with their container walls results in a **momentum transfer** (impulse) from molecules to the walls (Figure 6.7.2).

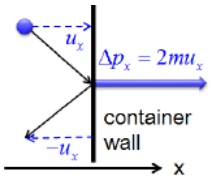


Figure **6.7.2**: Momentum transfer (impulse) from a molecule to the container wall as it bounces off the wall. u_x and Δp_x are the x component of the molecular velocity and the momentum transferred to the wall, respectively. The wall is perpendicular to x axis. Since the collisions are elastic, the molecule bounces back with the same velocity in the opposite direction.

The **momentum transfer** to the wall perpendicular to x axis as a molecule with an initial velocity u_x in x direction hits is expressed as:

$$\Delta p_x = 2mu_x \tag{6.7.1}$$

The **collision frequency**, a number of collisions of the molecules to the wall per unit area and per second, increases with the molecular speed and the number of molecules per unit volume.

$$f \propto (u_x) \times \left(\frac{N}{V}\right) \tag{6.7.2}$$

The pressure the gas exerts on the wall is expressed as the product of impulse and the collision frequency.

$$P \propto (2mu_x) \times (u_x) \times \left(\frac{N}{V}\right) \propto \left(\frac{N}{V}\right) mu_x^2 \tag{6.7.3}$$

At any instant, however, the molecules in a gas sample are traveling at different speed. Therefore, we must replace u_x^2 in the expression above with the average value of u_x^2, which is denoted by $\overline{u_x^2}$. The overbar designates the average value over all molecules.

The exact expression for pressure is given as :

$$P = \frac{N}{V} m\overline{u_x^2} \tag{6.7.4}$$

Finally, we must consider that there is nothing special about x direction. We should expect that

$$\overline{u_x^2} = \overline{u_y^2} = \overline{u_z^2} = \frac{1}{3}\overline{u^2}.$$

Here the quantity $\overline{u^2}$ is called the **mean-square speed** defined as the average value of square-speed (u^2) over all molecules. Since

$$u^2 = u_x^2 + u_y^2 + u_z^2$$

for each molecule, then

$$\overline{u^2} = \overline{u_x^2} + \overline{u_y^2} + \overline{u_z^2}.$$

By substituting $\frac{1}{3}\overline{u^2}$ for $\overline{u_x^2}$ in the expression above, we can get the final expression for the pressure:

$$P = \frac{1}{3}\frac{N}{V} m\overline{u^2} \tag{6.7.5}$$

Because volumes and intermolecular interactions are negligible, postulates 2 and 3 state that all gaseous particles behave identically, regardless of the chemical nature of their component molecules. This is the essence of the ideal gas law, which treats all gases as collections of particles that are identical in all respects except mass. Postulate 2 also explains why it is relatively easy to compress a gas; you simply decrease the distance between the gas molecules.

Postulate 5 provides a molecular explanation for the temperature of a gas. Postulate 5 refers to the *average translational* kinetic energy of the molecules of a gas ($\overline{e_K}$), which can be represented as *and states that at a given Kelvin temperature* (T), *all gases have the same value of*

$$\overline{e_K} = \frac{1}{2} m\overline{u^2} = \frac{3}{2}\frac{R}{N_A}T \tag{6.7.6}$$

where N_A is the Avogadro's constant. The total translational kinetic energy of 1 mole of molecules can be obtained by multiplying the equation by N_A:

$$N_A\overline{e_K} = \frac{1}{2} M\overline{u^2} = \frac{3}{2}RT \tag{6.7.7}$$

where M is the molar mass of the gas molecules and is related to the molecular mass by $M = N_A m$. By rearranging the equation, we can get the relationship between the root-mean square speed (u_{rms}) and the temperature. The rms speed (u_{rms}) is the square root of the sum of the squared speeds divided by the number of particles:

$$u_{rms} = \sqrt{\overline{u^2}} = \sqrt{\frac{u_1^2 + u_2^2 + \cdots u_N^2}{N}} \tag{6.7.8}$$

where N is the number of particles and u_i is the speed of particle i.

The relationship between u_{rms} and the temperature is given by:

$$u_{rms} = \sqrt{\frac{3RT}{M}} \tag{6.7.9}$$

In Equation 6.7.9, u_{rms} has units of meters per second; consequently, the units of molar mass M are kilograms per mole, temperature T is expressed in kelvins, and the ideal gas constant R has the value 8.3145 J/(K•mol). Equation 6.7.9 shows that u_{rms} of a gas is proportional to the square root of its Kelvin temperature and inversely proportional to the square root of its molar mass. The root mean-square speed of a gas increase with increasing temperature. At a given temperature, heavier gas molecules have slower speeds than do lighter ones.

The rms speed and the average speed do not differ greatly (typically by less than 10%). The distinction is important, however, because the rms speed is the speed of a gas particle that has average kinetic energy. Particles of different gases at the same temperature have the same average kinetic energy, not the same average speed. In contrast, the most probable speed (vp) is the speed at which the greatest number of particles is moving. If the average kinetic energy of the particles of a gas increases linearly with increasing temperature, then Equation 6.7.8 tells us that the rms speed must also increase with temperature because the mass of the particles is constant. At higher temperatures, therefore, the molecules of a gas move more rapidly than at lower temperatures, and vp increases.

> *At a given temperature, all gaseous particles have the same average kinetic energy but not the same average speed.*

EXAMPLE 6.7.1

The speeds of eight particles were found to be 1.0, 4.0, 4.0, 6.0, 6.0, 6.0, 8.0, and 10.0 m/s. Calculate their average speed (v_{av}) root mean square speed (v_{rms}), and most probable speed (v_m).

Given: particle speeds

Asked for: average speed (v_{av}), root mean square speed (v_{rms}), and most probable speed (v_m)

Strategy:

Use Equation 6.7.6 to calculate the average speed and Equation 6.7.8 to calculate the rms speed. Find the most probable speed by determining the speed at which the greatest number of particles is moving.

Solution:

The average speed is the sum of the speeds divided by the number of particles:

$$v_{av} = \frac{(1.0 + 4.0 + 4.0 + 6.0 + 6.0 + 6.0 + 8.0 + 10.0)\ \text{m/s}}{8} = 5.6\ \text{m/s}$$

The rms speed is the square root of the sum of the squared speeds divided by the number of particles:

$$v_{rms} = \sqrt{\frac{(1.0^2 + 4.0^2 + 4.0^2 + 6.0^2 + 6.0^2 + 6.0^2 + 8.0^2 + 10.0^2)\ \text{m}^2/\text{s}^2}{8}} = 6.2\ \text{m/s}$$

The most probable speed is the speed at which the greatest number of particles is moving. Of the eight particles, three have speeds of 6.0 m/s, two have speeds of 4.0 m/s, and the other three particles have different speeds. Hence $v_m = 6.0$ m/s. The v_{rms} of the particles, which is related to the average kinetic energy, is greater than their average speed.

6.7.2 BOLTZMANN DISTRIBUTIONS

At any given time, what fraction of the molecules in a particular sample has a given speed? Some of the molecules will be moving more slowly than average, and some will be moving faster than average, but how many in each situation? Answers to questions such as these can have a substantial effect on the amount of product formed during a chemical reaction. This problem was solved mathematically by Maxwell

in 1866; he used statistical analysis to obtain an equation that describes the distribution of molecular speeds at a given temperature. Typical curves showing the distributions of speeds of molecules at several temperatures are displayed in Figure **6.7.3**. Increasing the temperature has two effects. First, the peak of the curve moves to the right because the most probable speed increases. Second, the curve becomes broader because of the increased spread of the speeds. Thus increased temperature increases the *value* of the most probable speed but decreases the relative number of molecules that have that speed. Although the mathematics behind curves such as those in Figure **6.7.3** were first worked out by Maxwell, the curves are almost universally referred to as Boltzmann distributions, after one of the other major figures responsible for the kinetic molecular theory of gases.

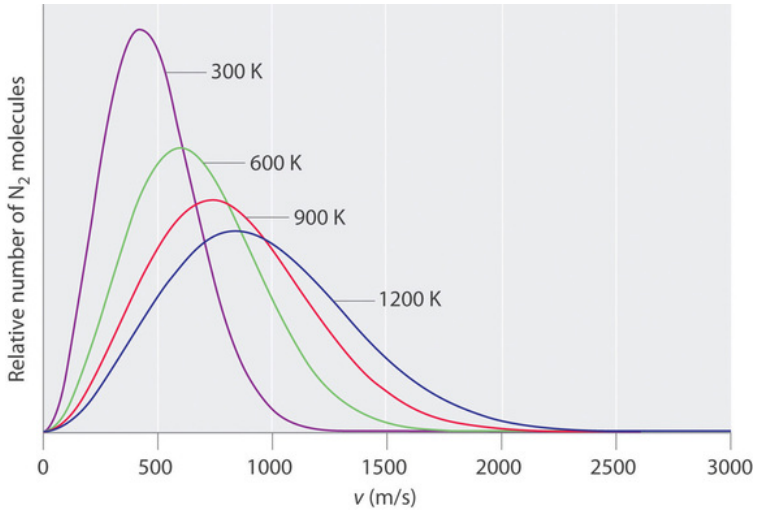


Figure **6.7.3**: The Distributions of Molecular Speeds for a Sample of Nitrogen Gas at Various Temperatures. Increasing the temperature increases both the most probable speed (given at the peak of the curve) and the width of the curve.

6.7.3 THE RELATIONSHIPS AMONG PRESSURE, VOLUME, AND TEMPERATURE

We now describe how the kinetic molecular theory of gases explains some of the important relationships we have discussed previously.

- **Pressure versus Volume**: At constant temperature, the kinetic energy of the molecules of a gas and hence the rms speed remain unchanged. If a given gas sample is allowed to occupy a larger volume, then the speed of the molecules does not change, but the density of the gas (number of particles per unit volume) decreases, and the average distance between the molecules increases. Hence the molecules must, on average, travel farther between collisions. They therefore collide with one another and with the walls of their containers less often, leading to a decrease in pressure. Conversely, increasing the pressure forces the molecules closer together and increases the density, until the collective impact of the collisions of the molecules with the container walls just balances the applied pressure.
- **Volume versus Temperature**: Raising the temperature of a gas increases the average kinetic energy and therefore the rms speed (and the average speed) of the gas molecules. Hence as the temperature increases, the molecules collide with the walls of their containers more frequently and with greater force. This increases the pressure, *unless* the volume increases to reduce the pressure, as we have just seen. Thus an increase in temperature must be offset by an increase in volume for the net impact (pressure) of the gas molecules on the container walls to remain unchanged.
- **Pressure of Gas Mixtures**: Postulate 3 of the kinetic molecular theory of gases states that gas molecules exert no attractive or repulsive forces on one another. If the gaseous molecules do not interact, then the presence of one gas in a gas mixture will have no effect on the pressure exerted by another, and Dalton's law of partial pressures holds.

✔ EXAMPLE **6.7.2**

The temperature of a 4.75 L container of N_2 gas is increased from 0°C to 117°C. What is the qualitative effect of this change on the

a. average kinetic energy of the N_2 molecules?
b. rms speed of the N_2 molecules?
c. average speed of the N_2 molecules?
d. impact of each N_2 molecule on the wall of the container during a collision with the wall?
e. total number of collisions per second of N_2 molecules with the walls of the entire container?
f. number of collisions per second of N_2 molecules with each square centimeter of the container wall?
g. pressure of the N_2 gas?

Given: temperatures and volume

Asked for: effect of increase in temperature

Strategy:

Use the relationships among pressure, volume, and temperature to predict the qualitative effect of an increase in the temperature of the gas.

Solution:

a. Increasing the temperature increases the average kinetic energy of the N_2 molecules.
b. An increase in average kinetic energy can be due only to an increase in the rms speed of the gas particles.
c. If the rms speed of the N_2 molecules increases, the average speed also increases.
d. If, on average, the particles are moving faster, then they strike the container walls with more energy.
e. Because the particles are moving faster, they collide with the walls of the container more often per unit time.
f. The number of collisions per second of N_2 molecules with each square centimeter of container wall increases because the total number of collisions has increased, but the volume occupied by the gas and hence the total area of the walls are unchanged.
g. The pressure exerted by the N_2 gas increases when the temperature is increased at constant volume, as predicted by the ideal gas law.

? EXERCISE 6.7.2

A sample of helium gas is confined in a cylinder with a gas-tight sliding piston. The initial volume is 1.34 L, and the temperature is 22°C. The piston is moved to allow the gas to expand to 2.12 L at constant temperature. What is the qualitative effect of this change on the

a. average kinetic energy of the He atoms?
b. rms speed of the He atoms?
c. average speed of the He atoms?
d. impact of each He atom on the wall of the container during a collision with the wall?
e. total number of collisions per second of He atoms with the walls of the entire container?
f. number of collisions per second of He atoms with each square centimeter of the container wall?
g. pressure of the He gas?

Answer a

no change

Answer b

no change

Answer c

no change

Answer d

no change

Answer e

decreases

Answer f

decreases

Answer g

decreases



6.7.4 SUMMARY

- The kinetic molecular theory of gases provides a molecular explanation for the observations that led to the development of the ideal gas law.
- **Average kinetic energy:**

$$\overline{e_K} = \frac{1}{2}m{u_{\text{rms}}}^2 = \frac{3}{2}\frac{R}{N_A}Tn$$

- **Root mean square speed:**

$$u_{\text{rms}} = \sqrt{\frac{u_1^2 + u_2^2 + \cdots u_N^2}{N}}$$

- **Kinetic molecular theory of gases:**

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

The behavior of ideal gases is explained by the **kinetic molecular theory of gases**. Molecular motion, which leads to collisions between molecules and the container walls, explains pressure, and the large intermolecular distances in gases explain their high compressibility. Although all gases have the same average kinetic energy at a given temperature, they do not all possess the same **root mean square (rms) speed (v_{rms})**. The actual values of speed and kinetic energy are not the same for all particles of a gas but are given by a **Boltzmann distribution**, in which some molecules have higher or lower speeds (and kinetic energies) than average.

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6.8: MOLECULAR EFFUSION AND DIFFUSION

LEARNING OBJECTIVES

- To understand the significance of the kinetic molecular theory of gases

We now describe how the kinetic molecular theory of gases explains some of the important relationships we have discussed previously.

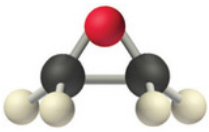
6.8.1 DIFFUSION AND EFFUSION

As you have learned, the molecules of a gas are *not* stationary but in constant and random motion. If someone opens a bottle of perfume in the next room, for example, you are likely to be aware of it soon. Your sense of smell relies on molecules of the aromatic substance coming into contact with specialized olfactory cells in your nasal passages, which contain specific receptors (protein molecules) that recognize the substance. How do the molecules responsible for the aroma get from the perfume bottle to your nose? You might think that they are blown by drafts, but, in fact, molecules can move from one place to another even in a draft-free environment.

Diffusion is the gradual mixing of gases due to the motion of their component particles even in the absence of mechanical agitation such as stirring. The result is a gas mixture with uniform composition. Diffusion is also a property of the particles in liquids and liquid solutions and, to a lesser extent, of solids and solid solutions. The related process, **effusion**, is the escape of gaseous molecules through a small (usually microscopic) hole, such as a hole in a balloon, into an evacuated space.

The phenomenon of effusion had been known for thousands of years, but it was not until the early 19th century that quantitative experiments related the rate of effusion to molecular properties. The rate of effusion of a gaseous substance is inversely proportional to the square root of its molar mass. This relationship *is referred to as Graham's law*, after the Scottish chemist Thomas Graham (1805–1869). The ratio of the effusion rates of two gases is the square root of the inverse ratio of their molar masses*:*

$$\frac{\text{rate of effusion A}}{\text{rate of effusion B}} = \sqrt{\frac{M_B}{M_A}} \tag{6.8.1}$$



Ethylene oxide

Helium (M = 4.00 g/mol) effuses much more rapidly than ethylene oxide (M = 44.0 g/mol). Because helium is less dense than air, helium-filled balloons "float" at the end of a tethering string. Unfortunately, rubber balloons filled with helium soon lose their buoyancy along with much of their volume. In contrast, rubber balloons filled with air tend to retain their shape and volume for a much longer time. Because helium has a molar mass of 4.00 g/mol, whereas air has an average molar mass of about 29 g/mol, pure helium effuses through the microscopic pores in the rubber balloon $\sqrt{\frac{29}{4.00}} = 2.7$ times faster than air. For this reason, high-quality helium-filled balloons are usually made of Mylar, a dense, strong, opaque material with a high molecular mass that forms films that have many fewer pores than rubber. Hence, mylar balloons can retain their helium for days.

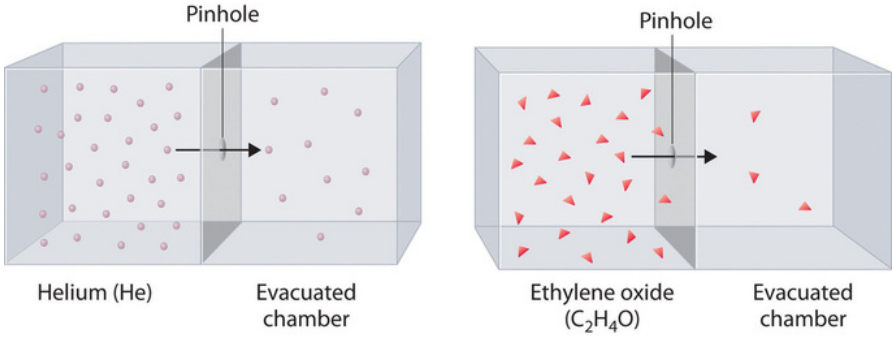


Figure **6.8.1**: The Relative Rates of Effusion of Two Gases with Different Masses. The lighter He atoms (M = 4.00 g/mol) effuse through the small hole more rapidly than the heavier ethylene oxide (C_2H_4O) molecules (M = 44.0 g/mol), as predicted by Graham's law (Equation **6.8.1**).

At a given temperature, heavier molecules move more slowly than lighter molecules.



EXAMPLE 6.8.1

During World War II, scientists working on the first atomic bomb were faced with the challenge of finding a way to obtain large amounts of ^{235}U. Naturally occurring uranium is only 0.720% ^{235}U, whereas most of the rest (99.275%) is ^{238}U, which is not fissionable (i.e., it will not break apart to release nuclear energy) and also actually poisons the fission process. Because both isotopes of uranium have the same reactivity, they cannot be separated chemically. Instead, a process of gaseous effusion was developed using the volatile compound UF_6 (boiling point = 56°C).

1. Calculate the ratio of the rates of effusion of $^{235}UF_6$ and $^{238}UF_6$ for a single step in which UF_6 is allowed to pass through a porous barrier. (The atomic mass of ^{235}U is 235.04, and the atomic mass of ^{238}U is 238.05.)
2. If *n* identical successive separation steps are used, the overall separation is given by the separation in a single step (in this case, the ratio of effusion rates) raised to the *n*th power. How many effusion steps are needed to obtain 99.0% pure $^{235}UF_6$?

Given: isotopic content of naturally occurring uranium and atomic masses of ^{235}U and ^{238}U

Asked for: ratio of rates of effusion and number of effusion steps needed to obtain 99.0% pure $^{235}UF_6$

Strategy:

A. Calculate the molar masses of $^{235}UF_6$ and $^{238}UF_6$, and then use Graham's law to determine the ratio of the effusion rates. Use this value to determine the isotopic content of $^{235}UF_6$ after a single effusion step.

B. Divide the final purity by the initial purity to obtain a value for the number of separation steps needed to achieve the desired purity. Use a logarithmic expression to compute the number of separation steps required.

Solution:

A The first step is to calculate the molar mass of UF_6 containing ^{235}U and ^{238}U. Luckily for the success of the separation method, fluorine consists of a single isotope of atomic mass 18.998. The molar mass of $^{235}UF_6$ is

$$234.04 + (6)(18.998) = 349.03 \text{ g/mol}$$

The molar mass of $^{238}UF_6$ is

$$238.05 + (6)(18.998) = 352.04 \text{ g/mol}$$

The difference is only 3.01 g/mol (less than 1%). The ratio of the effusion rates can be calculated from Graham's law using Equation 6.8.1:

$$\frac{\text{rate } ^{235}UF_6}{\text{rate } ^{238}UF_6} = \sqrt{\frac{352.04 \text{ g/mol}}{349.03 \text{ g/mol}}} = 1.0043$$

B To obtain 99.0% pure $^{235}UF_6$ requires many steps. We can set up an equation that relates the initial and final purity to the number of times the separation process is repeated:

final purity = (initial purity)(separation)^n

In this case, 0.990 = (0.00720)(1.0043)^n, which can be rearranged to give

$$1.0043^n = \frac{0.990}{0.00720} = 137.50$$

Taking the logarithm of both sides gives

$$n \ln(1.0043) = \ln(137.50) \tag{6.8.2}$$

$$n = \frac{\ln(137.50)}{\ln(1.0043)} \tag{6.8.3}$$

$$= 1148 \tag{6.8.4}$$

Thus at least a thousand effusion steps are necessary to obtain highly enriched ^{235}U. Below is a small part of a system that is used to prepare enriched uranium on a large scale.



A Portion of a Plant for Separating Uranium Isotopes by Effusion of UF_6. The large cylindrical objects (note the human for scale) are so-called diffuser (actually effuser) units, in which gaseous UF_6 is pumped through a porous barrier to partially separate the isotopes. The UF_6 must be passed through multiple units to become substantially enriched in ^{235}U.

? EXERCISE 6.8.1

Helium consists of two isotopes: ^3He (natural abundance = 0.000134%) and ^4He (natural abundance = 99.999866%). Their atomic masses are 3.01603 and 4.00260, respectively. Helium-3 has unique physical properties and is used in the study of ultralow temperatures. It is separated from the more abundant ^4He by a process of gaseous effusion.

a. Calculate the ratio of the effusion rates of ^3He and ^4He and thus the enrichment possible in a single effusion step.
b. How many effusion steps are necessary to yield 99.0% pure ^3He?

Answer a

ratio of effusion rates = 1.15200; one step gives 0.000154% ^3He

Answer b

96 steps

6.8.2 RATES OF DIFFUSION OR EFFUSION

Graham's law is an empirical relationship that states that the ratio of the rates of diffusion or effusion of two gases is the square root of the inverse ratio of their molar masses. The relationship is based on the postulate that all gases at the same temperature have the same average kinetic energy. We can write the expression for the average kinetic energy of two gases with different molar masses:

$$KE = \frac{1}{2}\frac{M_A}{N_A}v_{rms,A}^2 = \frac{1}{2}\frac{M_B}{N_A}v_{rms,B}^2 \tag{6.8.5}$$

Multiplying both sides by 2 and rearranging give

$$\frac{v_{rms,B}^2}{v_{rms,A}^2} = \frac{M_A}{M_B} \tag{6.8.6}$$

Taking the square root of both sides gives

$$\frac{v_{rms,B}}{v_{rms,A}} = \sqrt{\frac{M_A}{M_B}} \tag{6.8.7}$$

Thus the rate at which a molecule, or a mole of molecules, diffuses or effuses is directly related to the speed at which it moves. Equation 6.8.7 shows that Graham's law is a direct consequence of the fact that gaseous molecules at the same temperature have the same average kinetic energy.

Typically, gaseous molecules have a speed of hundreds of meters per second (hundreds of miles per hour). The effect of molar mass on these speeds is dramatic, as illustrated in Figure **6.8.3** for some common gases. Because all gases have the same average kinetic energy, according to the Boltzmann distribution, molecules with lower masses, such as hydrogen and helium, have a wider distribution of speeds.

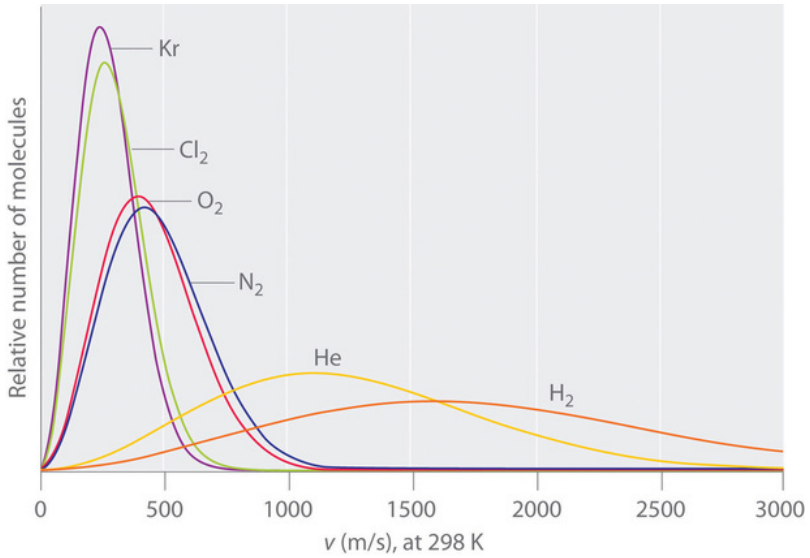


Figure **6.8.3**: The Wide Variation in Molecular Speeds Observed at 298 K for Gases with Different Molar Masses

The lightest gases have a wider distribution of speeds and the highest average speeds.

> *Molecules with lower masses have a wider distribution of speeds and a higher average speed.*

Gas molecules do not diffuse nearly as rapidly as their very high speeds might suggest. If molecules actually moved through a room at hundreds of miles per hour, we would detect odors faster than we hear sound. Instead, it can take several minutes for us to detect an aroma because molecules are traveling in a medium with other gas molecules. Because gas molecules collide as often as 10^{10} times per second, changing direction and speed with each collision, they do not diffuse across a room in a straight line, as illustrated schematically in Figure **6.8.4**.

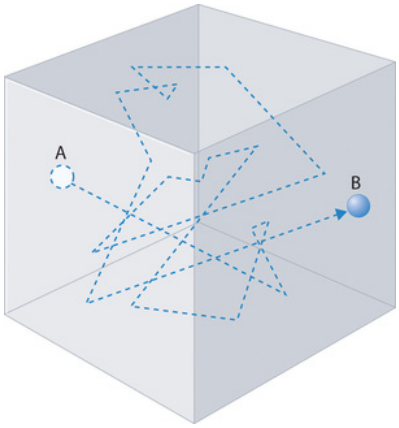


Figure **6.8.4**: The Path of a Single Particle in a Gas Sample. The frequent changes in direction are the result of collisions with other gas molecules and with the walls of the container.

The average distance traveled by a molecule between collisions is the mean free path. The denser the gas, the shorter the mean free path; conversely, as density decreases, the mean free path becomes longer because collisions occur less frequently. At 1 atm pressure and 25°C, for example, an oxygen or nitrogen molecule in the atmosphere travels only about 6.0×10^{-8} m (60 nm) between collisions. In the upper atmosphere at about 100 km altitude, where gas density is much lower, the mean free path is about 10 cm; in space between galaxies, it can be as long as 1×10^{10} m (about 6 million miles).

*The **denser** the gas, the **shorter** the mean free path.*

EXAMPLE 6.8.2

Calculate the rms speed of a sample -butene (C_4H_8) at 20°C.

Given: compound and temperature

Asked for: rms speed

Strategy:

Calculate the molar mass of cis-2-butene. Be certain that all quantities are expressed in the appropriate units and then use Equation 10.8.5 to calculate the rms speed of the gas.

Solution:

To use Equation 10.8.4, we need to calculate the molar mass of *cis*-2-butene and make sure that each quantity is expressed in the appropriate units. Butene is C_4H_8, so its molar mass is 56.11 g/mol. Thus

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}} \tag{6.8.8}$$

$$= \sqrt{\frac{3 \times 8.3145 \ \frac{\text{J}}{\text{K} \cdot \text{mol}} \times (20 + 273) \ \text{K}}{56.11 \times 10^{-3} \ \text{kg}}} \tag{6.8.9}$$

$$= 361 \ m/s \tag{6.8.10}$$

or approximately 810 mi/h.

EXERCISE 6.8.1

Calculate the rms speed of a sample of radon gas at 23°C.

Answer

$1.82 \times 10^2 \ m/s$ (about 410 mi/h)

The kinetic molecular theory of gases demonstrates how a successful theory can explain previously observed empirical relationships (laws) in an intuitively satisfying way. Unfortunately, the actual gases that we encounter are not “ideal,” although their behavior usually approximates that of an ideal gas.

6.8.3 SUMMARY

- The kinetic molecular theory of gases provides a molecular explanation for the observations that led to the development of the ideal gas law.
- **Average kinetic energy:**

$$\overline{e_K} = \frac{1}{2} m {u_{\text{rms}}}^2 = \frac{3}{2} \frac{R}{N_A} T,$$

- **Root mean square speed:**

$$u_{\text{rms}} = \sqrt{\frac{u_1^2 + u_2^2 + \cdots u_N^2}{N}},$$

- **Kinetic molecular theory of gases**:

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}.$$

- **Graham’s law for effusion:**

$$\frac{v_{\text{rms,B}}}{v_{\text{rms,A}}} = \sqrt{\frac{M_A}{M_B}}$$

Diffusion is the gradual mixing of gases to form a sample of uniform composition even in the absence of mechanical agitation. In contrast, **effusion** is the escape of a gas from a container through a tiny opening into an evacuated space. The rate of effusion of a gas is inversely proportional to the square root of its molar mass (**Graham's law**), a relationship that closely approximates the rate of diffusion. As a result, light gases tend to diffuse and effuse much more rapidly than heavier gases. The **mean free path** of a molecule is the average distance it travels between collisions.

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6.9: REAL GASES - DEVIATIONS FROM IDEAL BEHAVIOR

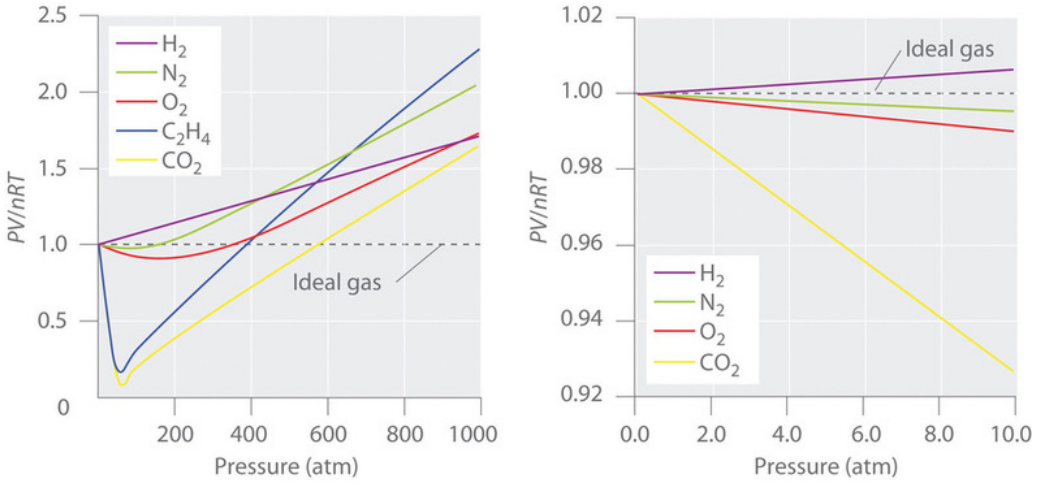
LEARNING OBJECTIVES

- To recognize the differences between the behavior of an ideal gas and a real gas
- To understand how molecular volumes and intermolecular attractions cause the properties of real gases to deviate from those predicted by the ideal gas law.

The postulates of the kinetic molecular theory of gases ignore both the volume occupied by the molecules of a gas and all interactions between molecules, whether attractive or repulsive. In reality, however, all gases have nonzero molecular volumes. Furthermore, the molecules of real gases interact with one another in ways that depend on the structure of the molecules and therefore differ for each gaseous substance. In this section, we consider the properties of real gases and how and why they differ from the predictions of the ideal gas law. We also examine liquefaction, a key property of real gases that is not predicted by the kinetic molecular theory of gases.

6.9.1 PRESSURE, VOLUME, AND TEMPERATURE RELATIONSHIPS IN REAL GASES

For an ideal gas, a plot of PV/nRT versus P gives a horizontal line with an intercept of 1 on the PV/nRT axis. Real gases, however, show significant deviations from the behavior expected for an ideal gas, particularly at high pressures (Figure 6.9.1*a*). Only at relatively low pressures (less than 1 atm) do real gases approximate ideal gas behavior (Figure 6.9.1*b*).



(a) *PV/nRT* at high pressures **(b) *PV/nRT* at low pressures**

Figure 6.9.1: Real Gases Do Not Obey the Ideal Gas Law, Especially at High Pressures. (a) In these plots of PV/nRT versus P at 273 K for several common gases, there are large negative deviations observed for C_2H_4 and CO_2 because they liquefy at relatively low pressures. (b) These plots illustrate the relatively good agreement between experimental data for real gases and the ideal gas law at low pressures.

Real gases also approach ideal gas behavior more closely at higher temperatures, as shown in Figure 6.9.2 for N_2. Why do real gases behave so differently from ideal gases at high pressures and low temperatures? Under these conditions, the two basic assumptions behind the ideal gas law—namely, that gas molecules have negligible volume and that intermolecular interactions are negligible—are no longer valid.

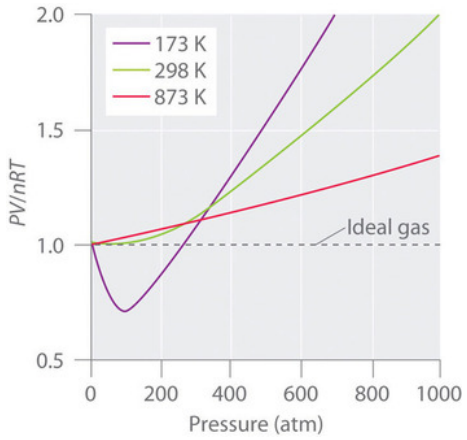


Figure 6.9.2: The Effect of Temperature on the Behavior of Real Gases. A plot of PV/nRT versus P for nitrogen gas at three temperatures shows that the approximation to ideal gas behavior becomes better as the temperature increases.

Because the molecules of an ideal gas are assumed to have zero volume, the volume available to them for motion is always the same as the volume of the container. In contrast, the molecules of a real gas have small but measurable volumes. At low pressures, the gaseous molecules are relatively far apart, but as the pressure of the gas increases, the intermolecular distances become smaller and smaller (Figure 6.9.3). As a result, the volume occupied by the molecules becomes significant compared with the volume of the container. Consequently, the total volume occupied by the gas is greater than the volume predicted by the ideal gas law. Thus at very high pressures, the experimentally measured value of *PV*/*nRT* is greater than the value predicted by the ideal gas law.

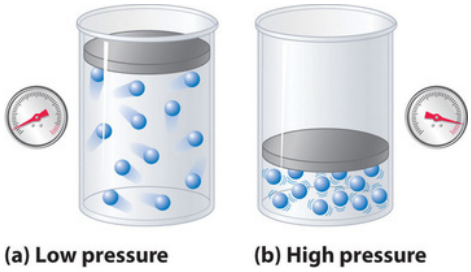


Figure 6.9.3: The Effect of Nonzero Volume of Gas Particles on the Behavior of Gases at Low and High Pressures. (a) At low pressures, the volume occupied by the molecules themselves is small compared with the volume of the container. (b) At high pressures, the molecules occupy a large portion of the volume of the container, resulting in significantly decreased space in which the molecules can move.

Moreover, all molecules are attracted to one another by a combination of forces. These forces become particularly important for gases at low temperatures and high pressures, where intermolecular distances are shorter. Attractions between molecules reduce the number of collisions with the container wall, an effect that becomes more pronounced as the number of attractive interactions increases. Because the average distance between molecules decreases, the pressure exerted by the gas on the container wall decreases, and the observed pressure is *less* than expected (Figure 6.9.4). Thus as shown in Figure 6.9.2, at low temperatures, the ratio of \(PV/nRT\) is lower than predicted for an ideal gas, an effect that becomes particularly evident for complex gases and for simple gases at low temperatures. At very high pressures, the effect of nonzero molecular volume predominates. The competition between these effects is responsible for the minimum observed in the PV/nRT versus P plot for many gases.

> *Nonzero molecular volume makes the actual volume greater than predicted at high pressures; intermolecular attractions make the pressure less than predicted.*

At high temperatures, the molecules have sufficient kinetic energy to overcome intermolecular attractive forces, and the effects of nonzero molecular volume predominate. Conversely, as the temperature is lowered, the kinetic energy of the gas molecules decreases. Eventually, a point is reached where the molecules can no longer overcome the intermolecular attractive forces, and the gas liquefies (condenses to a liquid).

6.9.2 THE VAN DER WAALS EQUATION

The Dutch physicist Johannes van der Waals (1837–1923; Nobel Prize in Physics, 1910) modified the ideal gas law to describe the behavior of real gases by explicitly including the effects of molecular size and intermolecular forces. In his description of gas behavior, the so-called *van der Waals* equation,

$$\underbrace{\left(P+\frac{an^2}{V^2}\right)}_{\text{Pressure Term}}\overbrace{(V-nb)}^{\text{Pressure Term}}=nRT \tag{6.9.1}$$

a and b are empirical constants that are different for each gas. The values of a and b are listed in Table **6.9.1** for several common gases.

Table **6.9.1**:: van der Waals Constants for Some Common Gases (see Table A8 for more complete list)

Gas	a (L^2·atm)/mol^2)	b (L/mol)
He	0.03410	0.0238
Ne	0.205	0.0167
Ar	1.337	0.032
H_2	0.2420	0.0265
N_2	1.352	0.0387
O_2	1.364	0.0319
Cl_2	6.260	0.0542
NH_3	4.170	0.0371
CH_4	2.273	0.0430
CO_2	3.610	0.0429

The pressure term in Equation 6.9.1 corrects for intermolecular attractive forces that tend to reduce the pressure from that predicted by the ideal gas law. Here, n^2/V^2 represents the concentration of the gas (n/V) squared because it takes two particles to engage in the pairwise intermolecular interactions of the type shown in Figure **6.9.4**. The volume term corrects for the volume occupied by the gaseous molecules.

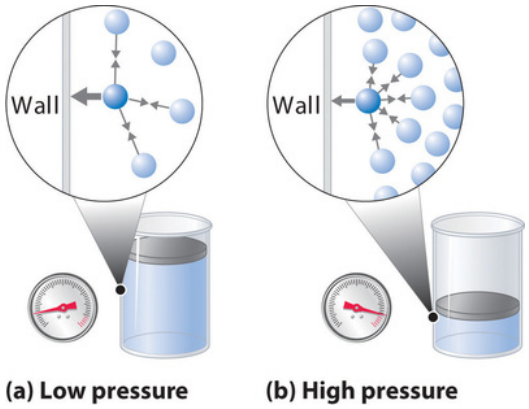


Figure **6.9.4**: The Effect of Intermolecular Attractive Forces on the Pressure a Gas Exerts on the Container Walls. (a) At low pressures, there are relatively few attractive intermolecular interactions to lessen the impact of the molecule striking the wall of the container, and the pressure is close to that predicted by the ideal gas law. (b) At high pressures, with the average intermolecular distance relatively small, the effect of intermolecular interactions is to lessen the impact of a given molecule striking the container wall, resulting in a lower pressure than predicted by the ideal gas law.

The correction for volume is negative, but the correction for pressure is positive to reflect the effect of each factor on V and P, respectively. Because nonzero molecular volumes produce a measured volume that is *larger* than that predicted by the ideal gas law, we must subtract the molecular volumes to obtain the actual volume available. Conversely, attractive intermolecular forces produce a pressure that is *less* than that expected based on the ideal gas law, so the an^2/V^2 term must be added to the measured pressure to correct for these effects.

✔ EXAMPLE 6.9.1

You are in charge of the manufacture of cylinders of compressed gas at a small company. Your company president would like to offer a 4.00 L cylinder containing 500 g of chlorine in the new catalog. The cylinders you have on hand have a rupture pressure of 40 atm. Use both the ideal gas law and the van der Waals equation to calculate the pressure in a cylinder at 25°C. Is this cylinder likely to be safe against sudden rupture (which would be disastrous and certainly result in lawsuits because chlorine gas is highly toxic)?

Given: volume of cylinder, mass of compound, pressure, and temperature

Asked for: safety

Strategy:

A Use the molar mass of chlorine to calculate the amount of chlorine in the cylinder. Then calculate the pressure of the gas using the ideal gas law.

B Obtain *a* and *b* values for Cl_2 from Table **6.9.1**. Use the van der Waals equation (6.9.1) to solve for the pressure of the gas. Based on the value obtained, predict whether the cylinder is likely to be safe against sudden rupture.

Solution:

A We begin by calculating the amount of chlorine in the cylinder using the molar mass of chlorine (70.906 g/mol):

$$n = \frac{m}{M} \tag{6.9.2}$$

$$= \frac{500\ \text{g}}{70.906\ \text{g/mol}} \tag{6.9.3}$$

$$= 7.052\ mol$$

Using the ideal gas law and the temperature in kelvin (298 K), we calculate the pressure:

$$P = \frac{nRT}{V} \tag{6.9.4}$$

$$= \frac{7.052\ \text{mol} \times 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 298\ \text{K}}{4.00\ \text{L}} \tag{6.9.5}$$

$$= 43.1\ atm \tag{6.9.6}$$

If chlorine behaves like an ideal gas, you have a real problem!

B Now let's use the van der Waals equation with the *a* and *b* values for Cl_2 from Table **6.9.1**. Solving for P gives

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2} \tag{6.9.7}$$

$$= \frac{7.052\ \text{mol} \times 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 298\ \text{K}}{4.00\ \text{L} - 7.052\ \text{mol} \times 0.0542 \frac{\text{L}}{\text{mol}}} - \frac{6.260 \frac{\text{L}^2\text{atm}}{\text{mol}^2} \times (7.052\ \text{mol})^2}{(4.00\ \text{L})^2} \tag{6.9.8}$$

$$= 28.2\ \text{atm} \tag{6.9.9}$$

This pressure is well within the safety limits of the cylinder. The ideal gas law predicts a pressure 15 atm higher than that of the van der Waals equation.

? EXERCISE 6.9.1

A 10.0 L cylinder contains 500 g of methane. Calculate its pressure to two significant figures at 27°C using the

a. ideal gas law.
b. van der Waals equation.

Answer a

77 atm

Answer b

67 atm

6.9.3 LIQUEFACTION OF GASES

Liquefaction of gases is the condensation of gases into a liquid form, which is neither anticipated nor explained by the kinetic molecular theory of gases. Both the theory and the ideal gas law predict that gases compressed to very high pressures and cooled to very low temperatures should still behave like gases, albeit cold, dense ones. As gases are compressed and cooled, however, they invariably condense to form liquids, although very low temperatures are needed to liquefy light elements such as helium (for He, 4.2 K at 1 atm pressure).

Liquefaction can be viewed as an extreme deviation from ideal gas behavior. It occurs when the molecules of a gas are cooled to the point where they no longer possess sufficient kinetic energy to overcome intermolecular attractive forces. The precise combination of temperature and pressure needed to liquefy a gas depends strongly on its molar mass and structure, with heavier and more complex molecules usually liquefying at higher temperatures. In general, substances with large van der Waals a coefficients are relatively easy to liquefy because large

a coefficients indicate relatively strong intermolecular attractive interactions. Conversely, small molecules with only light elements have small *a* coefficients, indicating weak intermolecular interactions, and they are relatively difficult to liquefy. Gas liquefaction is used on a massive scale to separate O_2, N_2, Ar, Ne, Kr, and Xe. After a sample of air is liquefied, the mixture is warmed, and the gases are separated according to their boiling points.

> *A large value of a in the van der Waals equation indicates the presence of relatively strong intermolecular attractive interactions.*

The ultracold liquids formed from the liquefaction of gases are called cryogenic liquids, from the Greek *kryo*, meaning "cold," and *genes*, meaning "producing." They have applications as refrigerants in both industry and biology. For example, under carefully controlled conditions, the very cold temperatures afforded by liquefied gases such as nitrogen (boiling point = 77 K at 1 atm) can preserve biological materials, such as semen for the artificial insemination of cows and other farm animals. These liquids can also be used in a specialized type of surgery called *cryosurgery*, which selectively destroys tissues with a minimal loss of blood by the use of extreme cold.



Figure **6.9.5**: A Liquid Natural Gas Transport Ship.

Moreover, the liquefaction of gases is tremendously important in the storage and shipment of fossil fuels (Figure **6.9.5**). Liquefied natural gas (LNG) and liquefied petroleum gas (LPG) are liquefied forms of hydrocarbons produced from natural gas or petroleum reserves. LNG consists mostly of methane, with small amounts of heavier hydrocarbons; it is prepared by cooling natural gas to below about −162°C. It can be stored in double-walled, vacuum-insulated containers at or slightly above atmospheric pressure. Because LNG occupies only about 1/600 the volume of natural gas, it is easier and more economical to transport. LPG is typically a mixture of propane, propene, butane, and butenes and is primarily used as a fuel for home heating. It is also used as a feedstock for chemical plants and as an inexpensive and relatively nonpolluting fuel for some automobiles.

6.9.4 SUMMARY

No real gas exhibits ideal gas behavior, although many real gases approximate it over a range of conditions. Deviations from ideal gas behavior can be seen in plots of PV/nRT versus P at a given temperature; for an ideal gas, PV/nRT versus $P = 1$ under all conditions. At high pressures, most real gases exhibit larger PV/nRT values than predicted by the ideal gas law, whereas at low pressures, most real gases exhibit PV/nRT values close to those predicted by the ideal gas law. Gases most closely approximate ideal gas behavior at high temperatures and low pressures. Deviations from ideal gas law behavior can be described by the **van der Waals equation**, which includes empirical constants to correct for the actual volume of the gaseous molecules and quantify the reduction in pressure due to intermolecular attractive forces. If the temperature of a gas is decreased sufficiently, **liquefaction** occurs, in which the gas condenses into a liquid form. Liquefied gases have many commercial applications, including the transport of large amounts of gases in small volumes and the uses of ultracold **cryogenic liquids**.

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6.E: EXERCISES

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6.E.1 CHARACTERISTICS OF GASES

6.E.1.1 CONCEPTUAL PROBLEMS

1. Explain the differences between the microscopic and the macroscopic properties of matter. Is the boiling point of a compound a microscopic or macroscopic property? molecular mass? Why?
2. How do the microscopic properties of matter influence the macroscopic properties? Can you relate molecular mass to boiling point? Why or why not?
3. For a substance that has gas, liquid, and solid phases, arrange these phases in order of increasing density.
    1. strength of intermolecular interactions.
    2. compressibility.
    3. molecular motion.
    4. order in the arrangement of the molecules or atoms.
4. Which elements of the periodic table exist as gases at room temperature and pressure? Of these, which are diatomic molecules and which are monatomic? Which elements are liquids at room temperature and pressure? Which portion of the periodic table contains elements whose binary hydrides are most likely gases at room temperature?

6.E.2 PRESSURE

6.E.2.1 CONCEPTUAL PROBLEMS

5. What four quantities must be known to completely describe a sample of a gas? What units are commonly used for each quantity?
6. If the applied force is constant, how does the pressure exerted by an object change as the area on which the force is exerted decreases? In the real world, how does this relationship apply to the ease of driving a small nail versus a large nail?
7. As the force on a fixed area increases, does the pressure increase or decrease? With this in mind, would you expect a heavy person to need smaller or larger snowshoes than a lighter person? Explain.
8. What do we mean by *barometric pressure*? Is the barometric pressure at the summit of Mt. Rainier greater than or less than the pressure in Miami, Florida? Why?
9. Which has the highest barometric pressure—a cave in the Himalayas, a mine in South Africa, or a beach house in Florida? Which has the lowest?
10. Mars has an average barometric pressure of 0.007 atm. Would it be easier or harder to drink liquid from a straw on Mars than on Earth? Explain your answer.
11. Is the pressure exerted by a 1.0 kg mass on a 2.0 m^2 area greater than or less than the pressure exerted by a 1.0 kg mass on a 1.0 m^2 area? What is the difference, if any, between the pressure of the atmosphere exerted on a 1.0 m^2 piston and a 2.0 m^2 piston?
12. If you used water in a barometer instead of mercury, what would be the major difference in the instrument?

6.E.2.2 NUMERICAL PROBLEMS

13. Calculate the pressure in pascals and in atmospheres exerted by a carton of milk that weighs 1.5 kg and has a base of 7.0 cm × 7.0 cm. If the carton were lying on its side (height = 25 cm), would it exert more or less pressure? Explain your reasoning.
14. If barometric pressure at sea level is 1.0×10^5 Pa, what is the mass of air in kilograms above a 1.0 cm^2 area of your skin as you lie on the beach? If barometric pressure is 8.2×10^4 Pa on a mountaintop, what is the mass of air in kilograms above a 4.0 cm^2 patch of skin?
15. Complete the following table:

atm	kPa	mmHg	torr
1.40			
		723	
	43.2		

16. The SI unit of pressure is the pascal, which is equal to 1 N/m^2. Show how the product of the mass of an object and the acceleration due to gravity result in a force that, when exerted on a given area, leads to a pressure in the correct SI units. What mass in kilograms applied

to a 1.0 cm^2 area is required to produce a pressure of

a. 1.0 atm?
b. 1.0 torr?
c. 1 mmHg?
d. 1 kPa?

17. If you constructed a manometer to measure gas pressures over the range 0.60–1.40 atm using the liquids given in the following table, how tall a column would you need for each liquid? The density of mercury is 13.5 g/cm^3. Based on your results, explain why mercury is still used in barometers, despite its toxicity.

	Liquid Density (20°C)	Column Height (m)
isopropanol	0.785	
coconut oil	0.924	
glycerine	1.259	

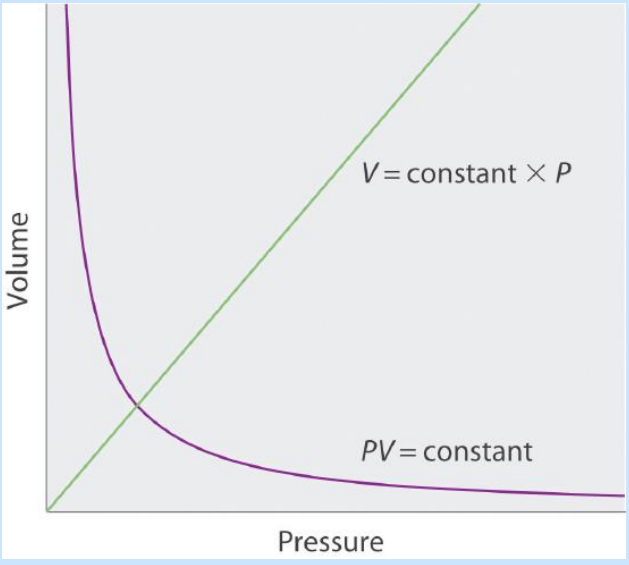
6.E.3 THE GAS LAWS

6.E.3.1 CONCEPTUAL PROBLEMS

18. Sketch a graph of the volume of a gas versus the pressure on the gas. What would the graph of V versus P look like if volume was directly proportional to pressure?
19. What properties of a gas are described by Boyle's law, Charles's law, and Avogadro's law? In each law, what quantities are held constant? Why does the constant in Boyle's law depend on the amount of gas used and the temperature at which the experiments are carried out?
20. Use Charles's law to explain why cooler air sinks.
21. Use Boyle's law to explain why it is dangerous to heat even a small quantity of water in a sealed container.

6.E.3.2 CONCEPTUAL ANSWERS

18.



6.E.3.3 NUMERICAL PROBLEMS

22. A 1.00 mol sample of gas at 25°C and 1.0 atm has an initial volume of 22.4 L. Calculate the results of each change, assuming all the other conditions remain constant.

a. The pressure is changed to 85.7 mmHg. How many milliliters does the gas occupy?
b. The volume is reduced to 275 mL. What is the pressure in millimeters of mercury?
c. The pressure is increased to 25.3 atm. What is the temperature in degrees Celsius?
d. The sample is heated to 30°C. What is the volume in liters?
e. The sample is compressed to 1255 mL, and the pressure is increased to 2555 torr. What is the temperature of the gas in kelvins?

23. A 1.00 mol sample of gas is at 300 K and 4.11 atm. What is the volume of the gas under these conditions? The sample is compressed to 6.0 atm at constant temperature, giving a volume of 3.99 L. Is this result consistent with Boyle's law?

6.E.3.4 NUMERICAL ANSWERS

22. a. 1.99×10^5 mL
    b. 6.19×10^4 mmHg
    c. 7270°C
    d. 22.8 L
    e. 51.4 K

6.E.4 THE IDEAL GAS EQUATION

6.E.4.1 CONCEPTUAL PROBLEMS

24. For an ideal gas, is volume directly proportional or inversely proportional to temperature? What is the volume of an ideal gas at absolute zero?
25. What is meant by STP? If a gas is at STP, what further information is required to completely describe the state of the gas?
26. For a given amount of a gas, the volume, temperature, and pressure under any one set of conditions are related to the volume, the temperature, and the pressure under any other set of conditions by the equation

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \tag{6.E.1}$$

27. Derive this equation from the ideal gas law. At constant temperature, this equation reduces to one of the gas laws discussed previosuly; which one? At constant pressure, this equation reduces to one of the laws discussed in Section 10.3"; which one?
28. Predict the effect of each change on one variable if the other variables are held constant.
    a. If the number of moles of gas increases, what is the effect on the temperature of the gas?
    b. If the temperature of a gas decreases, what is the effect on the pressure of the gas?
    c. If the volume of a gas increases, what is the effect on the temperature of the gas?
    d. If the pressure of a gas increases, what is the effect on the number of moles of the gas?
29. What would the ideal gas law be if the following were true?
    a. volume were proportional to pressure
    b. temperature were proportional to amount
    c. pressure were inversely proportional to temperature
    d. volume were inversely proportional to temperature
    e. both pressure and volume were inversely proportional to temperature
30. Given the following initial and final values, what additional information is needed to solve the problem using the ideal gas law?

Given	Solve for
V_1, T_1, T_2, n_1	n_2
P_1, P_2, T_2, n_2	n_1
T_1, T_2	V_2
P_1, n_1	P_2

31. Given the following information and using the ideal gas law, what equation would you use to solve the problem?

Given	Solve for
P_1, P_2, T_1	T_2
V_1, n_1, n_2	V_2
T_1, T_2, V_1, V_2, n_2	n_1

32. Using the ideal gas law as a starting point, derive the relationship between the density of a gas and its molar mass. Which would you expect to be denser—nitrogen or oxygen? Why does radon gas accumulate in basements and mine shafts?
33. Use the ideal gas law to derive an equation that relates the remaining variables for a sample of an ideal gas if the following are held constant.
    a. amount and volume

b. pressure and amount
c. temperature and volume
d. temperature and amount
e. pressure and temperature

34. Tennis balls that are made for Denver, Colorado, feel soft and do not bounce well at lower altitudes. Use the ideal gas law to explain this observation. Will a tennis ball designed to be used at sea level be harder or softer and bounce better or worse at higher altitudes?

6.E.4.2 CONCEPTUAL ANSWERS

33. a. P/T = constant
b. V/T = constant (Charles' law)
c. P/n = constant
d. PV = constant (Boyle's law)
e. V/n = constant (Avogadro's law)

6.E.4.3 NUMERICAL PROBLEMS

35. Calculate the number of moles in each sample at STP.
a. 1580 mL of NO_2
b. 847 cm^3 of HCl
c. 4.792 L of H_2
d. a 15.0 cm × 6.7 cm × 7.5 cm container of ethane

36. Calculate the number of moles in each sample at STP.
a. 2200 cm^3 of CO_2
b. 1200 cm^3 of N_2
c. 3800 mL of SO_2
d. 13.75 L of NH_3

37. Calculate the mass of each sample at STP.
a. 36 mL of HI
b. 550 L of H_2S
c. 1380 cm^3 of CH_4

38. Calculate the mass of each sample at STP.
a. 3.2 L of N_2O
b. 65 cm^3 of Cl_2
c. 3600 mL of HBr

39. Calculate the volume in liters of each sample at STP.
a. 1.68 g of Kr
b. 2.97 kg of propane (C_3H_8)
c. 0.643 mg of $(CH_3)_2O$

40. Calculate the volume in liters of each sample at STP.
a. 3.2 g of Xe
b. 465 mg of CS_2
c. 5.34 kg of acetylene (C_2H_2)

41. Calculate the volume of each gas at STP.
a. 1.7 L at 28°C and 96.4 kPa
b. 38.0 mL at 17°C and 103.4 torr
c. 650 mL at −15°C and 723 mmHg

42. Calculate the volume of each gas at STP.
a. 2.30 L at 23°C and 740 mmHg
b. 320 mL at 13°C and 97.2 kPa
c. 100.5 mL at 35°C and 1.4 atm

43. A 8.60 L tank of nitrogen gas at a pressure of 455 mmHg is connected to an empty tank with a volume of 5.35 L. What is the final pressure in the system after the valve connecting the two tanks is opened? Assume that the temperature is constant.

44. At constant temperature, what pressure in atmospheres is needed to compress 14.2 L of gas initially at 25.2 atm to a volume of 12.4 L? What pressure is needed to compress 27.8 L of gas to 20.6 L under similar conditions?
45. One method for preparing hydrogen gas is to pass HCl gas over hot aluminum; the other product of the reaction is $AlCl_3$. If you wanted to use this reaction to fill a balloon with a volume of 28,500 L at sea level and a temperature of 78°F, what mass of aluminum would you need? What volume of HCl at STP would you need?
46. An 3.50 g sample of acetylene is burned in excess oxygen according to the following reaction:

$$2\,C_2H_2\,(g) + 5\,O_2\,(g) \longrightarrow 4\,CO_2\,(g) + 2\,H_2O\,(l) \tag{6.E.2}$$

At STP, what volume of CO_2(g) is produced?

47. Calculate the density of ethylene (C_2H_4) under each set of conditions.
    a. 7.8 g at 0.89 atm and 26°C
    b. 6.3 mol at 102.6 kPa and 38°C
    c. 9.8 g at 3.1 atm and −45°C
48. Determine the density of O_2 under each set of conditions.
    a. 42 g at 1.1 atm and 25°C
    b. 0.87 mol at 820 mmHg and 45°C
    c. 16.7 g at 2.4 atm and 67°C
49. At 140°C, the pressure of a diatomic gas in a 3.0 L flask is 635 kPa. The mass of the gas is 88.7 g. What is the most likely identity of the gas?
50. What volume must a balloon have to hold 6.20 kg of H_2 for an ascent from sea level to an elevation of 20,320 ft, where the temperature is −37°C and the pressure is 369 mmHg?
51. What must be the volume of a balloon that can hold 313.0 g of helium gas and ascend from sea level to an elevation of 1.5 km, where the temperature is 10.0°C and the pressure is 635.4 mmHg?
52. A typical automobile tire is inflated to a pressure of 28.0 lb/in.^{2} Assume that the tire is inflated when the air temperature is 20°C; the car is then driven at high speeds, which increases the temperature of the tire to 43°C. What is the pressure in the tire? If the volume of the tire had increased by 8% at the higher temperature, what would the pressure be?
53. The average respiratory rate for adult humans is 20 breaths per minute. If each breath has a volume of 310 mL of air at 20°C and 0.997 atm, how many moles of air does a person inhale each day? If the density of air is 1.19 kg/m^3, what is the average molecular mass of air?
54. Kerosene has a self-ignition temperature of 255°C. It is a common accelerant used by arsonists, but its presence is easily detected in fire debris by a variety of methods. If a 1.0 L glass bottle containing a mixture of air and kerosene vapor at an initial pressure of 1 atm and an initial temperature of 23°C is pressurized, at what pressure would the kerosene vapor ignite?

6.E.4.4 NUMERICAL ANSWERS

35. a. 7.05×10^{-2} mol
    b. 3.78×10^{-2} mol
    c. 0.2138 mol
    d. 3.4×10^{-2} mol
36.
37. a. 0.21 g HI;
    b. 840 g H_2S;
    c. 0.988 g CH_4
38.
39. a. 0.449 L Kr
    b. 1510 L C_3H_8
    c. 3.13×10^{-4} L $(CH_3)_2O$
40.
41.
42. a. 1.5 L
    b. 4.87 mL
    c. 650 mL
43. 281 mmHg

44.
45. 20.9 kg Al, 5.20×10^4 L HCl
46.
47. a. 1.0 g/L
    b. 1.1 g/L
    c. 4.6 g/L
48.
49.
50.
51. 2174 L

6.E.5 FURTHER APPLICATIONS OF THE IDEAL-GAS EQUATIONS

6.E.5.1 CONCEPTUAL PROBLEMS

55. Why are so many industrially important reactions carried out in the gas phase?
56. The volume of gas produced during a chemical reaction can be measured by collecting the gas in an inverted container filled with water. The gas forces water out of the container, and the volume of liquid displaced is a measure of the volume of gas. What additional information must be considered to determine the number of moles of gas produced? The volume of some gases cannot be measured using this method. What property of a gas precludes the use of this method?
57. Equal masses of two solid compounds (A and B) are placed in separate sealed flasks filled with air at 1 atm and heated to 50°C for 10 hours. After cooling to room temperature, the pressure in the flask containing A was 1.5 atm. In contrast, the pressure in the flask containing B was 0.87 atm. Suggest an explanation for these observations. Would the masses of samples A and B still be equal after the experiment? Why or why not?

6.E.5.2 NUMERICAL PROBLEMS

58. Balance each chemical equation and then determine the volume of the indicated reactant at STP that is required for complete reaction. Assuming complete reaction, what is the volume of the products?
    a. $SO_2(g) + O_2(g) \rightarrow SO_3(g)$ given 2.4 mol of O_2
    b. $H_2(g) + Cl_2(g) \rightarrow HCl(g)$ given 0.78 g of H_2
    c. $C_2H_6(g) + O_2(g) \rightarrow CO_2(g) + H_2O(g)$ given 1.91 mol of O_2
59. During the smelting of iron, carbon reacts with oxygen to produce carbon monoxide, which then reacts with iron(III) oxide to produce iron metal and carbon dioxide. If 1.82 L of CO_2 at STP is produced,
    a. what mass of CO is consumed?
    b. what volume of CO at STP is consumed?
    c. how much O_2 (in liters) at STP is used?
    d. what mass of carbon is consumed?
    e. how much iron metal (in grams) is produced?
60. Complete decomposition of a sample of potassium chlorate produced 1.34 g of potassium chloride and oxygen gas.
    a. What is the mass of $KClO_3$ in the original sample?
    b. What mass of oxygen is produced?
    c. What is the volume of oxygen produced at STP?
61. The combustion of a 100.0 mg sample of an herbicide in excess oxygen produced 83.16 mL of CO_2 and 72.9 mL of H_2O vapor at STP. A separate analysis showed that the sample contained 16.44 mg of chlorine. If the sample is known to contain only C, H, Cl, and N, determine the percent composition and the empirical formula of the herbicide.
62. The combustion of a 300.0 mg sample of an antidepressant in excess oxygen produced 326 mL of CO_2 and 164 mL of H_2O vapor at STP. A separate analysis showed that the sample contained 23.28% oxygen. If the sample is known to contain only C, H, O, and N, determine the percent composition and the empirical formula of the antidepressant.

6.E.5.3 NUMERICAL ANSWERS

60. 1. 2.20 g $KClO_3$
    2. 0.863 g O_2
    3. 604 mL O_2

61.

62. Percent composition: 58.3% C, 4.93% H, 23.28% O, and 13.5% N; empirical formula: $C_{10}H_{10}O_3N_2$

6.E.6 GAS MIXTURES AND PARTIAL PRESSURES

6.E.6.1 CONCEPTUAL PROBLEMS

63. Dalton's law of partial pressures makes one key assumption about the nature of the intermolecular interactions in a mixture of gases. What is it?
64. What is the relationship between the partial pressure of a gas and its mole fraction in a mixture?

6.E.6.2 NUMERICAL PROBLEMS

65. What is the partial pressure of each gas if the following amounts of substances are placed in a 25.0 L container at 25°C? What is the total pressure of each mixture?
    a. 1.570 mol of CH_4 and 0.870 mol of CO_2
    b. 2.63 g of CO and 1.24 g of NO_2
    c. 1.78 kg of CH_3Cl and 0.92 kg of SO_2
66. What is the partial pressure of each gas in the following 3.0 L mixtures at 37°C as well as the total pressure?
    a. 0.128 mol of SO_2 and 0.098 mol of methane (CH_4)
    b. 3.40 g of acetylene (C_2H_2) and 1.54 g of He
    c. 0.267 g of NO, 4.3 g of Ar, and 0.872 g of SO_2
67. In a mixture of helium, oxygen, and methane in a 2.00 L container, the partial pressures of He and O_2 are 13.6 kPa and 29.2 kPa, respectively, and the total pressure inside the container is 95.4 kPa. What is the partial pressure of methane? If the methane is ignited to initiate its combustion with oxygen and the system is then cooled to the original temperature of 30°C, what is the final pressure inside the container (in kilopascals)?
68. A 2.00 L flask originally contains 1.00 g of ethane (C_2H_6) and 32.0 g of oxygen at 21°C. During ignition, the ethane reacts completely with oxygen to produce CO_2 and water vapor, and the temperature of the flask increases to 200°C. Determine the total pressure and the partial pressure of each gas before and after the reaction.
69. If a 20.0 L cylinder at 19°C is charged with 5.0 g each of sulfur dioxide and oxygen, what is the partial pressure of each gas? The sulfur dioxide is ignited in the oxygen to produce sulfur trioxide gas, and the mixture is allowed to cool to 19°C at constant pressure. What is the final volume of the cylinder? What is the partial pressure of each gas in the piston?
70. The highest point on the continent of Europe is Mt. Elbrus in Russia, with an elevation of 18,476 ft. The highest point on the continent of South America is Mt. Aconcagua in Argentina, with an elevation of 22,841 ft.
    a. The following table shows the variation of atmospheric pressure with elevation. Use the data in the table to construct a plot of pressure versus elevation.

Elevation (km)	Pressure in Summer (mmHg)	Pressure in Winter (mmHg)
0.0	760.0	760.0
1.0	674.8	670.6
1.5	635.4	629.6
2.0	598.0	590.8
3.0	528.9	519.7
5.0	410.6	398.7
7.0	314.9	301.6
9.0	237.8	224.1

    b. Use your graph to estimate the pressures in millimeters of mercury during the summer and the winter at the top of both mountains in both atmospheres and kilopascals.
    c. Given that air is 20.95% O_2 by volume, what is the partial pressure of oxygen in atmospheres during the summer at each location?

6.E.6.3 NUMERICAL ANSWERS

67. 52.6 kPa, 66.2 kPa

6.E.7 KINETIC-MOLECULAR THEORY

6.E.8 MOLECULAR EFFUSION AND DIFFUSION

6.E.8.1 CONCEPTUAL PROBLEMS

71. Which of the following processes represents effusion, and which represents diffusion?
    a. helium escaping from a hole in a balloon
    b. vapor escaping from the surface of a liquid
    c. gas escaping through a membrane
72. Which postulate of the kinetic molecular theory of gases most readily explains the observation that a helium-filled balloon is round?
73. Why is it relatively easy to compress a gas? How does the compressibility of a gas compare with that of a liquid? A solid? Why? Which of the postulates of the kinetic molecular theory of gases most readily explains these observations?
74. What happens to the average kinetic energy of a gas if the rms speed of its particles increases by a factor of 2? How is the rms speed different from the average speed?
75. Which gas—radon or helium—has a higher average kinetic energy at 100°C? Which has a higher average speed? Why? Which postulate of the kinetic molecular theory of gases most readily supports your answer?
76. What is the relationship between the average speed of a gas particle and the temperature of the gas? What happens to the distribution of molecular speeds if the temperature of a gas is increased? Decreased?
77. Qualitatively explain the relationship between the number of collisions of gas particles with the walls of a container and the pressure of a gas. How does increasing the temperature affect the number of collisions?
78. What happens to the average kinetic energy of a gas at constant temperature if the
    a. volume of the gas is increased?
    b. pressure of the gas is increased?
79. What happens to the density of a gas at constant temperature if the
    a. volume of the gas is increased?
    b. pressure of the gas is increased?
80. Use the kinetic molecular theory of gases to describe how a decrease in volume produces an increase in pressure at constant temperature. Similarly, explain how a decrease in temperature leads to a decrease in volume at constant pressure.
81. Graham's law is valid only if the two gases are at the same temperature. Why?
82. If we lived in a helium atmosphere rather than in air, would we detect odors more or less rapidly than we do now? Explain your reasoning. Would we detect odors more or less rapidly at sea level or at high altitude? Why?

6.E.8.2 NUMERICAL PROBLEMS

83. At a given temperature, what is the ratio of the rms speed of the atoms of Ar gas to the rms speed of molecules of H_2 gas?
84. At a given temperature, what is the ratio of the rms speed of molecules of CO gas to the rms speed of molecules of H_2S gas?
85. What is the ratio of the rms speeds of argon and oxygen at any temperature? Which diffuses more rapidly?
86. What is the ratio of the rms speeds of Kr and NO at any temperature? Which diffuses more rapidly?
87. Deuterium (D) and tritium (T) are heavy isotopes of hydrogen. Tritium has an atomic mass of 3.016 amu and has a natural abundance of 0.000138%. The effusion of hydrogen gas (containing a mixture of H_2, HD, and HT molecules) through a porous membrane can be used to obtain samples of hydrogen that are enriched in tritium. How many membrane passes are necessary to give a sample of hydrogen gas in which 1% of the hydrogen molecules are HT?
88. Samples of HBr gas and NH_3 gas are placed at opposite ends of a 1 m tube. If the two gases are allowed to diffuse through the tube toward one another, at what distance from each end of the tube will the gases meet and form solid NH_4Br?

6.E.8.3 NUMERICAL ANSWERSS

83. At any temperature, the rms speed of hydrogen is 4.45 times that of argon.<

6.E.9 REAL GASES: DEVIATIONS FROM IDEAL BEHAVIOR

6.E.9.1 CONCEPTUAL PROBLEMS

89. What factors cause deviations from ideal gas behavior? Use a sketch to explain your answer based on interactions at the molecular level.
90. Explain the effect of nonzero atomic volume on the ideal gas law at high pressure. Draw a typical graph of volume versus $1/P$ for an ideal gas and a real gas.

91. For an ideal gas, the product of pressure and volume should be constant, regardless of the pressure. Experimental data for methane, however, show that the value of PV decreases significantly over the pressure range 0 to 120 atm at 0°C. The decrease in PV over the same pressure range is much smaller at 100°C. Explain why PV decreases with increasing temperature. Why is the decrease less significant at higher temperatures?
92. What is the effect of intermolecular forces on the liquefaction of a gas? At constant pressure and volume, does it become easier or harder to liquefy a gas as its temperature increases? Explain your reasoning. What is the effect of increasing the pressure on the liquefaction temperature?
93. Describe qualitatively what a and b, the two empirical constants in the van der Waals equation, represent.
94. In the van der Waals equation, why is the term that corrects for volume negative and the term that corrects for pressure positive? Why is n/V squared?
95. Liquefaction of a gas depends strongly on two factors. What are they? As temperature is decreased, which gas will liquefy first—ammonia, methane, or carbon monoxide? Why?
96. What is a cryogenic liquid? Describe three uses of cryogenic liquids.
97. Air consists primarily of O_2, N_2, Ar, Ne, Kr, and Xe. Use the concepts discussed in this chapter to propose two methods by which air can be separated into its components. Which component of air will be isolated first?
98. How can gas liquefaction facilitate the storage and transport of fossil fuels? What are the potential drawbacks to these methods?

6.E.9.2 NUMERICAL PROBLEMS

99. The van der Waals constants for xenon are $a = 4.19\ (L^2{\cdot}atm)/mol^2$ and $b = 0.0510$ L/mol. If a 0.250 mol sample of xenon in a container with a volume of 3.65 L is cooled to −90°C, what is the pressure of the sample assuming ideal gas behavior? What would be the *actual* pressure under these conditions?
100. The van der Waals constants for water vapor are $a = 5.46\ (L^2{\cdot}atm)/mol^2$ and $b = 0.0305$ L/mol. If a 20.0 g sample of water in a container with a volume of 5.0 L is heated to 120°C, what is the pressure of the sample assuming ideal gas behavior? What would be the *actual* pressure under these conditions?

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6.S: GASES (SUMMARY)

6.S.1 10.1: CHARACTERISTICS OF GASES

Bulk matter can exist in three states: gas, liquid, and solid. Gases have the lowest density of the three, are highly compressible, and fill their containers completely. Elements that exist as gases at room temperature and pressure are clustered on the right side of the periodic table; they occur as either monatomic gases (the noble gases) or diatomic molecules (some halogens, N_2, O_2).

- Gases expand spontaneously to fill containers in which they are held, equaling their volume. Consequently, they are highly compressible.
- Gases form homogeneous mixtures with each other *regardless* of the identities or relative proportions of the component gases
- The characteristic properties of gases arise because the individual molecules are relatively far apart, hence, acting largely as though they were alone.

6.S.2 10.2: PRESSURE

Pressure is defined as the force exerted per unit area; it can be measured using a barometer or manometer. Four quantities must be known for a complete physical description of a sample of a gas: temperature, volume, amount, and pressure. Pressure is force per unit area of surface; the SI unit for pressure is the pascal (Pa), defined as 1 newton per square meter (N/m^2). The pressure exerted by an object is proportional to the force it exerts and inversely proportional to the area.

- Pressure, *P*, is the Force, *F*, that acts on a given Area, *A*:

$$P = F/A$$

Atmospheric Pressure and the Barometer

- The force, *F*, exerted by any object is the product of its mass, *m*, times its acceleration, *a*: $F = ma$
- SI unit for force is kg-m/s^2 and is called the *Newton* (N)
- SI unit of pressure is N/m^2, called a Pascal
- **Standard atmospheric pressure**: defined as 760 torr (760 mm Hg), or, in SI units, 101.325 kPa
- **Atmosphere**: unit of pressure equal to 760 torr; 1 atm = 101.325 kPa

6.S.3 10.3: THE GAS LAWS

The volume of a gas is inversely proportional to its pressure and directly proportional to its temperature and the amount of gas. Boyle showed that the volume of a sample of a gas is inversely proportional to pressure (Boyle's law), Charles and Gay-Lussac demonstrated that the volume of a gas is directly proportional to its temperature at constant pressure (Charles's law), and Avogadro showed that the volume of a gas is directly proportional to the number of moles of gas (Avogadro's law).

The Pressure-Volume Relationship: Boyle's Law

- Boyle's law states that the volume of a fixed quantity of gas maintained at constant temperature is inversely proportional to the pressure. When two measurements are inversely proportional, one gets smaller as the other one gets larger.

$$PV = constant$$

where P = pressure, V = volume

The Temperature-Volume Relationship: Charles's Law

- **Charles's law**: states that the volume of a fixed amount of gas maintained at constant pressure is directly proportional to its absolute temperature. Thus, as the pressure gets higher, so does the temperature.

$$\frac{V}{T} = constant$$

where V = volume, T = Temperature

The Quantity-Volume Relationship: Avogadro's Law

- **Law of combining volumes**: at a given pressure and temperature, the volumes of gases that react with one another are in the ratios of small whole numbers. (ie: $2H_2 + O_2 = 2H_2O$)
- **Avogadro's hypothesis**: equal volumes of gases at the same temperature and pressure contain equal number of molecules
- **Avogadro's law**: The volume of a gas maintained at constant temperature and pressure is directly proportional to the number of moles of the gas

$$V = constant \times n$$

where V = volume, *n* = number of moles

6.S.4 10.4: THE IDEAL GAS EQUATION

The empirical relationships among the volume, the temperature, the pressure, and the amount of a gas can be combined into the ideal gas law, PV = nRT. The proportionality constant, R, is called the gas constant. The ideal gas law describes the behavior of an ideal gas, a hypothetical substance whose behavior can be explained quantitatively by the ideal gas law and the kinetic molecular theory of gases. Standard temperature and pressure (STP) is 0°C and 1 atm.

Ideal-gas equation

$$PV = nRT$$

where P = pressure, V = volume, n = number of moles, R = gas constant, T = Temperature (always expressed on absolute-temperature scale, usually Kelvin)

The *Gas constant* (***R***) is the constant of proportionality in the ideal-gas equation. Some values of R are given below

Some values of R

Units	Numerical value
L-atm/mol-K	0.08206
Cal/mol-K	1.987
J/mol-K	8.314
M^3-Pa/mol-K	8.314
L-torr/mol-K	62.36

Standard temperature and pressure (STP): 0°C and 1 atm. 1 mol of gas at STP has a volume of 22.41 L (*molar volume*)

6.S.5 10.5: FURTHER APPLICATIONS OF THE IDEAL-GAS EQUATIONS

The relationship between the amounts of products and reactants in a chemical reaction can be expressed in units of moles or masses of pure substances, of volumes of solutions, or of volumes of gaseous substances. The ideal gas law can be used to calculate the volume of gaseous products or reactants as needed. In the laboratory, gases produced in a reaction are often collected by the displacement of water from filled vessels; the amount of gas can be calculated from the volume of water displaced.

Density of a gas (*\rho\) = density, M = molar mass):

\[\rho = \dfrac{PM}{ RT} \nonumber \]

Molar mass of a gas:

$$M = \frac{\rho RT}{P}$$

6.S.6 10.6: GAS MIXTURES AND PARTIAL PRESSURES

The pressure exerted by each gas in a gas mixture is independent of the pressure exerted by all other gases present. Consequently, the total pressure exerted by a mixture of gases is the sum of the partial pressures of the components (Dalton's law of partial pressures). The amount of gas in a mixture may be described by its partial pressure or its mole fraction. In a mixture, the partial pressure of each gas is the product of the total pressure and the mole fraction.

- **Partial pressure**: the pressure exerted by a particular gas in a mixture
- **Dalton's law of partial pressures**: law stating that the total pressure of a mixture of gases equals the sum of the pressures that each would exert if it were present alone

The total pressure at constant temperature and volume is determined by the total number of moles of gas present, whether that total represents just one substance or a mixture

Partial Pressures and Mole Fractions

- **Mole fraction**: the ratio of the number of one component of a mixture to the total moles of all components; abbreviated χ, with a subscript to identify the components.

The partial pressure of a gas in a mixture is its mole fraction times the total pressure

6.S.7 10.7: KINETIC-MOLECULAR THEORY

The behavior of ideal gases is explained by the kinetic molecular theory of gases. Molecular motion, which leads to collisions between molecules and the container walls, explains pressure, and the large intermolecular distances in gases explain their high compressibility. Although all gases have the same average kinetic energy at a given temperature, they do not all possess the same root mean square speed. The actual values of speed and kinetic energy are not the same for all gas particles.

Kinetic-molecular theory: set of assumptions about the nature of gases. These assumptions, when translated into mathematical form, yield the ideal-gas equation

1. Gases consist of large numbers of molecules that are in continuous, random motion
2. The volume of all the molecules of the gas is negligible compared to the total volume in which the gas is contained
3. Attractive and repulsive forces between gas molecules are negligible
4. Energy can be transferred between molecules during collisions, but the *average* kinetic energy of the molecules does *not* change with time, as long as the temperature of the gas remains constant
5. The average kinetic energy of the molecules is proportional to absolute temperature. At any given temperature, the molecules of all gases have the same average kinetic energy

The pressure of a gas is caused by collisions of molecules with the walls of the container. The magnitude of the pressure is determined by how often and how "hard" the molecules strike the walls.

If two different gases are at the same temperature, they have the same average kinetic energy. If the temperature of a gas is doubled, its kinetic energy also doubles. Hence, molecular motion increases with increasing temperature.

- **Root-mean-square (rms) speed**: the square root of the squared speeds of the gas molecules in a gas sample. This quantity is the speed of a molecule possessing average kinetic energy.

The rms speed is important because the average kinetic energy of the gas molecules, ε, is related directly to u^2:

$$\varepsilon = \frac{1}{2}mu^2$$

where m is the mass of the molecule

Because mass doesn't change with temperature, the rms speed (and also the average speed) of molecules must increase as temperature increases

Applications to the Gas Laws

1. *Effect of a volume increase at constant temperature*: If the volume is increased, the molecules must move a longer distance between collisions. Consequently, there are fewer collisions per unit time with the container walls, and pressure decreases.
2. *Effect of a temperature increase at constant volume*: An increases in temperature means an increase in the average kinetic energy of the molecules. If there is no change in volume, there will be more collisions with the walls per unit time. Furthermore, the molecules strike harder, hence explaining how the observed pressure increases.

6.S.8 10.8: MOLECULAR EFFUSION AND DIFFUSION

Diffusion is the gradual mixing of gases to form a sample of uniform composition even in the absence of mechanical agitation. In contrast, effusion is the escape of a gas from a container through a tiny opening into an evacuated space. The rate of effusion of a gas is inversely proportional to the square root of its molar mass (Graham's law), a relationship that closely approximates the rate of diffusion. As a result, light gases tend to diffuse and effuse much more rapidly than heavier gases.

A gas composed of light gas particles will have the same average kinetic energy as one composed of much heavier particles, provided that the two gases are at the same temperature. The mass, m, of the particles in the lighter gas is smaller that that in the heavier gas. Consequently, the particles of the lighter gas must have a higher rms speed, u, than the heavier one:

$$u = \sqrt{\frac{3RT}{M}}$$

Since M is in the denominator, the less massive the gas molecules, the higher the rms speed

- **Effusion**: the escape of a gas through an orifice or hole. The rate of effusion depends on the molecular mass of the gas.
- **Diffusion**: the spreading of one substance through a space or through another substance

Graham's Law of Effusion

- **Graham's law**: law stating that the rate of effusion of a gas is inversely proportional to the square root of its molecular weight

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

where r is the rate of effusion

- The rate of effusion is also directly proportional to the rms speed of the molecules. This is because the only way for the molecule to escape is to "collide" with the opening. Hence, the faster the molecules are moving, the greater the likelihood that a molecule will hit the opening and effuse.

Diffusion and Mean Free Path

- Diffusion, like effusion, is faster for light molecules than for heavy ones. The diffusion of gases is much slower than molecular speeds because of molecular collisions. Because of these collisions, the direction of motion of a gas molecule is constantly changing, making this a slow process.
- **Mean free path**: average distance traveled by a molecule between collisions. The higher the density of a gas, the smaller the mean free path

6.S.9 10.9: REAL GASES - DEVIATIONS FROM IDEAL BEHAVIOR

No real gas exhibits ideal gas behavior, although many real gases approximate it over a range of conditions. Gases most closely approximate ideal gas behavior at high temperatures and low pressures. Deviations from ideal gas law behavior can be described by the van der Waals equation, which includes empirical constants to correct for the actual volume of the gaseous molecules and quantify the reduction in pressure due to intermolecular attractive forces.

The ideal gas equation may be rearranged as follows to understand deviations from ideal-gas behavior:

$$\frac{PV}{RT} = n$$

- For a mole of ideal gas (n = 1), the quantity PV / RT = 1 at all pressures. However, real gases do not behave in such a way. At high pressures, the deviation is very high, however it is less with lower pressures. In general, the deviations from idea behavior increase as temperature decreases, becoming significant near the temperature at which the gas is converted into a liquid.
- Basic assumptions in the kinetic molecular theory suggest that molecules of an ideal gas occupy no space and have no attraction for each other. *Real molecules, however, do have finite volumes, and they do attract one another*.
- Also, if the volume of the container in which the gas is contained is large, the molecules have plenty of free space, and do not take much of the container's volume itself. However, as pressure increases, the gas molecules occupy a much larger fraction of the container's volume.
- In addition, the attractive forces between molecules come into play at short distances, as when molecules are crowded together at high pressures. Because of these attractive forces, the impact of a given molecule with the wall of the container is lessened.
- Temperature determines how effective attractive forces between gas molecules are. As the gas is cooled, the average kinetic energy decreases, while intermolecular attractions remain constant.

The Van der Walls Equation

According to the ideal gas equation:

$$\underbrace{P = \frac{nRT}{V}}_{\text{ideal gas}}$$

According to Van der Waals:

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

Correction for volume of molecules – Correction for molecular attractions

- The Van der Waals constant b is a measure of the actual volume occupied by a mole of gas molecules; b has units of L/mol.
- The Van der Walls constant a has units of L^2-atm/mol^2. The magnitude of a reflects how strongly the gas molecules attract each other

Van der Waals equation

$$\left[P + \left(\frac{n^2 a}{V^2}\right)\right](V - nb) = nRT$$

The Van der Waals constants *a* and *b* are different for each gas. The values of these constants generally increase with an increase in mass of the molecule and with an increase in the complexity of its structures.

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CHAPTER OVERVIEW

7: FUNDAMENTALS OF THERMOCHEMISTRY (HEAT AND ENTHALPY)

This chapter introduces you to **thermochemistry**, a branch of chemistry that describes the energy changes that occur during chemical reactions. In some situations, the energy produced by chemical reactions is actually of greater interest to chemists than the material products of the reaction. For example, the controlled combustion of organic molecules, primarily sugars and fats, within our cells provides the energy for physical activity, thought, and other complex chemical transformations that occur in our bodies. Similarly, our energy-intensive society extracts energy from the combustion of fossil fuels, such as coal, petroleum, and natural gas, to manufacture clothing and furniture, heat your home in winter and cool it in summer, and power the car or bus that gets you to class and to the movies.

7.1: Systems, States and Processes
7.2: Heat as a Mechanism to Transfer Energy
7.3: Work as a Mechanism to Transfer Energy
7.4: The First Law of Thermodynamics
7.5: Heat Capacity and Calorimetry
7.6: Molecules as Energy Carriers and Converters
7.7: Heats of Reactions - ΔU and ΔH
7.8: Indirect Determination of ΔH - Hess's Law
7.9: Standard Enthalpies of Formation
7.E: Fundamentals of Thermochemistry (Exercises)

Thumbnail: Dancing Flames of burning charcoal in the dark. (CC SA-BY 3.0; Oscar),

7.1 OUTSIDE LINKS

- Barrow, Gordon M. "Thermodynamics should be built on energy-not on heat and work." J. Chem. Educ. **1988**: 65, 122.
- Brouwer, Henry. "Small-scale thermochemistry experiment (ML)." J. Chem. Educ. **1991**:68, A178.
- King, Edward L. "Thermodynamics of the thermal decomposition of water by closed chemical cycles." *J. Chem. Educ.* **1981**, *58*, 975.
- Peckham, G. D., McNaught, Ian J. 'Heat and work are not "forms of energy".' J. Chem. Educ. **1993**: 70, 103.

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7.1: SYSTEMS, STATES AND PROCESSES

LEARNING OBJECTIVES

- To understand the concept of energy and its various forms.
- To know the relationship between energy, work, and heat.

Because energy takes many forms, only some of which can be seen or felt, it is defined by its effect on matter. For example, microwave ovens produce energy to cook food, but we cannot see that energy. In contrast, we can see the energy produced by a light bulb when we switch on a lamp. In this section, we describe the forms of energy and discuss the relationship between energy, heat, and work.

7.1.1 FORMS OF ENERGY

The forms of energy include thermal energy, radiant energy, electrical energy, nuclear energy, and chemical energy (Figure **7.1.1**). Thermal energy results from atomic and molecular motion; the faster the motion, the greater the thermal energy. The temperature of an object is a measure of its thermal energy content. Radiant energy is the energy carried by light, microwaves, and radio waves. Objects left in bright sunshine or exposed to microwaves become warm because much of the radiant energy they absorb is converted to thermal energy. Electrical energy results from the flow of electrically charged particles. When the ground and a cloud develop a separation of charge, for example, the resulting flow of electrons from one to the other produces lightning, a natural form of electrical energy. Nuclear energy is stored in the nucleus of an atom, and chemical energy is stored within a chemical compound because of a particular arrangement of atoms.

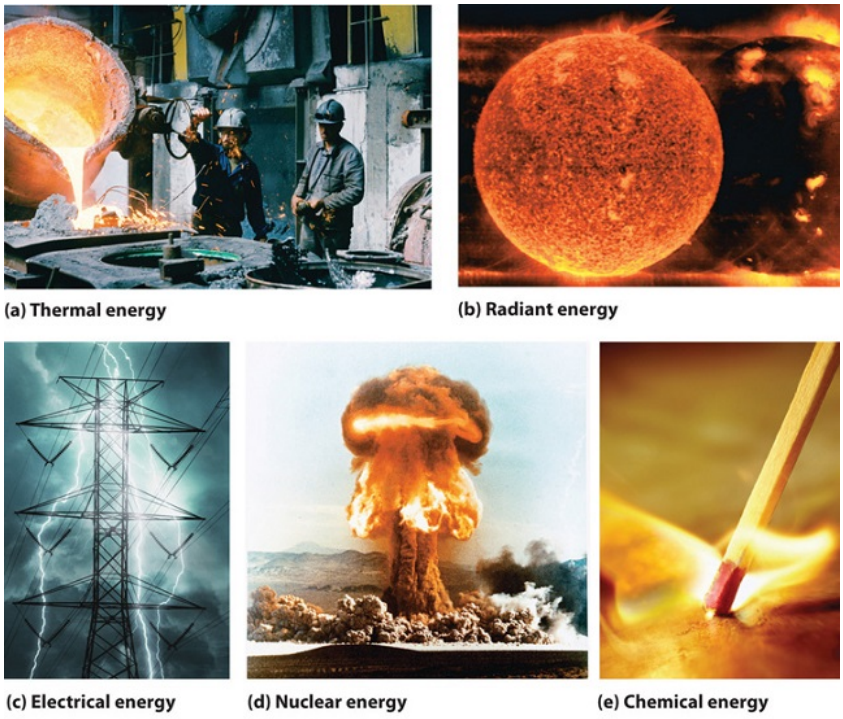


Figure **7.1.1**: Forms of Energy. (a) *Thermal energy* results from atomic and molecular motion; molten steel at 2,000°C has high thermal energy. (b) *Radiant energy* (e.g., from the sun) is the energy in light, microwaves, and radio waves. (c) Lightning is an example of *electrical energy*, which is due to the flow of electrically charged particles. (d) *Nuclear energy* is released when particles in the nucleus of the atom are rearranged. (e) *Chemical energy* results from the particular arrangement of atoms in a chemical compound; the heat and light produced in this reaction are due to energy released during the breaking and reforming of chemical bonds. (CC BY-SA-NC; anonymous)

Electrical energy, nuclear energy, and chemical energy are different forms of potential energy (PE), which is energy stored in an object because of the relative positions or orientations of its components. A brick lying on the windowsill of a 10th-floor office has a great deal of potential energy, but until its position changes by falling, the energy is contained. In contrast, kinetic energy (KE) is energy due to the motion of an object. When the brick falls, its potential energy is transformed to kinetic energy, which is then transferred to the object on the ground that it strikes. The electrostatic attraction between oppositely charged particles is a form of potential energy, which is converted to kinetic energy when the charged particles move toward each other.

Energy can be converted from one form to another (Figure **7.1.2**) or, as we saw with the brick, transferred from one object to another. For example, when you climb a ladder to a high diving board, your body uses chemical energy produced by the combustion of organic molecules. As you climb, the chemical energy is converted to *mechanical work* to overcome the force of gravity. When you stand on the end of the diving board, your potential energy is greater than it was before you climbed the ladder: the greater the distance from the water, the greater the potential energy. When you then dive into the water, your potential energy is converted to kinetic energy as you fall, and when you hit the surface, some of that energy is transferred to the water, causing it to splash into the air. Chemical energy can also be converted to radiant energy; one common example is the light emitted by fireflies, which is produced from a chemical reaction.

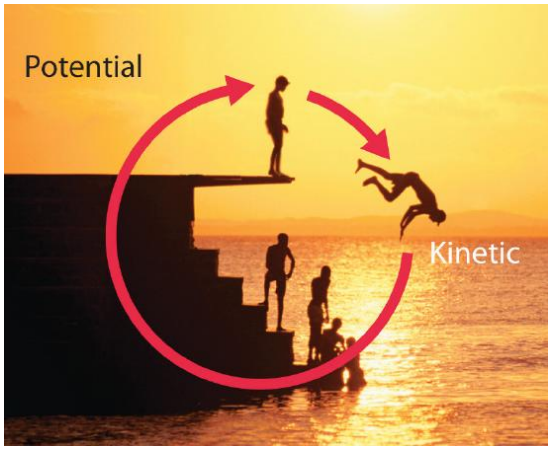


Figure **7.1.2**: Interconversion of Forms of Energy. When a swimmer steps off the platform to dive into the water, potential energy is converted to kinetic energy. As the swimmer climbs back up to the top of the diving platform, chemical energy is converted to mechanical work. (CC BY-SA-NC; anonymous)

Although energy can be converted from one form to another, *the total amount of energy in the universe remains constant*. This is known as the **law of conservation of energy**: *Energy cannot be created or destroyed.*

7.1.2 KINETIC AND POTENTIAL ENERGY

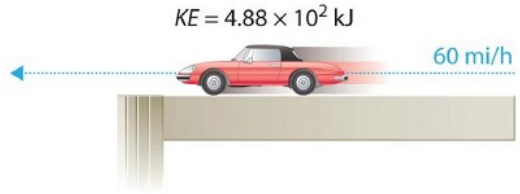
The kinetic energy of an object is related to its mass m and velocity v:

$$KE = \frac{1}{2}mv^2 \tag{7.1.1}$$

For example, the kinetic energy of a 1360 kg (approximately 3000 lb) automobile traveling at a velocity of 26.8 m/s (approximately 60 mi/h) is

$$\begin{aligned} KE &= \frac{1}{2}(1360\,kg)(26.8\,ms)^2 \\ &= 4.88 \times 10^5 g \cdot m^2 \end{aligned} \tag{7.1.2}$$

Because all forms of energy can be interconverted, energy in any form can be expressed using the same units as kinetic energy. The SI unit of energy, the joule (J), is named after the British physicist James Joule (1818–1889), an early worker in the field of energy, is defined as 1 kilogram·meter^2/second^2 (kg·m^2/s^2). Because a joule is such a small quantity of energy, chemists usually express energy in kilojoules (1 kJ = 10^3 J). For example, the kinetic energy of the 1360 kg car traveling at 26.8 m/s is 4.88 × 10^5 J or 4.88 × 10^2 kJ. It is important to remember that *the units of energy are the same regardless of the form of energy*, whether thermal, radiant, chemical, or any other form. Because heat and work result in changes in energy, their units must also be the same.



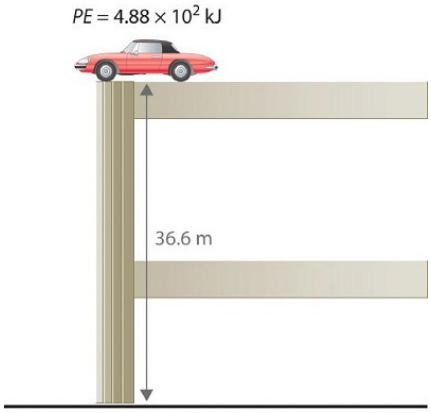
To demonstrate, let's calculate the potential energy of the same 1360 kg automobile if it were parked on the top level of a parking garage 36.6 m (120 ft) high. Its potential energy is equivalent to the amount of work required to raise the vehicle from street level to the top level of the parking garage, which is

$$w = F\,d. \tag{7.1.3}$$

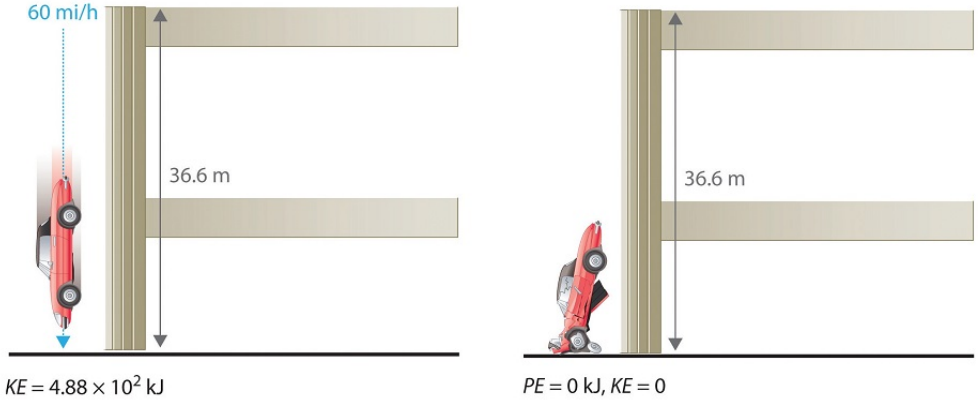
The force (F) exerted by gravity on any object is equal to its mass (m, in this case, 1360 kg) times the acceleration (a) due to gravity (g, 9.81 m/s^2 at Earth's surface). The distance (d) is the height (h) above street level (in this case, 36.6 m). Thus the potential energy of the car is as follows:

$$\begin{aligned} PE = F\,d = m\,a\,d = m\,g\,h \\ &= (1360\,Kg)\left(\frac{9.81\,m}{s^2}\right)(36.6\,m) \\ &= 4.88 \times 10^5\,\frac{Kg \cdot m^2}{s^2} \\ &= 4.88 \times 10^5 J = 488\,kJ \end{aligned} \tag{7.1.4}$$

The units of potential energy are the same as the units of kinetic energy. Notice that in this case the potential energy of the stationary automobile at the top of a 36.6 m high parking garage is the same as its kinetic energy at 60 mi/h.



If the vehicle fell from the roof of the parking garage, its potential energy would be converted to kinetic energy, and it is reasonable to infer that the vehicle would be traveling at 60 mi/h just before it hit the ground, neglecting air resistance. After the car hit the ground, its potential and kinetic energy would both be zero.



Potential energy is usually defined relative to an arbitrary standard position (in this case, the street was assigned an elevation of zero). As a result, we usually calculate only differences in potential energy: in this case, the difference between the potential energy of the car on the top level of the parking garage and the potential energy of the same car on the street at the base of the garage.

7.1.3 UNITS OF ENERGY

The units of energy are the same for all forms of energy. Energy can also be expressed in the non-SI units of calories (cal), where 1 cal was originally defined as the amount of energy needed to raise the temperature of exactly 1 g of water from 14.5 °C to 15.5 °C.We specify the exact temperatures because the amount of energy needed to raise the temperature of 1 g of water 1 °C varies slightly with elevation. To three significant figures, however, this amount is 1.00 cal over the temperature range 0 °C–100 °C. The name is derived from the Latin *calor*, meaning "heat." Although energy may be expressed as either calories or joules, calories were defined in terms of heat, whereas joules were defined in terms of motion. Because calories and joules are both units of energy, however, the calorie is now defined in terms of the joule:

$$1\ cal \equiv 4.184\ J \quad \text{(exactly)} \tag{7.1.5}$$

$$1\ J = 0.2390\ cal \tag{7.1.6}$$

In this text, we will use the SI units—joules (J) and kilojoules (kJ)—exclusively, except when we deal with nutritional information.

EXAMPLE 7.1.1: KINETIC ENERGY OF BASEBALLS

a. If the mass of a baseball is 149 g, what is the kinetic energy of a fastball clocked at 100 mi/h?

b. A batter hits a pop fly, and the baseball (with a mass of 149 g) reaches an altitude of 250 ft. If we assume that the ball was 3 ft above home plate when hit by the batter, what is the increase in its potential energy?

Given

- mass and velocity or height

Asked for

- kinetic and potential energy

Strategy

Use Equation 7.1.1 to calculate the kinetic energy and Equation 7.1.4 to calculate the potential energy, as appropriate.

Solution

a. The kinetic energy of an object is given by $\frac{1}{2}mv^2$ In this case, we know both the mass and the velocity, but we must convert the velocity to SI units:

$$\begin{aligned} v &= \left(\frac{100\ \cancel{mi}}{1\ \cancel{h}}\right)\left(\frac{1\ \cancel{h}}{60\ \cancel{min}}\right)\left(\frac{1\ \cancel{min}}{60\ s}\right)\left(\frac{1.61\ \cancel{km}}{1\ \cancel{mi}}\right)\left(\frac{1000\ m}{1\ \cancel{km}}\right) \\ &= 44.7\ m/s \end{aligned}$$

The kinetic energy of the baseball is therefore (via Equation 7.1.1)

$$\begin{aligned} KE &= \frac{1}{2}149\ \cancel{g}\left(\frac{1\ kg}{1000\ \cancel{g}}\right)\left(\frac{44.7\ m}{s}\right)^2 \\ &= 1.49 \times 10^2\ \frac{kg \cdot m^2}{s^2} \\ &= 1.49 \times 10^2\ J \end{aligned}$$

b. The increase in potential energy is the same as the amount of work required to raise the ball to its new altitude, which is (250 − 3) = 247 feet above its initial position. Thus

$$\begin{aligned} PE &= 149\ \cancel{g}\left(\frac{1\ kg}{1000\ \cancel{g}}\right)\left(\frac{9.81\ m}{s^2}\right)(247\ \cancel{ft})\left(\frac{0.3048\ m}{1\ \cancel{ft}}\right) \\ &= 1.10 \times 10^2\ \frac{kg \cdot m^2}{s^2} \\ &= 1.10 \times 10^2\ J \end{aligned}$$

EXERCISE 7.1.1

a. In a bowling alley, the distance from the foul line to the head pin is $59\ ft$ and $10\ \frac{13}{16}in.$ (18.26 m). If a 16 lb (7.3 kg) bowling ball takes 2.0 s to reach the head pin, what is its kinetic energy at impact? (Assume its speed is constant.)

b. What is the potential energy of a 16 lb bowling ball held 3.0 ft above your foot?

Answer a

3.10×10^2 J

Answer b

65 J

7.1.4 SYSTEMS AND SURROUNDINGS

To study the flow of energy during a chemical reaction, we need to distinguish between a system, the small, well-defined part of the universe in which we are interested (such as a chemical reaction), and its surroundings, the rest of the universe, including the container in which the reaction is carried out (Figure **7.1.3**). In the discussion that follows, the mixture of chemical substances that undergoes a reaction is always the system, and the flow of heat can be from the system to the surroundings or vice versa.

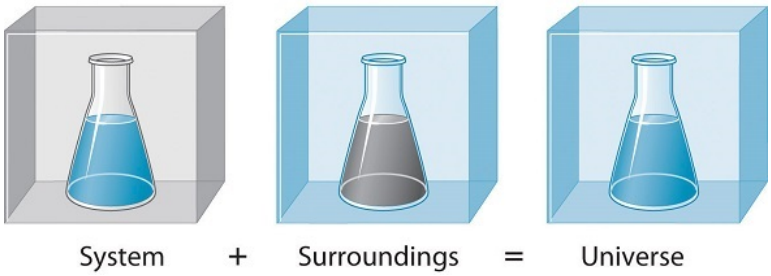


Figure **7.1.3**: A System and Its Surroundings. The system is that part of the universe we are interested in studying, such as a chemical reaction inside a flask. The surroundings are the rest of the universe, including the container in which the reaction is carried out. (CC BY-SA-NC; anonymous)

Three kinds of systems are important in chemistry. An open system can exchange both matter and energy with its surroundings. A pot of boiling water is an open system because a burner supplies energy in the form of heat, and matter in the form of water vapor is lost as the water boils. A closed system can exchange energy but not matter with its surroundings. The sealed pouch of a ready-made dinner that is dropped into a pot of boiling water is a closed system because thermal energy is transferred to the system from the boiling water but no matter is exchanged (unless the pouch leaks, in which case it is no longer a closed system). An isolated system exchanges neither energy nor matter with the surroundings. Energy is always exchanged between a system and its surroundings, although this process may take place very slowly. A truly isolated system does not actually exist. An insulated thermos containing hot coffee approximates an isolated system, but eventually the coffee cools as heat is transferred to the surroundings. In all cases, the amount of heat lost by a system is equal to the amount of heat gained by its surroundings and vice versa. That is, *the total energy of a system plus its surroundings is constant*, which must be true if *energy is conserved*.

The state of a system is a complete description of a system at a given time, including its temperature and pressure, the amount of matter it contains, its chemical composition, and the physical state of the matter. A state function is a property of a system whose magnitude depends on only the present state of the system, not its previous history. Temperature, pressure, volume, and potential energy are all state functions. The temperature of an oven, for example, is independent of however many steps it may have taken for it to reach that temperature. Similarly, the pressure in a tire is independent of how often air is pumped into the tire for it to reach that pressure, as is the final volume of air in the tire. Heat and work, on the other hand, are not state functions because they are *path dependent*. For example, a car sitting on the top level of a parking garage has the same potential energy whether it was lifted by a crane, set there by a helicopter, driven up, or pushed up by a group of students (Figure **7.1.4**). The amount of work expended to get it there, however, can differ greatly depending on the path chosen. If the students decided to carry the car to the top of the ramp, they would perform a great deal more work than if they simply pushed the car up the ramp (unless, of course, they neglected to release the parking brake, in which case the work expended would increase substantially!). The potential energy of the car is the same, however, no matter which path they choose.

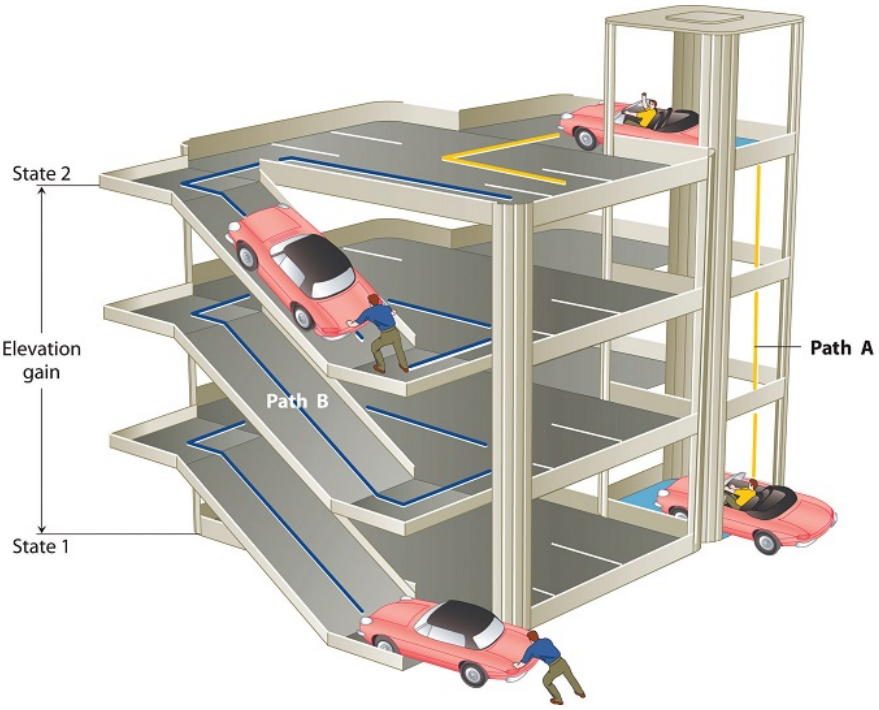


Figure **7.1.4**: Elevation as an Example of a State Function. The change in elevation between state 1 (at the bottom of the parking garage) and state 2 (at the top level of the parking garage) is the same for both paths A and B; it does not depend on which path is taken from the bottom to the top. In contrast, the distance traveled and the work needed to reach the top do depend on which path is taken. Elevation is a state function, but distance and work are *not* state functions. (CC BY-SA-NC; anonymous)

7.1.5 SUMMARY

Thermochemistry is a branch of chemistry that qualitatively and quantitatively describes the energy changes that occur during chemical reactions. **Energy** is the capacity to do work. **Mechanical work** is the amount of energy required to move an object a given distance when opposed by a force. **Thermal energy** is due to the random motions of atoms, molecules, or ions in a substance. The **temperature** of an object is a measure of the amount of thermal energy it contains. **Heat (*q*)** is the transfer of thermal energy from a hotter object to a cooler one. Energy can take many forms; most are different varieties of **potential energy (*PE*)**, energy caused by the relative position or orientation of an object. **Kinetic energy (*KE*)** is the energy an object possesses due to its motion. Energy can be converted from one form to another, but the **law of conservation of energy** states that energy can be neither created nor destroyed. The most common units of energy are the **joule (J)**, defined as 1 $(kg \cdot m^2)/s^2$, and the **calorie**, defined as the amount of energy needed to raise the temperature of 1 g of water by 1°C (1 cal = 4.184 J).

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7.2: HEAT AS A MECHANISM TO TRANSFER ENERGY

LEARNING OBJECTIVES

- To calculate changes in internal energy
- Distinguish the related properties of heat, thermal energy, and temperature
- Define and distinguish specific heat and heat capacity, and describe the physical implications of both
- Perform calculations involving heat, specific heat, and temperature change

Thermal energy is kinetic energy associated with the random motion of atoms and molecules. Temperature is a quantitative measure of "hot" or "cold." When the atoms and molecules in an object are moving or vibrating quickly, they have a higher average kinetic energy (KE), and we say that the object is "hot." When the atoms and molecules are moving slowly, they have lower KE, and we say that the object is "cold" (Figure **7.2.1**). Assuming that no chemical reaction or phase change (such as melting or vaporizing) occurs, increasing the amount of thermal energy in a sample of matter will cause its temperature to increase. And, assuming that no chemical reaction or phase change (such as condensation or freezing) occurs, decreasing the amount of thermal energy in a sample of matter will cause its temperature to decrease.

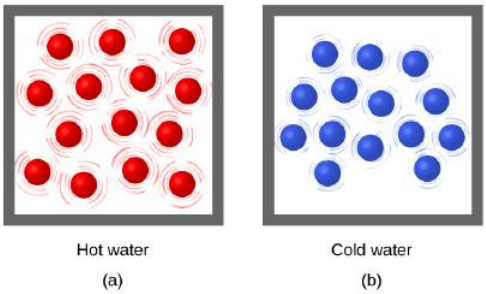


Figure **7.2.1**: (a) The molecules in a sample of hot water move more rapidly than (b) those in a sample of cold water.

Heat (q) is the transfer of thermal energy between two bodies at different temperatures. Heat flow (a redundant term, but one commonly used) increases the thermal energy of one body and decreases the thermal energy of the other. Suppose we initially have a high temperature (and high thermal energy) substance (H) and a low temperature (and low thermal energy) substance (L). The atoms and molecules in H have a higher average KE than those in L. If we place substance H in contact with substance L, the thermal energy will flow spontaneously from substance H to substance L. The temperature of substance H will decrease, as will the average KE of its molecules; the temperature of substance L will increase, along with the average KE of its molecules. Heat flow will continue until the two substances are at the same temperature (Figure **7.2.2**).

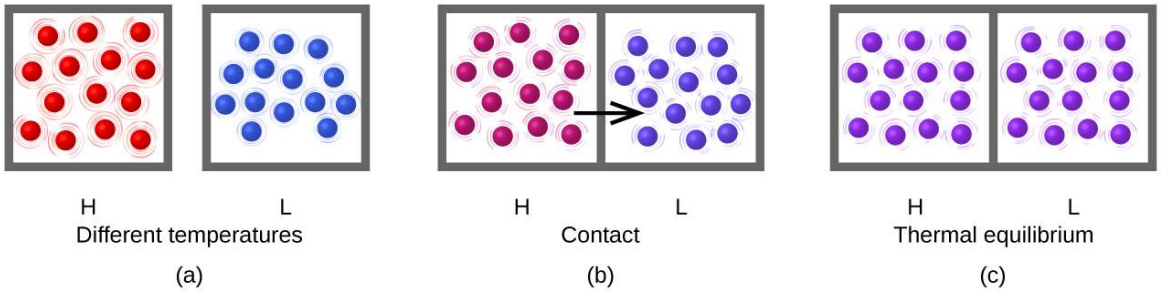


Figure **7.2.2**: (a) Substances H and L are initially at different temperatures, and their atoms have different average kinetic energies. (b) When they are put into contact with each other, collisions between the molecules result in the transfer of kinetic (thermal) energy from the hotter to the cooler matter. (c) The two objects reach "thermal equilibrium" when both substances are at the same temperature, and their molecules have the same average kinetic energy.

Matter undergoing chemical reactions and physical changes can release or absorb heat. A change that releases heat is called an **exothermic process**. For example, the combustion reaction that occurs when using an oxyacetylene torch is an exothermic process—this process also releases energy in the form of light as evidenced by the torch's flame (Figure **7.2.3*a***). A reaction or change that absorbs heat is an endothermic process. A cold pack used to treat muscle strains provides an example of an endothermic process. When the substances in the cold pack (water and a salt like ammonium nitrate) are brought together, the resulting process absorbs heat, leading to the sensation of cold.



Figure **7.2.3**: (a) An oxyacetylene torch produces heat by the combustion of acetylene in oxygen. The energy released by this exothermic reaction heats and then melts the metal being cut. The sparks are tiny bits of the molten metal flying away. (b) A cold pack uses an endothermic process to create the sensation of cold. (credit a: modification of work by “Skatebiker”/Wikimedia commons).

HEAT DOES NOT "FLOW" NOR DOES HEAT "TRANSFER"

The definition of heat is the transfer of *thermal energy* between two bodies at different temperatures, since temperature is a measure of the average kinetic energy of a sample, this means that heat is the flow of kinetic energy from one spot to another. Therefore, heat is the process of the energy flow and a specific system; a system does not "contain" heat, therefore heat cannot be "transferred" nor does not "flow."

The concept of heat flow originates from the incorrect theory in the 19th century called caloric theory that postulated that heat was connect to a mythical fluid that flows from hotter systems to colder systems. Unfortunately, the vernacular usage of terms involving heat flowing is ingrained in the English language and it is difficulty to avoid them in scientific discussions of thermodynamics. Nevertheless, it is important to emphasize that the important concept that heat does not flow.

7.2.1 DIRECTION OF HEAT "FLOW": ENDOTHERMIC VS. EXOTHERMIC PROCESSES

The reaction of powdered aluminum with iron(III) oxide, known as the thermite reaction, generates an enormous amount of heat—enough, in fact, to melt steel. The balanced chemical equation for the reaction is as follows:

$$2\,Al\,(s) + Fe_2O_3\,(s) \rightarrow 2\,Fe\,(s) + Al_2O_3\,(s) \tag{7.2.1}$$

We can also write this chemical equation as

$$2\,Al\,(s) + Fe_2O_3\,(s) \rightarrow 2\,Fe\,(s) + Al_2O_3\,(s) + heat \tag{7.2.2}$$

to indicate that heat is one of the products. Chemical equations in which heat is shown as either a reactant or a product are called *thermochemical equations*. In this reaction, the system consists of aluminum, iron, and oxygen atoms; everything else, including the container, makes up the surroundings. During the reaction, so much heat is produced that the iron liquefies. Eventually, the system cools; the iron solidifies as heat is transferred to the surroundings. A process in which heat (q) is transferred *from* a system *to* its surroundings is described as exothermic. By convention, $q < 0$ for an exothermic reaction.



When you hold an ice cube in your hand, heat from the surroundings (including your hand) is transferred to the system (the ice), causing the ice to melt and your hand to become cold. We can describe this process by the following thermochemical equation:

$$\text{heat} + \text{H}_2\text{O}\,(\text{s}) \rightarrow \text{H}_2\text{O}\,(\text{l}) \tag{7.2.3}$$

When heat is transferred *to* a system *from* its surroundings, the process is endothermic. By convention, $q > 0$ for an endothermic reaction. It is poor form to have a ***heat*** term in the chemical reaction like in Equations 7.2.2 and 7.2.3 since heat is it not a true species in the reaction. However, this is a convenient approach to represent exothermic and endothermic behavior and is commonly used by chemists.

> *By convention, $q < 0$ for an exothermic reaction and $q > 0$ for an endothermic reaction.*

? EXERCISE 7.2.1

Decide whether the following are endothermic or exothermic processes

a. water evaporates off a shower door
b. an acid tablet being added to a pool and the surrounding water heats up
c. NH_4Cl is dissolved in water and the solution cools
d. the burning of a log in a campfire

Hint

During an endothermic process heat is absorbed from surroundings, causing them to cool, so in every case where there is cooling there is most likely an endothermic process taking place. For exothermic reactions energy is being released to the surroundings and so the surroundings feel like they have been heated by the process.

Answer a

endothermic

Answer b

exothermic

Answer c

endothermic

Answer d

exothermic

APPLICATION: HEAT CAN DO MORE THAN INCREASE TEMPERATURE

Most substances expand as their temperature increases and contract as their temperature decreases. This property can be used to measure temperature changes, as shown in Figure 7.2.4. The operation of many thermometers depends on the expansion and contraction of substances in response to temperature changes.

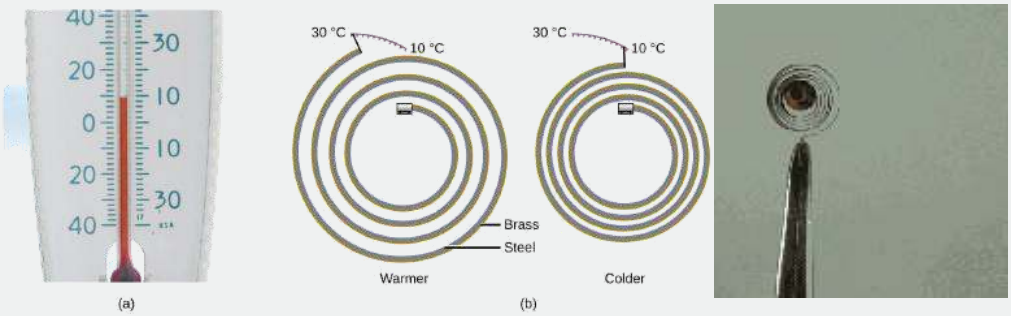


Figure 7.2.4: (a) In an alcohol or mercury thermometer, the liquid (dyed red for visibility) expands when heated and contracts when cooled, much more so than the glass tube that contains the liquid. (b) In a bimetallic thermometer, two different metals (such as brass and steel) form a two-layered strip. When heated or cooled, one of the metals (brass) expands or contracts more than the other metal (steel), causing the strip to coil or uncoil. Both types of thermometers have a calibrated scale that indicates the temperature. (credit a: modification of work by "dwstucke"/Flickr). (c) The demonstration allows one to view the effects of heating and cooling a coiled bimetallic strip.A bimetallic coil from a thermometer reacts to the heat from a lighter, by uncoiling and then coiling back up when the lighter is removed. Animation used with permission from Hustvedt (via Wikipedia)

7.2.2 CONTRIBUTORS AND ATTRIBUTIONS

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

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7.3: WORK AS A MECHANISM TO TRANSFER ENERGY

LEARNING OBJECTIVES

- To define work
- To identify mechanical and pressure-volume work

One definition of energy is the capacity to do work. There are many kinds of work, including mechanical work, electrical work, and work against a gravitational or a magnetic field. Here we will consider only mechanical work and focus on the work done during changes in the pressure or the volume of a gas.

7.3.1 MECHANICAL WORK

The easiest form of work to visualize is mechanical work (Figure 7.3.1), which is the energy required to move an object a distance d when *opposed* by a force F, such as gravity (Figure 7.3.1):

$$w = F\,d \tag{7.3.1}$$

with w is work, F is opposing force, and d is distance.

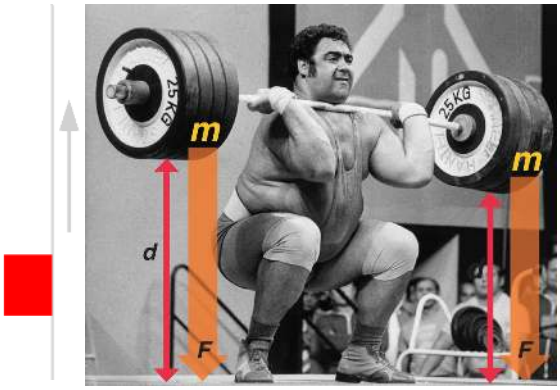


Figure 7.3.1: One form of energy is mechanical work, the energy required to move an object of mass m through distance d when opposed by a force F, i.e., as gravity. (CC BY-SA-NC; anonymous)

Because the force (F) that opposes the action is equal to the mass (m) of the object times its acceleration (a), Equation 7.3.1 can be rewritten to:

$$w = m\,a\,d \tag{7.3.2}$$

with w is work, m is mass, a is acceleration, and d is distance.

Recall from that weight is a force caused by the gravitational attraction between two masses, such as you and Earth. Hence for works against gravity (on Earth), a can be set to $g = 9.8\ m/s^2$. Consider the mechanical work required for you to travel from the first floor of a building to the second. Whether you take an elevator or an escalator, trudge upstairs, or leap up the stairs two at a time, energy is expended to overcome the opposing force of gravity. The amount of work done (w) and thus the energy required depends on three things:

1. the height of the second floor (the distance d);
2. your mass, which must be raised that distance against the downward acceleration due to gravity; and
3. your path.

7.3.2 PRESSURE-VOLUME (PV) WORK

To describe this pressure–volume work (PV work), we will use such imaginary oddities as frictionless pistons, which involve no component of resistance, and ideal gases, which have no attractive or repulsive interactions. Imagine, for example, an ideal gas, confined by a frictionless piston, with internal pressure P_{int} and initial volume V_i (Figure 7.3.2). If $P_{ext} = P_{int}$, the system is at equilibrium; the piston does not move, and no work is done. If the external pressure on the piston (P_{ext}) is less than P_{int}, however, then the ideal gas inside the piston will expand, forcing the piston to perform work on its surroundings; that is, the final volume (V_f) will be greater than V_i. If $P_{ext} > P_{int}$, then the gas will be compressed, and the surroundings will perform work on the system.

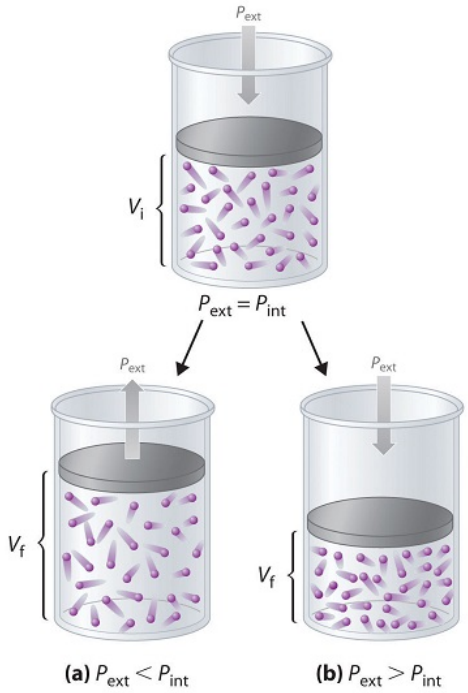


Figure **7.3.2**: PV Work demonstrated with a frictionless piston. (a) if the external pressure is less than P_{int}, the ideal gas inside the piston will expand, forcing the piston to perform work on its surroundings. The final volume (V_f) will be greater than V_i. (b) Alternatively, if the external pressure is greater than P_{int}, the gas will be compressed, and the surroundings will perform work on the system.

If the piston has cross-sectional area A, the external pressure exerted by the piston is, by definition, the force per unit area:

$$P_{ext} = \frac{F}{A} \tag{7.3.3}$$

The volume of any three-dimensional object with parallel sides (such as a cylinder) is the cross-sectional area times the height ($V = Ah$). Rearranging Equation 7.3.3 to give

$$F = P_{ext}A \tag{7.3.4}$$

and defining the distance the piston moves (d) as Δh, we can calculate the magnitude of the work performed by the piston by substituting into Equation 7.3.1:

$$w = Fd = P_{ext}A\Delta h \tag{7.3.5}$$

The change in the volume of the cylinder (ΔV) as the piston moves a distance d is $\Delta V = A\Delta h$, as shown in Figure **7.3.3**.

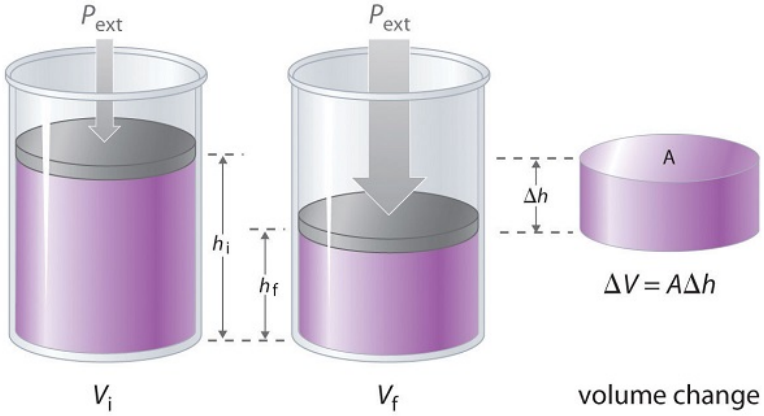


Figure **7.3.3**: Work Performed with a change in volume. The change in the volume (ΔV) of the cylinder housing a piston is $\Delta V = A\Delta h$ as the piston moves. The work performed by the surroundings on the system as the piston moves inward is given by Equation 7.3.6.

The PV work performed is thus

$$w = P_{ext}\Delta V \tag{7.3.6}$$

The units of work obtained using this definition are correct for energy: pressure is force per unit area (newton/m^2) and volume has units of cubic meters, so

$$w = \left(\frac{F}{A}\right)_{ext}(\Delta V) = \frac{\text{newton}}{\text{m}^2} \times \text{m}^3 = \text{newton} \cdot \text{m} = \text{joule} \tag{7.3.7}$$

If we use atmospheres for P and liters for V, we obtain units of L·atm for work. These units correspond to units of energy, as shown in the different values of the ideal gas constant R:

$$R = \frac{0.08206\ \text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} = \frac{8.314\ \text{J}}{\text{mol} \cdot \text{K}} \tag{7.3.8}$$

Thus 0.08206 L·atm = 8.314 J and 1 L·atm = 101.3 J.

Whether work is defined as having a positive sign or a negative sign is a matter of convention. Heat flow is defined from a system to its surroundings as negative; using that same sign convention, we define work done by a system on its surroundings as having a negative sign because it results in a transfer of energy from a system to its surroundings. This is an arbitrary convention and one that is not universally used. Some engineering disciplines are more interested in the work done on the surroundings than in the work done by the system and therefore use the opposite convention. Because $\Delta V > 0$ for an expansion, Equation 7.3.6 must be written with a negative sign to describe PV work done by the system as negative:

$$w = -P_{ext}\Delta V \tag{7.3.9}$$

The work done by a gas expanding against an external pressure is therefore negative, corresponding to work done by a system on its surroundings. Conversely, when a gas is compressed by an external pressure, $\Delta V < 0$ and the work is positive because work is being done on a system by its surroundings.

A MATTER OF CONVENTION

For the thermochemistry

- Heat is positive when energy is transferred from the surroundings to the system
- Work is positive when energy is transferred from the surroundings to the system

EXAMPLE 7.3.2: INTERNAL COMBUSTION ENGINE

A small high-performance internal combustion engine has six cylinders with a total nominal displacement (volume) of 2.40 L and a 10:1 compression ratio (meaning that the volume of each cylinder decreases by a factor of 10 when the piston compresses the air–gas mixture inside the cylinder prior to ignition). How much work in joules is done when a gas in one cylinder of the engine expands at constant temperature against an opposing pressure of 40.0 atm during the engine cycle? Assume that the gas is ideal, the piston is frictionless, and no energy is lost as heat.

Given: final volume, compression ratio, and external pressure

Asked for: work done

Strategy

Calculate the final volume of gas in a single cylinder. Then compute the initial volume of gas in a single cylinder from the compression ratio. Use Equation 7.3.9 to calculate the work done in liter-atmospheres. Convert from liter-atmospheres to joules.

Solution

A To calculate the work done, we need to know the initial and final volumes. The final volume is the volume of one of the six cylinders with the piston all the way down: V_f = 2.40 L/6 = 0.400 L. With a 10:1 compression ratio, the volume of the same cylinder with the piston all the way up is V_i = 0.400 L/10 = 0.0400 L. Work is done by the system on its surroundings, so work is negative.

$$\begin{aligned} w &= -P_{ext}\Delta V \\ &= -(40.0\,atm)(0.400\,L - 0.0400\,L) \\ &= -14.4\,L \cdot atm \end{aligned}$$

Converting from liter-atmospheres to joules,

$$\begin{aligned} w &= -(14.4\ \text{L} \cdot \text{atm})[101.3\ \text{J}/(\text{L} \cdot \text{atm})] \\ &= -1.46 \times 10^3\ \text{J} \end{aligned}$$

In the following exercise, you will see that the concept of work is not confined to engines and pistons. It is found in other applications as well.

EXERCISE 7.3.2: WORK REQUIRED TO BREATH

Breathing requires work, even if you are unaware of it. The lung volume of a 70 kg man at rest changed from 2200 mL to 2700 mL when he inhaled, while his lungs maintained a pressure of approximately 1.0 atm.

a. How much work in liter-atmospheres and joules was required to take a single breath?
b. During exercise, his lung volume changed from 2200 mL to 5200 mL on each in-breath.
c. How much additional work in joules did he require to take a breath while exercising?

Answer

−0.500 L·atm, or −50.7 J; −304 J; if he takes a breath every three seconds, this corresponds to 1.4 Calories per minute (1.4 kcal).

EXAMPLE 7.3.1: EXPANSION (PV) WORK

a. How much work is done by a gas that expands from 2 liters to 5 liters against an external pressure of 750 mmHg?
b. How much work is done by 0.54 moles of a gas that has an initial volume of 8 liters and expands under the following conditions: 30 ^{o}C and 1.3 atm?
c. How much work is done by a gas (P=1.7 atm, V=1.56 L) that expands against an external pressure of 1.8 atm?

Solution a

$$w = -P\Delta V$$

$$\Delta V = V_{final} - V_{Initial} = 5\,L - 2\,L = 3L$$

Convert 750 mmHg to atm:

$$750mmHg * 1/760(atm/mmHg) = 0.9868atm.$$

$$W = -p\Delta V = -(.9868\,atm)(3\,L) = -2.96\,L\,atm.$$

Solution b

First we must find the final volume using the ideal gas law:

$$pV = nRT$$

or

$$V = \frac{nRT}{P}$$

$$= \frac{(0.54\,moles)(0.082057(L\,atm)/(mol\,K))(303\,K)}{1.3\,atm} = 10.33\,L$$

$$\Delta V = V_{final} - V_{initial}$$

$$= 10.3\,L - 8\,L = 2.3\,L$$

Then from Equation 7.3.6

$$w = -p\Delta V = -(1.3\,atm)(2.3\,L) = -3\,L\cdot atm.$$

Solution c

$$w = -p\Delta V = -(1.8\,atm)\,\Delta V.$$

Given p_1, V_1, and p_2, find V_2: $p_1V_1 = p_2V_2$ (at constant T and n)

$$V_2 = \frac{V_1P_1}{P_2} = (1.56L * 1.7atm)/1.8atm = 1.47L$$

Now,

$$\Delta V = V_2 - V_1 = 1.47\,L - 1.56\,L = -0.09$$

$$w = -(1.8atm) * (-0.09L) = 0.162Latm.$$

7.3.3 WORK IN CHEMICAL TRANSFORMATIONS

Suppose, for example, that the system under study is a mass of steam heated by the combustion of several hundred pounds of coal and enclosed within a cylinder housing a piston attached to the crankshaft of a large steam engine. The gas is not ideal, and the cylinder is not frictionless. Nonetheless, as steam enters the engine chamber and the expanding gas pushes against the piston, the piston moves, so useful work is performed. In fact, PV work launched the Industrial Revolution of the 19th century and powers the internal combustion engine on which most of us still rely for transportation.

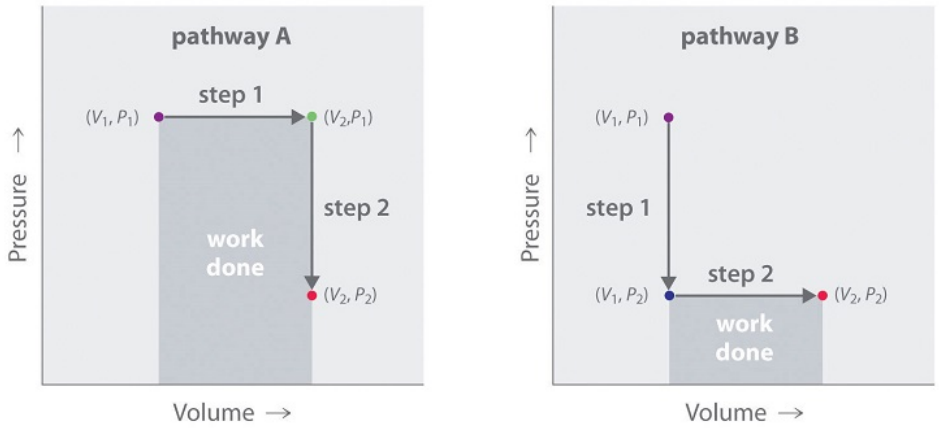


Figure 7.3.4: Work Is Not a State Function. In pathway A, the volume of a gas is initially increased while its pressure stays constant (step 1). Its pressure is then decreased while the volume remains constant (step 2). Pathway B reverses these steps. Although (V_1, P_1) and (V_2, P_2) are identical in both cases, the amount of work done (shaded area) depends on the pathway taken. (Cc BY-NC-SA; Anonymous by request)

In contrast to internal energy, work is not a state function. We can see this by examining Figure 7.3.4, in which two different, two-step pathways take a gaseous system from an initial state to a final state with corresponding changes in temperature. In pathway A, the volume of a gas is initially increased while its pressure stays constant (step 1); then its pressure is decreased while the volume remains constant (step 2). In pathway B, the order of the steps is reversed. The temperatures, pressures, and volumes of the initial and final states are identical in both cases, but the amount of work done, indicated by the shaded areas in the figure, is substantially different. As we can see, the amount of work done depends on the pathway taken from (V_1, P_1) to (V_2, P_2), which means that work is **not** a state function.

> *Internal energy is a state function, whereas work is not.*

7.3.4 WORK AND CHEMICAL REACTIONS

Consider, for example, a reaction that produces a gas, such as dissolving a piece of copper in concentrated nitric acid. The chemical equation for this reaction is as follows:

$$\mathrm{Cu\,(s) + 4\,HNO_3\,(aq) \longrightarrow Cu(NO_3)_2\,(aq) + 2\,H_2O\,(l) + 2\,NO_2\,(g)} \tag{7.3.10}$$

If the reaction is carried out in a closed system that is maintained at constant pressure by a movable piston, the piston will rise as nitrogen dioxide gas is formed (Figure 7.3.5). The system is performing work by lifting the piston against the downward force exerted by the atmosphere (i.e., *atmospheric pressure*). We find the amount of *PV* work done by multiplying the external pressure *P* by the change in volume caused by movement of the piston (ΔV). At a constant external pressure (here, atmospheric pressure)

$$w = -P\Delta V \tag{7.3.11}$$

The negative sign associated with PV work done indicates that the system loses energy. If the volume increases at constant pressure ($\Delta V > 0$), the work done by the system is negative, indicating that a system has lost energy by performing work on its surroundings. Conversely, if the volume decreases ($\Delta V < 0$), the work done by the system is positive, which means that the surroundings have performed work on the system, thereby increasing its energy.

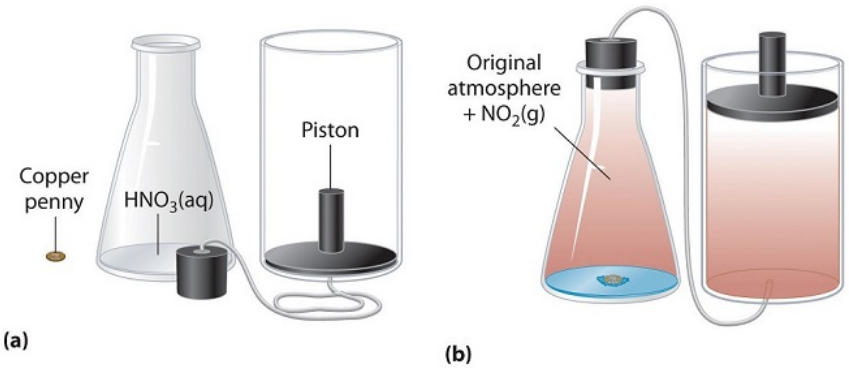


Figure **7.3.5**: An Example of Work Performed by a Reaction Carried Out at Constant Pressure. (a) Initially, the system (a copper penny and concentrated nitric acid) is at atmospheric pressure. (b) When the penny is added to the nitric acid, the volume of $\mathbf{NO_2}$ gas that is formed causes the piston to move upward to maintain the system at atmospheric pressure. In doing so, the system is performing work on its surroundings.

7.3.5 ENTHALPY

The symbol U represents the internal energy of a system, which is the sum of the kinetic energy and potential energy of all its components. It is the change in internal energy that produces heat plus work. To measure the energy changes that occur in chemical reactions, chemists usually use a related thermodynamic quantity called enthalpy (H) (from the Greek *enthalpein*, meaning "to warm"). The enthalpy of a system is defined as the sum of its internal energy U plus the product of its pressure P and volume V:

$$H = U + PV \tag{7.3.12}$$

Because internal energy, pressure, and volume are all state functions, enthalpy is also a state function.

If a chemical change occurs at constant pressure (i.e., for a fixed P, $\Delta P = 0$), the change in enthalpy (ΔH) is

$$\Delta H = \Delta(U + PV) \tag{7.3.13}$$
$$= \Delta U + \Delta(PV) \tag{7.3.14}$$
$$= \Delta U + P\Delta V \tag{7.3.15}$$

Substituting $q + w$ for ΔU (Equation 7.3.15) and $-w$ for $P\Delta V$ (Equation 7.3.11), we obtain

$$\Delta H = \Delta U + P\Delta V$$
$$= q_p + \cancel{w} - \cancel{w}$$
$$= q_p \tag{7.3.16}$$

The subscript p is used here to emphasize that this equation is true only for a process that occurs at constant pressure. From Equation 7.3.16 we see that at constant pressure the change in enthalpy, ΔH of the system, defined as $H_{final} - H_{initial}$, is equal to the heat gained or lost.

$$\Delta H = H_{final} - H_{initial} = q_p \tag{7.3.17}$$

Just as with ΔU, because enthalpy is a state function, the magnitude of ΔH depends on only the initial and final states of the system, not on the path taken. Most important, the enthalpy change is the same even if the process does *not* occur at constant pressure.

> *To find ΔH for a reaction, measure q_p under constant pressure.*

7.3.6 SUMMARY

All forms of energy can be interconverted. Three things can change the energy of an object: the transfer of heat, work performed on or by an object, or some combination of heat and work.

7.3.7 OUTSIDE LINKS

- Gasparro, Frances P. "Remembering the sign conventions for q and w in deltaU = q - w." J. Chem. Educ. 1976: 53, 389.
- Koubek, E. "PV work demonstration (TD)." J. Chem. Educ. 1980: 57, 374. '

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7.4: THE FIRST LAW OF THERMODYNAMICS

LEARNING OBJECTIVES

- To calculate changes in internal energy
- Distinguish the related properties of heat, thermal energy, and temperature
- Define and distinguish specific heat and heat capacity, and describe the physical implications of both
- Perform calculations involving heat, specific heat, and temperature change

The relationship between the energy change of a system and that of its surroundings is given by the first law of thermodynamics, which states that the energy of the universe is constant. We can express this law mathematically as follows:

$$\Delta U_{univ} = \Delta U_{sys} + \Delta U_{surr} = 0 \tag{7.4.1}$$

or

$$\Delta U_{sys} = -\Delta U_{surr} \tag{7.4.2}$$

where the subscripts *univ*, *sys*, and *surr* refer to the universe, the system, and the surroundings, respectively. Thus the change in energy of a system is identical in magnitude but opposite in sign to the change in energy of its surroundings.

> *The tendency of all systems, chemical or otherwise, is to move toward the state with the lowest possible energy.*

An important factor that determines the outcome of a chemical reaction is the tendency of all systems, chemical or otherwise, to move toward the lowest possible overall energy state. As a brick dropped from a rooftop falls, its potential energy is converted to kinetic energy; when it reaches ground level, it has achieved a state of lower potential energy. Anyone nearby will notice that energy is transferred to the surroundings as the noise of the impact reverberates and the dust rises when the brick hits the ground. Similarly, if a spark ignites a mixture of isooctane and oxygen in an internal combustion engine, carbon dioxide and water form spontaneously, while potential energy (in the form of the relative positions of atoms in the molecules) is released to the surroundings as heat and work. The internal energy content of the CO_2/H_2O product mixture is less than that of the isooctane O_2 reactant mixture. The two cases differ, however, in the form in which the energy is released to the surroundings. In the case of the falling brick, the energy is transferred as work done on whatever happens to be in the path of the brick; in the case of burning isooctane, the energy can be released as solely heat (if the reaction is carried out in an open container) or as a mixture of heat and work (if the reaction is carried out in the cylinder of an internal combustion engine). Because heat and work are the only two ways in which energy can be transferred between a system and its surroundings, any change in the internal energy of the system is the sum of the heat transferred (q) and the work done (w):

$$\underbrace{\Delta U_{sys} = q + w}_{\text{First Law of Thermodynamics}} \tag{7.4.3}$$

Although q and w are not state functions on their own, their sum (ΔU_{sys}) is independent of the path taken and is therefore a state function. A major task for the designers of any machine that converts energy to work is to maximize the amount of work obtained and minimize the amount of energy released to the environment as heat. An example is the combustion of coal to produce electricity. Although the maximum amount of energy available from the process is fixed by the energy content of the reactants and the products, the fraction of that energy that can be used to perform useful work is not fixed. Because we focus almost exclusively on the changes in the energy of a system, we will not use "sys" as a subscript unless we need to distinguish explicitly between a system and its surroundings.

> *Although q and w are not state functions, their sum (ΔU_{sys}) is independent of the path taken and therefore is a difference of a state function.*

EXAMPLE 7.4.1

A sample of an ideal gas in the cylinder of an engine is compressed from 400 mL to 50.0 mL during the compression stroke against a constant pressure of 8.00 atm. At the same time, 140 J of energy is transferred from the gas to the surroundings as heat. What is the total change in the internal energy (ΔU) of the gas in joules?

Given: initial volume, final volume, external pressure, and quantity of energy transferred as heat

Asked for: total change in internal energy

Strategy:

A. Determine the sign of q to use in Equation 7.4.3.

B. From Equation 7.4.3 calculate w from the values given. Substitute this value into Equation 7.4.3 to calculate ΔU.

Solution

A From Equation 7.4.3, we know that $\Delta U = q + w$ (First Law of Thermodynamics). We are given the magnitude of q (140 J) and need only determine its sign. Because energy is transferred from the system (the gas) to the surroundings, q is negative by convention.

B Because the gas is being compressed, we know that work is being done on the system, so w must be positive. From Equation 7.4.3,

$$\begin{aligned} w &= -P_{\text{ext}}\Delta V \\ &= -8.00\ \text{atm}(0.0500\ \text{L} - 0.400\ \text{L})\left(\frac{101.3\ \text{J}}{\text{L}\cdot\text{atm}}\right) \\ &= 284\ \text{J} \end{aligned}$$

Thus

$$\begin{aligned} \Delta U &= q + w \\ &= -140\ J + 284\ J \\ &= 144\ J \end{aligned}$$

In this case, although work is done on the gas, increasing its internal energy, heat flows from the system to the surroundings, decreasing its internal energy by 144 J. The work done and the heat transferred can have opposite signs.

? EXERCISE 7.4.1

A sample of an ideal gas is allowed to expand from an initial volume of 0.200 L to a final volume of 3.50 L against a constant external pressure of 0.995 atm. At the same time, 117 J of heat is transferred from the surroundings to the gas. What is the total change in the internal energy (ΔU) of the gas in joules?

Answer

−216 J

By convention, both heat flow and work have a negative sign when energy is transferred from a system to its surroundings and vice versa.

7.4.1 SUMMARY

The first law of thermodynamics states that the energy of the universe is constant. The change in the internal energy of a system is the sum of the heat transferred and the work done. The heat flow is equal to the change in the internal energy of the system plus the PV work done. When the volume of a system is constant, changes in its internal energy can be calculated by substituting the ideal gas law into the equation for ΔU.

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7.5: HEAT CAPACITY AND CALORIMETRY

LEARNING OBJECTIVES

- Explain the technique of calorimetry
- Calculate and interpret heat and related properties using typical calorimetry data
- To use calorimetric data to calculate enthalpy changes.

7.5.1 HEAT CAPACITY

We now introduce two concepts useful in describing heat flow and temperature change. The **heat capacity** (C) of a body of matter is the quantity of heat (q) it absorbs or releases when it experiences a temperature change (ΔT) of 1 degree Celsius (or equivalently, 1 kelvin)

$$C = \frac{q}{\Delta T} \tag{7.5.1}$$

Heat capacity is determined by both the type and amount of substance that absorbs or releases heat. It is therefore an **extensive property**—its value is proportional to the amount of the substance.

For example, consider the heat capacities of two cast iron frying pans. The heat capacity of the large pan is five times greater than that of the small pan because, although both are made of the same material, the mass of the large pan is five times greater than the mass of the small pan. More mass means more atoms are present in the larger pan, so it takes more energy to make all of those atoms vibrate faster. The heat capacity of the small cast iron frying pan is found by observing that it takes 18,140 J of energy to raise the temperature of the pan by 50.0 °C

$$C_{\text{small pan}} = \frac{18,140\ J}{50.0\ °C} = 363\ J/°C$$

The larger cast iron frying pan, while made of the same substance, requires 90,700 J of energy to raise its temperature by 50.0 °C. The larger pan has a (proportionally) larger heat capacity because the larger amount of material requires a (proportionally) larger amount of energy to yield the same temperature change:

$$C_{\text{large pan}} = \frac{90,700\ J}{50.0\ °C} = 1814\ J/°C$$

The *specific heat capacity* (c) of a substance, commonly called its **specific heat**, is the quantity of heat required to raise the temperature of 1 gram of a substance by 1 degree Celsius (or 1 kelvin):

$$c = \frac{q}{m\Delta T} \tag{7.5.2}$$

Specific heat capacity depends only on the kind of substance absorbing or releasing heat. It is an intensive property—the type, but not the amount, of the substance is all that matters. For example, the small cast iron frying pan has a mass of 808 g. The specific heat of iron (the material used to make the pan) is therefore:

$$c_{iron} = \frac{18,140\ J}{(808\ g)(50.0\ °C)} = 0.449\ J/g\ °C$$

The large frying pan has a mass of 4040 g. Using the data for this pan, we can also calculate the specific heat of iron:

$$c_{iron} = \frac{90,700 J}{(4,040\ g)(50.0\ °C)} = 0.449\ J/g\ °C$$

Although the large pan is more massive than the small pan, since both are made of the same material, they both yield the same value for specific heat (for the material of construction, iron). Note that specific heat is measured in units of energy per temperature per mass and is an intensive property, being derived from a ratio of two extensive properties (heat and mass). The molar heat capacity, also an intensive property, is the heat capacity per mole of a particular substance and has units of J/mol °C (Figure 7.5.1).



Figure 7.5.1: Due to its larger mass, a large frying pan has a larger heat capacity than a small frying pan. Because they are made of the same material, both frying pans have the same specific heat. (CC BY; Mark Blaser via OpenStax).

The heat capacity of an object depends on both its *mass* and its *composition*. For example, doubling the mass of an object doubles its heat capacity. Consequently, the amount of substance must be indicated when the heat capacity of the substance is reported. The molar heat capacity (C_p) is the amount of energy needed to increase the temperature of 1 mol of a substance by 1°C; the units of C_p are thus J/(mol•°C).The subscript *p* indicates that the value was measured at constant pressure. The specific heat (c_s) is the amount of energy needed to increase the temperature of 1 g of a substance by 1°C; its units are thus J/(g•°C).

We can relate the quantity of a substance, the amount of heat transferred, its heat capacity, and the temperature change either via moles (Equation 7.5.3) or mass (Equation 7.5.4):

$$q = nc_p\Delta T \tag{7.5.3}$$

where

- n is the number of moles of substance and
- c_p is the *molar heat capacity* (i.e., heat capacity per **mole** of substance), and
- $\Delta T = T_{final} - T_{initial}$ is the temperature change.

$$q = mc_s\Delta T \tag{7.5.4}$$

where

- m is the mass of substance in grams,
- c_s is the *specific heat* (i.e., heat capacity per **gram** of substance), and
- $\Delta T = T_{final} - T_{initial}$ is the temperature change.

Both Equations 7.5.3 and 7.5.4 are under constant pressure (which matters) and both show that we know the amount of a substance and its specific heat (for mass) or molar heat capcity (for moles), we can determine the amount of heat, q, entering or leaving the substance by measuring the temperature change before and after the heat is gained or lost.

The specific heats of some common substances are given in Table 7.5.1. Note that the specific heat values of most solids are less than 1 J/(g•°C), whereas those of most liquids are about 2 J/(g•°C). Water in its solid and liquid states is an exception. The heat capacity of ice is twice as high as that of most solids; the heat capacity of liquid water, 4.184 J/(g•°C), is one of the highest known. The specific heat of a substance varies somewhat with temperature. However, this variation is usually small enough that we will treat specific heat as constant over the range of temperatures that will be considered in this chapter. Specific heats of some common substances are listed in Table 7.5.1.

Table 7.5.1: Specific Heats of Common Substances at 25 °C and 1 bar

Substance	Symbol (state)	Specific Heat (J/g °C)
helium	$He(g)$	5.193
water	$H_2O(l)$	4.184
ethanol	$C_2H_6O(l)$	2.376
ice	$H_2O(s)$	2.093 (at −10 °C)
water vapor	$H_2O(g)$	1.864
nitrogen	$N_2(g)$	1.040
air	mixture	1.007
oxygen	$O_2(g)$	0.918
aluminum	$Al(s)$	0.897
carbon dioxide	$CO_2(g)$	0.853
argon	$Ar(g)$	0.522
iron	$Fe(s)$	0.449
copper	$Cu(s)$	0.385
lead	$Pb(s)$	0.130
gold	$Au(s)$	0.129
silicon	$Si(s)$	0.712
quartz	$\mathbf{SiO_2\,(s)}$	0.730

The value of C is intrinsically a positive number, but ΔT and q can be either positive or negative, and they both must have the same sign. If ΔT and q are positive, then *heat flows from the surroundings into an object*. If ΔT and q are negative, then *heat flows from an object into its surroundings*.

If a substance gains thermal energy, its temperature increases, its final temperature is higher than its initial temperature, then $\Delta T > 0$ and q is positive. If a substance loses thermal energy, its temperature decreases, the final temperature is lower than the initial temperature, so $\Delta T < 0$ and q is negative.

EXAMPLE 7.5.1: MEASURING HEAT

A flask containing $8.0 \times 10^2\ g$ of water is heated, and the temperature of the water increases from $21\,°C$ to $85\,°C$. How much heat did the water absorb?

Solution

To answer this question, consider these factors:

- the specific heat of the substance being heated (in this case, water)
- the amount of substance being heated (in this case, 800 g)
- the magnitude of the temperature change (in this case, from 21 °C to 85 °C).

The specific heat of water is 4.184 J/g °C (Table 7.5.1), so to heat 1 g of water by 1 °C requires 4.184 J. We note that since 4.184 J is required to heat 1 g of water by 1 °C, we will need 800 times as much to heat 800 g of water by 1 °C. Finally, we observe that since 4.184 J are required to heat 1 g of water by 1 °C, we will need 64 times as much to heat it by 64 °C (that is, from 21 °C to 85 °C).

This can be summarized using Equation 7.5.4:

$$\begin{aligned} q &= mc_s\Delta T \\ &= mc_s(T_{\text{final}} - T_{\text{initial}}) \\ &= (4.184\ \text{J}/\cancel{g}^\circ\text{C}) \times (800\ \cancel{g}) \times (85-21)^\circ\text{C} \\ &= (4.184\ \text{J}/\cancel{g}^\circ\cancel{\text{C}}) \times (800\ \cancel{g}) \times (64)^\circ\cancel{\text{C}} \\ &= 210,000\ \text{J} (= 210\ \text{kJ}) \end{aligned}$$

Because the temperature increased, the water absorbed heat and q is positive.

EXERCISE 7.5.1

How much heat, in joules, must be added to a $5.00 \times 10^2\ g$ iron skillet to increase its temperature from 25 °C to 250 °C? The specific heat of iron is 0.451 J/g °C.

Answer

$5.07 \times 10^4\ J$

Note that the relationship between heat, specific heat, mass, and temperature change can be used to determine any of these quantities (not just heat) if the other three are known or can be deduced.

EXAMPLE 7.5.2: DETERMINING OTHER QUANTITIES

A piece of unknown metal weighs 348 g. When the metal piece absorbs 6.64 kJ of heat, its temperature increases from 22.4 °C to 43.6 °C. Determine the specific heat of this metal (which might provide a clue to its identity).

Solution

Since mass, heat, and temperature change are known for this metal, we can determine its specific heat using Equation 7.5.4:

$$q = mc_s\Delta T \qquad = mc_s(T_{final} - T_{initial})$$

Substituting the known values:

$$6,640\ J = (348\ g)c_s(43.6 - 22.4)\ °C$$

Solving:

$$c = \frac{6,640\ J}{(348\ g)(21.2°C)} = 0.900\ J/g\ °C$$

Comparing this value with the values in Table 7.5.1, this value matches the specific heat of aluminum, which suggests that the unknown metal may be aluminum.

EXERCISE 7.5.2

A piece of unknown metal weighs 217 g. When the metal piece absorbs 1.43 kJ of heat, its temperature increases from 24.5 °C to 39.1 °C. Determine the specific heat of this metal, and predict its identity.

Answer

$c = 0.45\ J/g\ °C$; the metal is likely to be iron from checking Table 7.5.1.

EXAMPLE 7.5.3: SOLAR HEATING

A home solar energy storage unit uses 400 L of water for storing thermal energy. On a sunny day, the initial temperature of the water is 22.0°C. During the course of the day, the temperature of the water rises to 38.0°C as it circulates through the water wall. How much energy has been stored in the water? (The density of water at 22.0°C is 0.998 g/mL.)



Passive solar system. During the day (a), sunlight is absorbed by water circulating in the water wall. At night (b), heat stored in the water wall continues to warm the air inside the house.

Given: volume and density of water and initial and final temperatures

Asked for: amount of energy stored

Strategy:

A. Use the density of water at 22.0°C to obtain the mass of water (m) that corresponds to 400 L of water. Then compute ΔT for the water.

B. Determine the amount of heat absorbed by substituting values for m, c_s, and ΔT into Equation 7.5.1.

Solution:

A The mass of water is

$$mass\ of\ H_2O = 400\ \cancel{L}\left(\frac{1000\ \cancel{mL}}{1\ \cancel{L}}\right)\left(\frac{0.998\ g}{1\ \cancel{mL}}\right) = 3.99 \times 10^5 g\ H_2O$$

The temperature change (ΔT) is 38.0°C − 22.0°C = +16.0°C.

B From Table 7.5.1, the specific heat of water is 4.184 J/(g•°C). From Equation 7.5.4, the heat absorbed by the water is thus

$$q = mc_s\Delta T = \left(3.99 \times 10^5\ \cancel{g}\right)\left(\frac{4.184\ J}{\cancel{g}\cdot\cancel{^\circ C}}\right)\left(16.0\ \cancel{^\circ C}\right) = 2.67 \times 10^7 J = 2.67 \times 10^4 kJ$$

Both q and ΔT are positive, consistent with the fact that the water has absorbed energy.

? EXERCISE 7.5.3: SOLAR HEATING

Some solar energy devices used in homes circulate air over a bed of rocks that absorb thermal energy from the sun. If a house uses a solar heating system that contains 2500 kg of sandstone rocks, what amount of energy is stored if the temperature of the rocks increases from 20.0°C to 34.5°C during the day? Assume that the specific heat of sandstone is the same as that of quartz (SiO_2) in Table 7.5.1.

Answer

$2.7 \times 10^4\ kJ$

Even though the mass of sandstone is more than six times the mass of the water in Example 7.5.1, the amount of thermal energy stored is the same to two significant figures.

7.5.2 HEAT "FLOW" TO THERMAL EQUILIBRIUM

When two objects at different temperatures are placed in contact, heat flows from the warmer object to the cooler one until the temperature of both objects is the same. The law of conservation of energy says that the total energy cannot change during this process:

$$q_{cold} + q_{hot} = 0 \tag{7.5.5}$$

The equation implies that the amount of heat that flows *from* a warmer object is the same as the amount of heat that flows *into* a cooler object. Because the direction of heat flow is opposite for the two objects, the sign of the heat flow values must be opposite:

$$q_{cold} = -q_{hot} \tag{7.5.6}$$

Thus heat is conserved in any such process, consistent with the law of conservation of energy.

> *The amount of heat lost by a warmer object equals the amount of heat gained by a cooler object.*

Substituting for q from Equation 7.5.4 gives

$$[mc_s\Delta T]_{cold} + [mc_s\Delta T]_{hot} = 0$$

which can be rearranged to give

$$[mc_s\Delta T]_{cold} = -[mc_s\Delta T]_{hot} \tag{7.5.7}$$

When two objects initially at different temperatures are placed in contact, we can use Equation 7.5.7 to calculate the final temperature if we know the chemical composition and mass of the objects.

✔ EXAMPLE 7.5.4: THERMAL EQUILIBRATION OF COPPER AND WATER

If a 30.0 g piece of copper pipe at 80.0°C is placed in 100.0 g of water at 27.0°C, what is the final temperature? Assume that no heat is transferred to the surroundings.

Given: mass and initial temperature of two objects

Asked for: final temperature

Strategy: Using Equation 7.5.7 and writing $\Delta T = T_{final} - T_{initial}$ for both the copper and the water, substitute the appropriate values of m, c_s, and $T_{initial}$ into the equation and solve for T_{final}.

Solution

We can adapt Equation 7.5.7 to solve this problem, remembering that $\Delta T = T_{final} - T_{initial}$:

$$[mc_s(T_{final} - T_{initial})]_{Cu} + [mc_s(T_{final} - T_{initial})]_{H_2O} = 0$$

Substituting the data provided in the problem and Table 7.5.1 gives

$$(30\ g)\,(0.385\ J/(g°C))(T_{final} - 80°C) + (100\ g)(4.184\ J/(g°C))(T_{final} - 27.0°C) = 0$$

$$T_{final}\,(11.6\ J/°C) - 924\ J + T_{final}\,(418.4\ J/°C) - 11,300\ J = 0$$

$$T_{final}\,(430\ J/(g \cdot °C)) = 12,224\ J$$

$$T_{final} = 28.4\ °C$$

? EXERCISE 7.5.4A: THERMAL EQUILIBRATION OF GOLD AND WATER

If a 14.0 g chunk of gold at 20.0°C is dropped into 25.0 g of water at 80.0°C, what is the final temperature if no heat is transferred to the surroundings?

Answer

80.0°C

? EXERCISE 7.5.4B: THERMAL EQUILIBRATION OF ALUMINUM AND WATER

A 28.0 g chunk of aluminum is dropped into 100.0 g of water with an initial temperature of 20.0°C. If the final temperature of the water is 24.0°C, what was the initial temperature of the aluminum? (Assume that no heat is transferred to the surroundings.)

Answer

90.6°C

7.5.3 MEASURING HEAT "FLOW"

One technique we can use to measure the amount of heat involved in a chemical or physical process is known as calorimetry. Calorimetry is used to measure amounts of heat transferred to or from a substance. To do so, the heat is exchanged with a calibrated object (calorimeter).

The change in temperature of the measuring part of the calorimeter is converted into the amount of heat (since the previous calibration was used to establish its heat capacity). The measurement of heat transfer using this approach requires the definition of a system (the substance or substances undergoing the chemical or physical change) and its surroundings (the other components of the measurement apparatus that serve to either provide heat to the system or absorb heat from the system). Knowledge of the heat capacity of the surroundings, and careful measurements of the masses of the system and surroundings and their temperatures before and after the process allows one to calculate the heat transferred as described in this section.

A calorimeter is a device used to measure the amount of heat involved in a chemical or physical process.

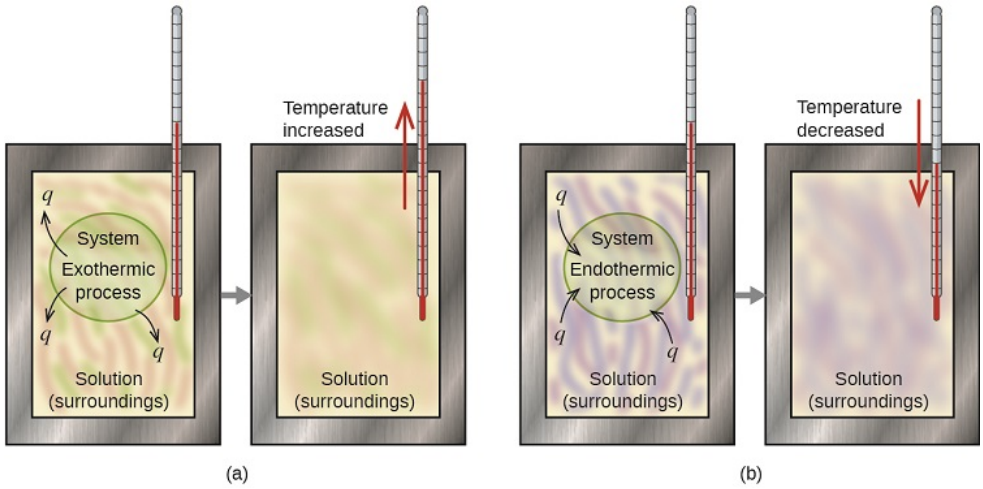


Figure **7.5.2**: In a calorimetric determination, either (a) an exothermic process occurs and heat, q, is negative, indicating that thermal energy is transferred from the system to its surroundings, or (b) an endothermic process occurs and heat, q, is positive, indicating that thermal energy is transferred from the surroundings to the system.

The thermal energy change accompanying a chemical reaction is responsible for the change in temperature that takes place in a calorimeter. If the reaction releases heat ($q_{rxn} < 0$), then heat is absorbed by the calorimeter ($q_{calorimeter} > 0$) and its temperature increases. Conversely, if the reaction absorbs heat ($q_{rxn} > 0$), then heat is transferred from the calorimeter to the system ($q_{calorimeter} < 0$) and the temperature of the calorimeter decreases. In both cases, *the amount of heat absorbed or released by the calorimeter is equal in magnitude and opposite in sign to the amount of heat produced or consumed by the reaction*. The heat capacity of the calorimeter or of the reaction mixture may be used to calculate the amount of heat released or absorbed by the chemical reaction. The amount of heat released or absorbed per gram or mole of reactant can then be calculated from the mass of the reactants.

> *The amount of heat absorbed or released by the calorimeter is equal in magnitude and opposite in sign to the amount of heat produced or consumed by the reaction.*

7.5.3.1 CONSTANT-PRESSURE CALORIMETRY

Because ΔH is defined as the heat flow at constant pressure, measurements made using a constant-pressure calorimeter (a device used to measure enthalpy changes in chemical processes at constant pressure) give ΔH values directly. This device is particularly well suited to studying reactions carried out in solution at a constant atmospheric pressure. A “student” version, called a *coffee-cup calorimeter* (Figure **7.5.3**), is often encountered in general chemistry laboratories. Commercial calorimeters operate on the same principle, but they can be used with smaller volumes of solution, have better thermal insulation, and can detect a change in temperature as small as several millionths of a degree (10^{-6} °C).

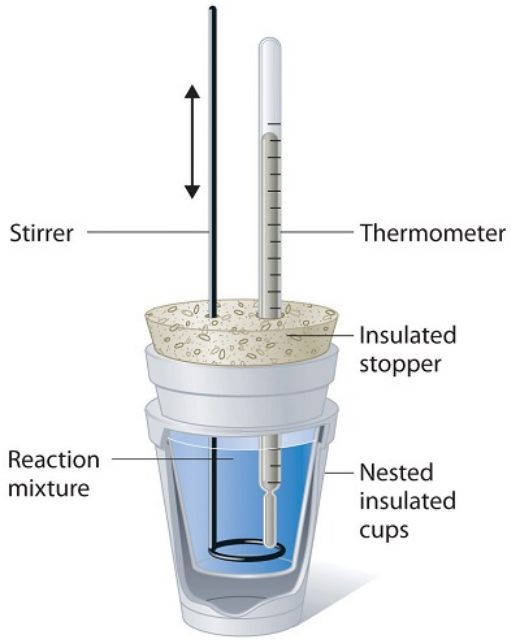


Figure 7.5.3: A Coffee-Cup Calorimeter. This simplified version of a constant-pressure calorimeter consists of two Styrofoam cups nested and sealed with an insulated stopper to thermally isolate the system (the solution being studied) from the surroundings (the air and the laboratory bench). Two holes in the stopper allow the use of a thermometer to measure the temperature and a stirrer to mix the reactants.

Before we practice calorimetry problems involving chemical reactions, consider a simpler example that illustrates the core idea behind calorimetry. Suppose we initially have a high-temperature substance, such as a hot piece of metal (M), and a low-temperature substance, such as cool water (W). If we place the metal in the water, heat will flow from M to W. The temperature of M will decrease, and the temperature of W will increase, until the two substances have the same temperature—that is, when they reach thermal equilibrium. If this occurs in a calorimeter, ideally all of this heat transfer occurs between the two substances, with no heat gained or lost by either the calorimeter or the calorimeter's surroundings. Under these ideal circumstances, the net heat change is zero:

$$q_{\text{substance M}} + q_{\text{substance W}} = 0 \tag{7.5.8}$$

This relationship can be rearranged to show that the heat gained by substance M is equal to the heat lost by substance W:

$$q_{\text{substance M}} = -q_{\text{substance W}} \tag{7.5.9}$$

The magnitude of the heat (change) is therefore the same for both substances, and the negative sign merely shows that $q_{substance\ M}$ and $q_{substance\ W}$ are opposite in direction of heat flow (gain or loss) but does not indicate the arithmetic sign of either q value (that is determined by whether the matter in question gains or loses heat, per definition). In the specific situation described, $q_{substance\ M}$ is a negative value and $q_{\text{substance W}}$ is positive, since heat is transferred from M to W.

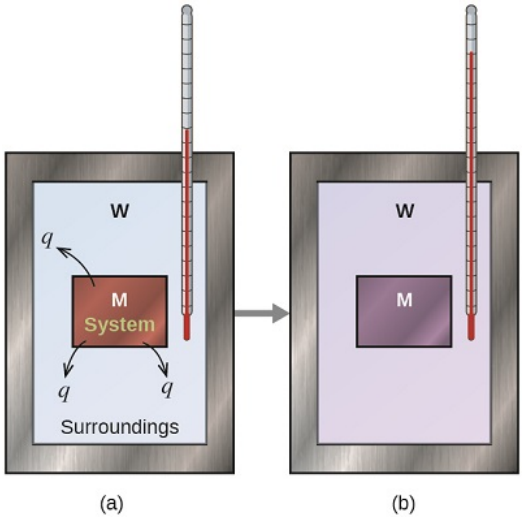


Figure 7.5.4: In a simple calorimetry process, (a) heat, q, is transferred from the hot metal, M, to the cool water, W, until (b) both are at the same temperature.

EXAMPLE 7.5.5: HEAT BETWEEN SUBSTANCES AT DIFFERENT TEMPERATURES

A 360-g piece of rebar (a steel rod used for reinforcing concrete) is dropped into 425 mL of water at 24.0 °C. The final temperature of the water was measured as 42.7 °C. Calculate the initial temperature of the piece of rebar. Assume the specific heat of steel is approximately the same as that for iron (Table T4), and that all heat transfer occurs between the rebar and the water (there is no heat exchange with the surroundings).

Solution

The temperature of the water increases from 24.0 °C to 42.7 °C, so the water absorbs heat. That heat came from the piece of rebar, which initially was at a higher temperature. Assuming that all heat transfer was between the rebar and the water, with no heat "lost" to the surroundings, then heat given off by rebar = −heat taken in by water, or:

$$q_{\text{rebar}} = -q_{\text{water}}$$

Since we know how heat is related to other measurable quantities, we have:

$$(c \times m \times \Delta T)_{\text{rebar}} = -(c \times m \times \Delta T)_{\text{water}}$$

Letting f = final and i = initial, in expanded form, this becomes:

$$c_{\text{rebar}} \times m_{\text{rebar}} \times (T_{\text{f,rebar}} - T_{\text{i,rebar}}) = -c_{\text{water}} \times m_{\text{water}} \times (T_{\text{f,water}} - T_{\text{i,water}})$$

The density of water is 1.0 g/mL, so 425 mL of water = 425 g. Noting that the final temperature of both the rebar and water is 42.7 °C, substituting known values yields:

$$(0.449\ \text{J/g °C})(360\text{g})(42.7\text{°C} - T_{\text{i,rebar}}) = -(4.184\ \text{J/g °C})(425\ \text{g})(42.7\text{°C} - 24.0\text{°C})$$

$$T_{\text{i,rebar}} = \frac{(4.184\ \text{J/g °C})(425\ \text{g})(42.7\text{°C} - 24.0\text{°C})}{(0.449\ \text{J/g °C})(360\ \text{g})} + 42.7\text{°C}$$

Solving this gives $T_{i,rebar}$= 248 °C, so the initial temperature of the rebar was 248 °C.

EXERCISE 7.5.5A

A 248-g piece of copper is dropped into 390 mL of water at 22.6 °C. The final temperature of the water was measured as 39.9 °C. Calculate the initial temperature of the piece of copper. Assume that all heat transfer occurs between the copper and the water.

Answer

The initial temperature of the copper was 335.6 °C.

EXERCISE 7.5.5B

A 248-g piece of copper initially at 314 °C is dropped into 390 mL of water initially at 22.6 °C. Assuming that all heat transfer occurs between the copper and the water, calculate the final temperature.

Answer

The final temperature (reached by both copper and water) is 38.8 °C.

This method can also be used to determine other quantities, such as the specific heat of an unknown metal.

EXAMPLE 7.5.6: IDENTIFYING A METAL BY MEASURING SPECIFIC HEAT

A 59.7 g piece of metal that had been submerged in boiling water was quickly transferred into 60.0 mL of water initially at 22.0 °C. The final temperature is 28.5 °C. Use these data to determine the specific heat of the metal. Use this result to identify the metal.

Solution

Assuming perfect heat transfer, heat given off by metal = −heat taken in by water, or:

$$q_{\text{metal}} = -q_{\text{water}}$$

In expanded form, this is:

$$c_{\text{metal}} \times m_{\text{metal}} \times (T_{\text{f,metal}} - T_{\text{i,metal}}) = -c_{\text{water}} \times m_{\text{water}} \times (T_{\text{f,water}} - T_{\text{i,water}})$$

Noting that since the metal was submerged in boiling water, its initial temperature was 100.0 °C; and that for water, 60.0 mL = 60.0 g; we have:

$$(c_{\text{metal}})(59.7\ \text{g})(28.5°\text{C} - 100.0°\text{C}) = -(4.18\ \text{J/g °C})(60.0\ \text{g})(28.5°\text{C} - 22.0°\text{C})$$

Solving this:

$$c_{\text{metal}} = \frac{-(4.184\ \text{J/g °C})(60.0\ \text{g})(6.5°\text{C})}{(59.7\ \text{g})(-71.5°\text{C})} = 0.38\ \text{J/g °C}$$

Comparing this with values in Table T4, our experimental specific heat is closest to the value for copper (0.39 J/g °C), so we identify the metal as copper.

EXERCISE 7.5.6

A 92.9-g piece of a silver/gray metal is heated to 178.0 °C, and then quickly transferred into 75.0 mL of water initially at 24.0 °C. After 5 minutes, both the metal and the water have reached the same temperature: 29.7 °C. Determine the specific heat and the identity of the metal. (Note: You should find that the specific heat is close to that of two different metals. Explain how you can confidently determine the identity of the metal).

Answer

$$c_{metal} = 0.13\ J/g\ °C$$

This specific heat is close to that of either gold or lead. It would be difficult to determine which metal this was based solely on the numerical values. However, the observation that the metal is silver/gray in addition to the value for the specific heat indicates that the metal is lead.

When we use calorimetry to determine the heat involved in a chemical reaction, the same principles we have been discussing apply. The amount of heat absorbed by the calorimeter is often small enough that we can neglect it (though not for highly accurate measurements, as discussed later), and the calorimeter minimizes energy exchange with the surroundings. Because energy is neither created nor destroyed during a chemical reaction, there is no overall energy change during the reaction. The heat produced or consumed in the reaction (the "system"), q_{reaction}, plus the heat absorbed or lost by the solution (the "surroundings"), q_{solution}, must add up to zero:

$$q_{\text{reaction}} + q_{\text{solution}} = 0 \tag{7.5.10}$$

This means that the amount of heat produced or consumed in the reaction equals the amount of heat absorbed or lost by the solution:

$$q_{reaction} = -q_{solution} \tag{7.5.11}$$

This concept lies at the heart of all calorimetry problems and calculations. Because the heat released or absorbed at constant pressure is equal to ΔH, the relationship between heat and ΔH_{rxn} is

$$\Delta H_{rxn} = q_{rxn} = -q_{calorimater} = -mc_s\Delta T \tag{7.5.12}$$

The use of a constant-pressure calorimeter is illustrated in Example 7.5.7.

EXAMPLE 7.5.7: HEAT OF SOLUTION

When 5.03 g of solid potassium hydroxide are dissolved in 100.0 mL of distilled water in a coffee-cup calorimeter, the temperature of the liquid increases from 23.0°C to 34.7°C. The density of water in this temperature range averages 0.9969 g/cm^3. What is ΔH_{soln} (in kilojoules per mole)? Assume that the calorimeter absorbs a negligible amount of heat and, because of the large volume of water, the specific heat of the solution is the same as the specific heat of pure water.

Given: mass of substance, volume of solvent, and initial and final temperatures

Asked for: ΔH_{soln}

Strategy:

A. Calculate the mass of the solution from its volume and density and calculate the temperature change of the solution.
B. Find the heat flow that accompanies the dissolution reaction by substituting the appropriate values into Equation 7.5.1.
C. Use the molar mass of **KOH** to calculate ΔH_{soln}.

Solution:

A To calculate ΔH_{soln}, we must first determine the amount of heat released in the calorimetry experiment. The mass of the solution is

$$\left(100.0\ \cancel{mL}\ H_2O\right)\left(0.9969\ g/\cancel{mL}\right) + 5.03\ g\ KOH = 104.72\ g$$

The temperature change is (34.7°C − 23.0°C) = +11.7°C.

B Because the solution is not very concentrated (approximately 0.9 M), we assume that the specific heat of the solution is the same as that of water. The heat flow that accompanies dissolution is thus

$$\begin{aligned} q_{calorimater} &= mc_s\Delta T \\ &= \left(104.72\ \cancel{g}\right)\left(\frac{4.184\ J}{\cancel{g}\cdot\cancel{^\circ C}}\right)\left(11.7\ \cancel{^\circ C}\right) \\ &= 5130\ J \\ &= 5.13\ kJ \end{aligned}$$

The temperature of the solution increased because heat was absorbed by the solution (q > 0). Where did this heat come from? It was released by KOH dissolving in water. From Equation 7.5.1, we see that

$$\Delta H_{rxn} = -q_{calorimeter} = -5.13\ kJ$$

This experiment tells us that dissolving 5.03 g of **KOH** in water is accompanied by the *release* of 5.13 kJ of energy. Because the temperature of the solution increased, the dissolution of KOH in water must be exothermic.

C The last step is to use the molar mass of **KOH** to calculate ΔH_{soln} - the heat associated when dissolving 1 mol of **KOH**:

$$\begin{aligned} \Delta H_{soln} &= \left(\frac{5.13\ kJ}{5.03\ \cancel{g}}\right)\left(\frac{56.11\ \cancel{g}}{1\ mol}\right) \\ &= -57.2\ kJ/mol \end{aligned}$$

EXERCISE 7.5.7: HEAT OF DISSOLVING

A coffee-cup calorimeter contains 50.0 mL of distilled water at 22.7°C. Solid ammonium bromide (3.14 g) is added and the solution is stirred, giving a final temperature of 20.3°C. Using the same assumptions as in Example 7.5.7, find ΔH_{soln} for NH_4Br (in kilojoules per mole).

Answer

16.6 kJ/mol

7.5.3.2 CONSTANT-VOLUME CALORIMETRY

Constant-pressure calorimeters are not very well suited for studying reactions in which one or more of the reactants is a gas, such as a combustion reaction. The enthalpy changes that accompany combustion reactions are therefore measured using a constant-volume calorimeter, such as the bomb calorimeter (A device used to measure energy changes in chemical processes. shown schematically in Figure **7.5.4**). The reactant is placed in a steel cup inside a steel vessel with a fixed volume (the "bomb"). The bomb is then sealed, filled with excess oxygen gas, and placed inside an insulated container that holds a known amount of water. Because combustion reactions are exothermic, the temperature of the bath and the calorimeter increases during combustion. If the heat capacity of the bomb and the mass of water are known, the heat released can be calculated.

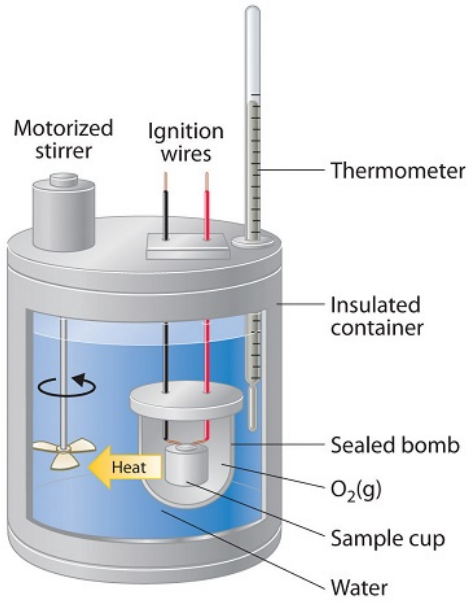


Figure **7.5.4**: A Bomb Calorimeter. After the temperature of the water in the insulated container has reached a constant value, the combustion reaction is initiated by passing an electric current through a wire embedded in the sample. Because this calorimeter operates at constant volume, the heat released is not precisely the same as the enthalpy change for the reaction. (CC BY-SA-NC; anonymous)

Because the volume of the system (the inside of the bomb) is fixed, the combustion reaction occurs under conditions in which the volume, but not the pressure, is constant. The heat released by a reaction carried out at constant volume is identical to the change in *internal energy* (ΔU) rather than the enthalpy change (ΔH); ΔU is related to ΔH by an expression that depends on the change in the number of moles of gas during the reaction. The difference between the heat flow measured at constant volume and the enthalpy change is usually quite small, however (on the order of a few percent). Assuming that $\Delta U < \Delta H$, the relationship between the measured temperature change and ΔH_{comb} is given in Equation **7.5.13**, where C_{bomb} is the total heat capacity of the steel bomb and the water surrounding it

$$\Delta H_{comb} < q_{comb} = q_{calorimater} = C_{bomb}\Delta T \tag{7.5.13}$$

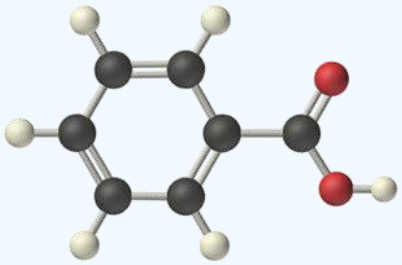
To measure the heat capacity of the calorimeter, we first burn a carefully weighed mass of a standard compound whose enthalpy of combustion is accurately known. Benzoic acid ($C_6H_5CO_2H$) is often used for this purpose because it is a crystalline solid that can be obtained in high purity. The combustion of benzoic acid in a bomb calorimeter releases 26.38 kJ of heat per gram (i.e., its ΔH_{comb} = −26.38 kJ/g). This value and the measured increase in temperature of the calorimeter can be used to determine C_{bomb}. The use of a bomb calorimeter to measure the ΔH_{comb} of a substance is illustrated in Example **7.5.8**.



***Video* 7.5.1:** *Video of view how a bomb calorimeter is prepared for action.*

EXAMPLE 7.5.8: COMBUSTION OF GLUCOSE

The combustion of 0.579 g of benzoic acid in a bomb calorimeter caused a 2.08°C increase in the temperature of the calorimeter. The chamber was then emptied and recharged with 1.732 g of glucose and excess oxygen. Ignition of the glucose resulted in a temperature increase of 3.64°C. What is the ΔH_{comb} of glucose?



Benzoic acid

Given: mass and ΔT for combustion of standard and sample

Asked for: ΔH_{comb} of glucose

Strategy:

A. Calculate the value of q_{rxn} for benzoic acid by multiplying the mass of benzoic acid by its ΔH_{comb}. Then use Equation 7.5.1 to determine the heat capacity of the calorimeter (C_{bomb}) from q_{comb} and ΔT.

B. Calculate the amount of heat released during the combustion of glucose by multiplying the heat capacity of the bomb by the temperature change. Determine the ΔH_{comb} of glucose by multiplying the amount of heat released per gram by the molar mass of glucose.

Solution:

The first step is to use Equation 7.5.1 and the information obtained from the combustion of benzoic acid to calculate C_{bomb}. We are given ΔT, and we can calculate q_{comb} from the mass of benzoic acid:

$$q_{comb} = \left(0.579 \cancel{g}\right)\left(-26.38\ kJ/\cancel{g}\right) = -15.3\ kJ$$

From Equation 7.5.1,

$$-C_{bomb} = \frac{q_{comb}}{\Delta T} = \frac{-15.3\ kJ}{2.08\ ^{o}C} = -7.34\ kJ/^{o}C$$

B According to the strategy, we can now use the heat capacity of the bomb to calculate the amount of heat released during the combustion of glucose:

$$q_{comb} = -C_{bomb}\Delta T = (-7.34\ kJ/^{o}C)\,(3.64\ ^{o}C) = -26.7\ kJ$$

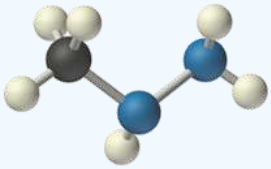
Because the combustion of 1.732 g of glucose released 26.7 kJ of energy, the ΔH_{comb} of glucose is

$$\Delta H_{comb} = \left(\frac{-26.7\ kJ}{1.732\ \cancel{g}}\right)\left(\frac{180.16\ \cancel{g}}{mol}\right) = -2780\ kJ/mol = 2.78 \times 10^3\ kJ/mol$$

This result is in good agreement (< 1% error) with the value of $\Delta H_{comb} = -2803\ kJ/mol$ that calculated using enthalpies of formation.

? EXERCISE 7.5.8: COMBUSTION OF BENZOIC ACID

When 2.123 g of benzoic acid is ignited in a bomb calorimeter, a temperature increase of 4.75°C is observed. When 1.932 g of methylhydrazine (CH_3NHNH_2) is ignited in the same calorimeter, the temperature increase is 4.64°C. Calculate the ΔH_{comb} of methylhydrazine, the fuel used in the maneuvering jets of the US space shuttle.



Methylhydrazine

Answer

-1.30×10^3 kJ/mol

7.5.4 SUMMARY

Calorimetry measures enthalpy changes during chemical processes, where the magnitude of the temperature change depends on the amount of heat released or absorbed and on the heat capacity of the system. **Calorimetry** is the set of techniques used to measure enthalpy changes during chemical processes. It uses devices called *calorimeters*, which measure the change in temperature when a chemical reaction is carried out. The magnitude of the temperature change depends on the amount of heat released or absorbed and on the heat capacity of the system. The **heat capacity (*C*)** of an object is the amount of energy needed to raise its temperature by 1°C; its units are joules per degree Celsius. The **specific heat** (c_s) of a substance is the amount of energy needed to raise the temperature of 1 g of the substance by 1°C, and the **molar heat capacity** (c_p) is the amount of energy needed to raise the temperature of 1 mol of a substance by 1°C. Liquid water has one of the highest specific heats known. Heat flow measurements can be made with either a **constant-pressure calorimeter**, which gives ΔH values directly, or a **bomb calorimeter**, which operates at constant volume and is particularly useful for measuring enthalpies of combustion.

Thermal energy itself cannot be measured easily, but the temperature change caused by the flow of thermal energy between objects or substances can be measured. Calorimetry describes a set of techniques employed to measure enthalpy changes in chemical processes using devices called *calorimeters*. To have any meaning, the quantity that is actually measured in a calorimetric experiment, the change in the temperature of the device, must be related to the heat evolved or consumed in a chemical reaction. We begin this section by explaining how the flow of thermal energy affects the temperature of an object.

7.5.5 CONTRIBUTORS AND ATTRIBUTIONS

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

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7.6: MOLECULES AS ENERGY CARRIERS AND CONVERTERS

LEARNING OBJECTIVES

Make sure you thoroughly understand the following essential concepts:

- Describe the sources of potential energy and kinetic energy contained in a molecule.
- Describe the nature of *"thermal" energy*, and how it relates to other forms of kinetic energy and to *temperature*.
- Explain why the simplest molecules (monatomic and diatomic) have smaller heat capacities than polyatomic molecules.
- Similarly, explain why the dependence of heat capacity on the temperature is different for monatomic and polyatomic molecules.

All molecules at temperatures above absolute zero possess *thermal energy*— the randomized kinetic energy associated with the various motions the molecules as a whole, and also the atoms within them, can undergo. Polyatomic molecules also possess *potential energy* in the form of chemical bonds. Molecules are thus both vehicles for **storing and transporting energy**, and the means of **converting it from one form to another** when the formation, breaking, or rearrangement of the chemical bonds within them is accompanied by the uptake or release of *heat*.

7.6.1 INTERNAL ENERGY: POTENTIAL + KINETIC

Chemical substances are made of atoms, or more generally, of positively charged nuclei surrounded by negatively charged electrons. A molecule such as dihydrogen, H_2, is held together by electrostatic attractions mediated by the electrons shared between the two nuclei. The total potential energy of the molecule is the sum of the repulsions between like charges and the attractions between electrons and nuclei:

$$PE_{total} = PE_{electron-electron} + PE_{nucleus-nucleus} + PE_{nucleus-electron} \tag{7.6.1}$$

In other words, the potential energy of a molecule depends on the time-averaged relative locations of its constituent nuclei and electrons. This dependence is expressed by the familiar potential energy curve which serves as an important description of the chemical bond between two atoms.

- ***Translation*** refers to movement of an object as a complete unit. Translational motions of molecules in solids or liquids are restricted to very short distances comparable to the dimensions of the molecules themselves, whereas in gases the molecules typically travel hundreds of molecular diameters between collisions. In gaseous hydrogen, for example, the molecules will be moving freely from one location to another; this is called *translational motion*, and the molecules therefore possess *translational kinetic energy*

  $$KE_{trans} = \frac{mv^2}{2} \tag{7.6.2}$$

  in which v stands for the average velocity of the molecules; you may recall from your study of gases that v, and therefore KE_{trans}, depends on the temperature.

In addition to translation, molecules composed of two or more atoms can possess other kinds of motion.

- Because a chemical bond acts as a kind of spring, the two atoms in H_2 will have a natural ***vibrational frequency***. In more complicated molecules, many different modes of vibration become possible, and these all contribute a vibrational term KE_{vib} to the total kinetic energy.
- Finally, a molecule can undergo ***rotational*** motions which give rise to a third term KE_{rot}.

Thus the total kinetic energy of a molecule is the sum

$$KE_{total} = KE_{trans} + KE_{vib} + KE_{rot} \tag{7.6.3}$$

The total energy of the molecule (i.e, its *internal energy* U) is just the sum of total kinetic and potential energies:

$$U = KE_{total} + PE_{total} \tag{7.6.4}$$

Although Equation 7.6.4 is simple and straightforward, it cannot take us very far in understanding and predicting the behavior of even one molecule, let alone a large number of them. The reason, of course, is the chaotic and unpredictable nature of molecular motion. Fortunately, the behavior of a large collection of molecules, like that of a large population of people, can be described by statistical methods.

7.6.2 HOW MOLECULES "STORE" THERMAL ENERGY

As noted previously, the *heat capacity* of a substance is a measure of how sensitively its temperature is affected by a change in heat content; the greater the heat capacity, the less effect a given flow of heat q will have on the temperature.

> *Thermal energy is randomized kinetic energy and temperature is a measure of it.*

For monatomic gases, temperature is a measure of the average kinetic energy due to *translational motions* of molecules. If vibrational or rotational motions are also active (e.g., diatomic gases), these motions will also accept thermal energy and reduce the amount that goes into translational motions. Because the temperature depends only on the latter, the effect of the other kinds of motions will be to reduce the dependence of the internal energy on the temperature, thus raising the *heat capacity* of a substance.

Table **7.6.1**: Molar heat capacities (kJ mol^{-1} K^{-1}) of some gaseous substances at constant pressure.

monatomic		diatomic		triatomic	
He	20.5	**CO**	29.3	**H_2O**	33.5
Ne	20.5	**N_2**	29.5	**D_2O**	34.3
Ar	20.5	**F_2**	31.4	**CO_2**	37.2
Kr	20.5	**Cl_2**	33.9	**CS_2**	45.6

Whereas monatomic molecules can only possess translational thermal energy, two additional kinds of motions become possible in polyatomic molecules. A linear molecule has an axis that defines two perpendicular directions in which rotations can occur; each represents an additional *degree of freedom*, so the two together contribute a total of ½ *R* to the heat capacity.

$$C_{trans} = \underbrace{\frac{1}{2}R}_{\text{x dimension}} + \underbrace{\frac{1}{2}R}_{\text{y dimension}} + \underbrace{\frac{1}{2}R}_{\text{z dimension}} = \underbrace{\frac{3}{2}R}_{\text{translation in 3D}} \tag{7.6.5}$$

Vibrational and rotational motions are not possible for monatomic species such as the noble gas elements, so these substances have the lowest heat capacities. Moreover, as you can see in the leftmost column of Table **7.6.1**, their heat capacities are all the same. This reflects the fact that translational motions are the same for all particles; all such motions can be resolved into three directions in space, each contributing one *degree of freedom* to the molecule and **½*R*** to its heat capacity (Equation 7.6.5) where R is the gas constant, $8.314\ J\ K^{-1}$.

> *Think of a "degree of freedom" as a motion that contributes to the total kinetic energy of a molecule.*

For a non-linear molecule, *rotations* are possible along all three directions of space, so these molecules have a rotational heat capacity of $3/2R$.

$$\underbrace{C_{rot}}_{\text{nonlinear molecules}} = \underbrace{\frac{1}{2}R}_{\text{x rotation}} + \underbrace{\frac{1}{2}R}_{\text{y rotation}} + \underbrace{\frac{1}{2}R}_{\text{z rotation}} = \frac{3}{2}R \tag{7.6.6}$$

Linear molecules can only rotate in two dimensions so rotational motions in linear molecules contribute less than rotational motions in nonlinear molecules to the heat capacity.

$$\underbrace{C_{rot}}_{\text{linear molecules}} = \underbrace{\frac{1}{2}R}_{\text{x rotation}} + \underbrace{\frac{1}{2}R}_{\text{y rotation}} = R \tag{7.6.7}$$

Finally, the individual atoms within a molecule can move relative to each other, producing a *vibrational motion*. A nonlinear molecule consisting of N atoms can vibrate in $3N-6$ different ways or modes, while a linear molecule has $3N-5$ modes. Each vibrational mode contributes R (rather than ½ *R*) to the total heat capacity (these results come from advanced mechanics and will not be proven here).

$$\underbrace{C_{vib}}_{\text{linear molecules}} = \overbrace{(3N-5)}^{\text{vib degrees of freedom}} R \tag{7.6.8}$$

and

$$\underbrace{C_{vib}}_{\text{nonlinear molecules}} = \overbrace{(3N-6)}^{\text{vib degrees of freedom}} R \tag{7.6.9}$$

The total heat capacity of a mole of gas molecules is then

$$C_p = C_{trans} + C_{rot} + C_{vib} \tag{7.6.10}$$

which differs based on the geometry and number of atoms in the molecule considered (Equations 7.6.6 - 7.6.9) as shown in Table **7.6.2**.

Table **7.6.2**: Contribution of molecular motions to heat capacity

type of motion →	translation 	Rotation 	vibration 
monatomic	$3/2R$	0	0
diatomic	$3/2R$	R	R ($N = 2$ in Equation 7.6.8)
polyatomic	$3/2R$	$3/2R$(nonlinear) or R (linear)	$(3N–6)R$ (nonlinear) or $(3N–5)R$ (linear)
separation between adjacent levels, (kJ mol^{-1})	6.0 × 10^{-17} J (O_2)	373 J (HCl)	26,000 J (HCl)

Now we are in a position to understand why more complicated molecules have higher heat capacities. The total kinetic energy of a molecule is the sum of those due to the various kinds of motions:

$$KE_{total} = KE_{trans} + KE_{rot} + KE_{vib} \tag{7.6.11}$$

When a monatomic gas absorbs heat, all of the energy ends up in translational motion, and thus goes to increase its temperature. In a polyatomic gas, by contrast, the absorbed energy is partitioned among the other kinds of motions; since only the translational motions contribute to the temperature, the temperature rise is smaller, and thus the heat capacity is larger. There is one very significant complication, however: classical mechanics predicts that the energy is always partitioned equally between all degrees of freedom. Experiments, however, show that this is observed only at quite high temperatures. The reason is that these motions are all *quantized*. This means that only certain increments of energy are possible for each mode of motion, and unless a certain minimum amount of energy is available, a given mode will not be active at all and will contribute nothing to the heat capacity.

7.6.3 TRANSLATIONAL ENERGY LEVELS ARE EFFECTIVELY CONTINUOUS

The shading in Figure **7.6.1** indicates the average thermal energy available at 300 K. Only those levels within this range will have significant occupancy as indicated by the thickness of the lines in the two rightmost columns. At 300 K, only the lowest vibrational states and the first few rotational states will be active. Most of the thermal energy will be confined to the translational levels whose minute spacing (10^{-17} J) causes them to appear as a continuum although technically quantized (by the particle in a box quantum model).

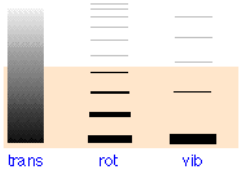


Figure **7.6.1**: Different energy levels associated with translation, rotation, and vibration compared to an arbitrary thermal energy (tan lelvel).

Heat capacity of dihydrogen as a function of temperature. Figure **7.6.2** is typical of those for other polyatomic molecules, and shows the practical consequences of the spacings of the various forms of thermal energy. Thus translational motions are available at virtually all temperatures, but contributions to heat capacity by rotational or vibrational motions can only develop at temperatures sufficiently large to excite these motions.

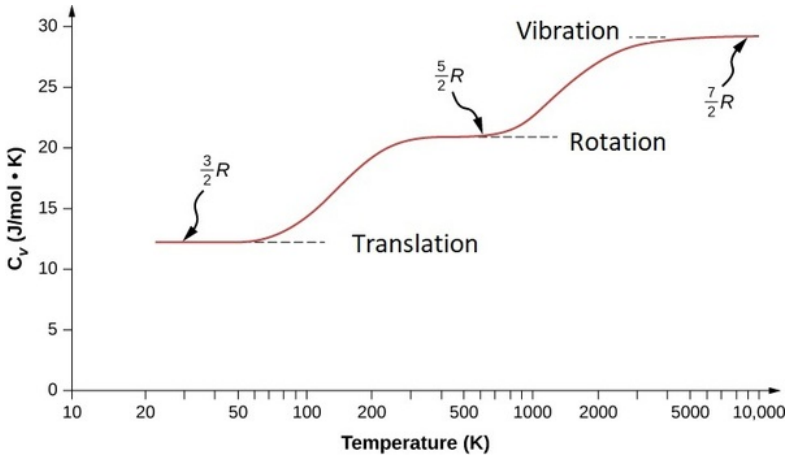


Figure **7.6.2**: The molar heat capacity of hydrogen as a function of temperature (on a logarithmic scale). The three “steps” or “plateaus” show different numbers of degrees of freedom that the typical energies of molecules must achieve to activate. Translational kinetic energy corresponds to three degrees of freedom, rotational to another two, and vibrational to yet another two. (CC BY; OpenStax).

It turns out that translational energy levels are spaced so closely that these motions are active almost down to absolute zero, so all gases possess a heat capacity of at least 3/2 *R* at all temperatures. Rotational motions do not get started until intermediate temperatures, typically 300-500K, so within this range heat capacities begin to increase with temperature. Finally, at very high temperatures, vibrations begin to make a significant contribution to the heat capacity

The strong intermolecular forces of liquids and many solids allow heat to be channeled into vibrational motions involving more than a single molecule, further increasing heat capacities. One of the well known "anomalous" properties of liquid water is its high heat capacity (75 J mol^{-1} K^{-1}) due to intermolecular hydrogen bonding, which is directly responsible for the moderating influence of large bodies of water on coastal climates.

HEAT CAPACITIES OF METALS

Metallic solids are a rather special case. In metals, the atoms oscillate about their equilibrium positions in a rather uniform way which is essentially the same for all metals, so they should all have about the same heat capacity. We can model the atoms of a solid as attached to neighboring atoms by springs (Figure **7.6.3**).

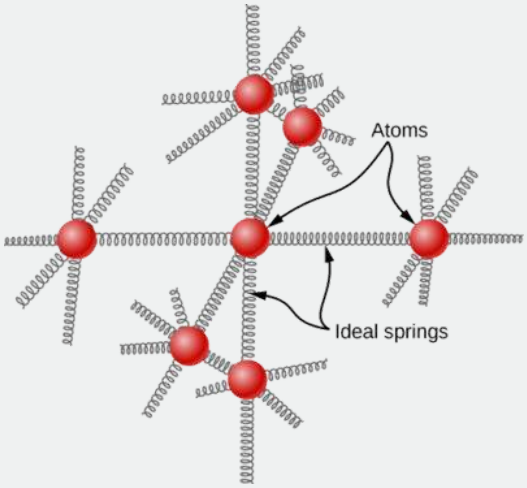


Figure **7.6.3**: In a simple model of a solid element, each atom is attached to others by six springs, two for each possible motion: x, y, and z. Each of the three motions corresponds to two degrees of freedom, one for kinetic energy and one for potential energy. (CC BY-SA OpenStax).

Analogously to the discussion of vibration in the previous module, each atom has six degrees of freedom: one kinetic and one potential for each of the *x*-, *y*-, and *z*-directions. Accordingly, the molar specific heat of a metal should be $3R$. This result, known as the *Law of Dulong and Petit*, works fairly well experimentally at room temperature. In the 19th century these workers discovered that the molar heat capacities of all the metallic elements they studied were around to 25 J mol^{-1} K^{-1}, which is close to what classical physics predicts for crystalline metals. This observation played an important role in characterizing new elements, for it provided a means of estimating their molar masses by a simple heat capacity measurement.

7.6.4 CONTRIBUTORS AND ATTRIBUTIONS

- Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook

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7.7: HEATS OF REACTIONS - ΔU AND ΔH

LEARNING OBJECTIVES

- To understand how enthalpy pertains to chemical reactions

When we study energy changes in chemical reactions, the most important quantity is usually the enthalpy of reaction (ΔH_{rxn}), the change in enthalpy that occurs during a reaction (such as the dissolution of a piece of copper in nitric acid). If heat flows from a system to its surroundings, the enthalpy of the system decreases, so ΔH_{rxn} is negative. Conversely, if heat flows from the surroundings to a system, the enthalpy of the system increases, so ΔH_{rxn} is positive. Thus $\Delta H_{rxn} < 0$ *for an exothermic reaction*, and $\Delta H_{rxn} > 0$ *for an endothermic reaction*. In chemical reactions, bond breaking requires an input of energy and is therefore an endothermic process, whereas bond making releases energy, which is an exothermic process. The sign conventions for heat flow and enthalpy changes are summarized in the following table:

Reaction Type	q	ΔH_{rxn}
exothermic	< 0	< 0 (heat flows from a system to its surroundings)
endothermic	> 0	> 0 (heat flows from the surroundings to a system)

If ΔH_{rxn} is negative, then the enthalpy of the products is less than the enthalpy of the reactants; that is, *an exothermic reaction is energetically downhill* (Figure **7.7.1***a*). Conversely, if ΔH_{rxn} is positive, then the enthalpy of the products is greater than the enthalpy of the reactants; thus, *an endothermic reaction is energetically uphill* (Figure **7.7.1***b*).

> *Bond breaking **ALWAYS** requires an input of energy; bond making **ALWAYS** releases energy.*

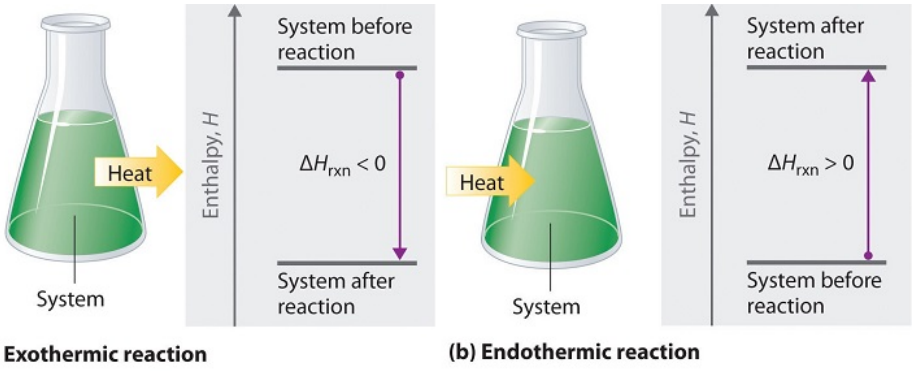


Figure **7.7.1**: The Enthalpy of Reaction. Energy changes in chemical reactions are usually measured as changes in enthalpy. (a) If heat flows from a system to its surroundings, the enthalpy of the system decreases, ΔH_{rxn} is negative, and the reaction is exothermic; it is energetically downhill. (b) Conversely, if heat flows from the surroundings to a system, the enthalpy of the system increases, ΔH_{rxn} is positive, and the reaction is endothermic; it is energetically uphill.

Two important characteristics of enthalpy and changes in enthalpy are summarized in the following discussion.

- **Reversing a reaction or a process changes the sign of ΔH.** Ice *absorbs* heat when it melts (electrostatic interactions are broken), so liquid water must *release* heat when it freezes (electrostatic interactions are formed):

$$\text{heat} + \text{H}_2\text{O}\,(\text{s}) \longrightarrow \text{H}_2\text{O}\,(\text{l}) \qquad \Delta H > 0 \tag{7.7.1}$$

$$\text{H}_2\text{O}\,(\text{l}) \longrightarrow \text{H}_2\text{O}\,(\text{s}) + \text{heat} \qquad \Delta H < 0 \tag{7.7.2}$$

  In both cases, the *magnitude* of the enthalpy change is the same; only the *sign* is different.

- **Enthalpy is an extensive property (like mass).** The magnitude of ΔH for a reaction is proportional to the amounts of the substances that react. For example, a large fire produces more heat than a single match, even though the chemical reaction—the combustion of wood—is the same in both cases. For this reason, the enthalpy change for a reaction is usually given in kilojoules per mole of a particular reactant or product. Consider Equation 7.7.3, which describes the reaction of aluminum with iron(III) oxide (Fe_2O_3) at constant pressure. According to the reaction stoichiometry, 2 mol of Fe, 1 mol of Al_2O_3, and 851.5 kJ of heat are produced for every 2 mol of Al and 1 mol of Fe_2O_3 consumed:

$$2\,\text{Al}\,(\text{s}) + \text{Fe}_2\text{O}_3\,(\text{s}) \longrightarrow 2\,\text{Fe}\,(\text{s}) + \text{Al}_2\text{O}_3\,(\text{s}) + 851.5\ kJ \tag{7.7.3}$$

Thus $\Delta H = -851.5\ kJ/mol$ of Fe_2O_3. We can also describe ΔH for the reaction as −425.8 kJ/mol of Al: because 2 mol of Al are consumed in the balanced chemical equation, we divide −851.5 kJ by 2. When a value for ΔH, in kilojoules rather than kilojoules per mole, is written after the reaction, as in Equation 7.7.3, it is the value of ΔH corresponding to the reaction of the molar quantities of reactants as given in the balanced chemical equation:

$$2\,Al(s) + Fe_2O_3(s) \longrightarrow 2\,Fe(s) + Al_2O_3(s) \qquad \Delta H_{rxn} = -851.5\ kJ \tag{7.7.4}$$

If 4 mol of Al and 2 mol of Fe_2O_3 react, the change in enthalpy is 2 × (−851.5 kJ) = −1703 kJ. We can summarize the relationship between the amount of each substance and the enthalpy change for this reaction as follows:

$$-\frac{851.5\ kJ}{2\ mol\ Al} = -\frac{425.8\ kJ}{1\ mol\ Al} = -\frac{1703\ kJ}{4\ mol\ Al} \tag{7.7.5}$$

The relationship between the magnitude of the enthalpy change and the mass of reactants is illustrated in Example 7.7.1.

7.7.1 EXAMPLE

Certain parts of the world, such as southern California and Saudi Arabia, are short of fresh water for drinking. One possible solution to the problem is to tow icebergs from Antarctica and then melt them as needed. If ΔH is 6.01 kJ/mol for the reaction $H_2O(s) \longrightarrow H_2O(l)$ at 0°C and constant pressure, how much energy would be required to melt a moderately large iceberg with a mass of 1.00 million metric tons (1.00×10^6 metric tons)? (A metric ton is 1000 kg.)

Given: energy per mole of ice and mass of iceberg

Asked for: energy required to melt iceberg

Strategy:

A. Calculate the number of moles of ice contained in 1 million metric tons (1.00×10^6 metric tons) of ice.

B. Calculate the energy needed to melt the ice by multiplying the number of moles of ice in the iceberg by the amount of energy required to melt 1 mol of ice.

Solution:

A Because enthalpy is an extensive property, the amount of energy required to melt ice depends on the amount of ice present. We are given ΔH for the process—that is, the amount of energy needed to melt 1 mol (or 18.015 g) of ice—so we need to calculate the number of moles of ice in the iceberg and multiply that number by ΔH (+6.01 kJ/mol):

$$moles\ H_2O = 1.00 \times 10^6\ \cancel{metric\ tons}\ H_2O \left(\frac{1000\ \cancel{kg}}{1\ \cancel{metric\ ton}}\right)\left(\frac{1000\ \cancel{g}}{1\ \cancel{kg}}\right)\left(\frac{1\ mol\ H_2O}{18.015\ \cancel{g\ H_2O}}\right)$$

$$= 5.55 \times 10^{10}\ mol H_2O$$

B The energy needed to melt the iceberg is thus

$$\left(\frac{6.01\ kJ}{\cancel{mol\ H_2O}}\right)\left(5.55 \times 10^{10}\ \cancel{mol\ H_2O}\right) = 3.34 \times 10^{11}\ kJ$$

Because so much energy is needed to melt the iceberg, this plan would require a relatively inexpensive source of energy to be practical. To give you some idea of the scale of such an operation, the amounts of different energy sources equivalent to the amount of energy needed to melt the iceberg are shown in the table below.

Possible sources of the approximately 3.34×10^{11} kJ needed to melt a 1.00×10^6 metric ton iceberg

- Combustion of 3.8×10^3 ft^3 of natural gas
- Combustion of 68,000 barrels of oil
- Combustion of 15,000 tons of coal
- 1.1×10^8 kilowatt-hours of electricity

7.7.1 EXERCISE

If 17.3 g of powdered aluminum are allowed to react with excess Fe_2O_3, how much heat is produced?

Answer

- 273 kJ

7.7.1 TYPES OF ENTHALPIES OF REACTIONS

One way to report the heat absorbed or released would be to compile a massive set of reference tables that list the enthalpy changes for all possible chemical reactions, which would require an incredible amount of effort. Fortunately, Hess's law allows us to calculate the enthalpy change for virtually any conceivable chemical reaction using a relatively small set of tabulated data, such as the following:

- **Enthalpy of combustion** (ΔH_{comb}) is the change in enthalpy that occurs during a combustion reaction. Enthalpy changes have been measured for the combustion of virtually any substance that will burn in oxygen; these values are usually reported as the enthalpy of combustion per mole of substance.
- **Enthalpy of fusion** (ΔH_{fus}) is the enthalpy change that accompanies the melting (fusion) of 1 mol of a substance. The enthalpy change that accompanies the melting, or fusion, of 1 mol of a substance; these values have been measured for almost all the elements and for most simple compounds.
- **Enthalpy of vaporization** (ΔH_{vap}) is the enthalpy change that accompanies the vaporization of 1 mol of a substance. The enthalpy change that accompanies the vaporization of 1 mol of a substance; these values have also been measured for nearly all the elements and for most volatile compounds.
- **Enthalpy of solution** (ΔH_{soln}) is the change in enthalpy that occurs when a specified amount of solute dissolves in a given quantity of solvent.

Table **7.7.1**: Enthalpies of Vaporization and Fusion for Selected Substances at Their Boiling Points and Melting Points

Substance	ΔH_{vap} (kJ/mol)	ΔH_{fus} (kJ/mol)
argon (Ar)	6.3	1.3
methane (CH_4)	9.2	0.84
ethanol (CH_3CH_2OH)	39.3	7.6
benzene (C_6H_6)	31.0	10.9
water (H_2O)	40.7	6.0
mercury (Hg)	59.0	2.29
iron (Fe)	340	14

> *The sign convention is the same for all enthalpy changes: negative if heat is released by the system and positive if heat is absorbed by the system.*



Enthalpy of Reaction: https://youtu.be/z2KUaIEF9qI

7.7.2 SUMMARY

Enthalpy is a state function used to measure the heat transferred from a system to its surroundings or vice versa at constant pressure. Only the **change in enthalpy** (ΔH) can be measured. A negative ΔH means that heat flows from a system to its surroundings; a positive ΔH means that heat flows into a system from its surroundings. For a chemical reaction, the **enthalpy of reaction** (ΔH_{rxn}) is the difference in enthalpy between products and reactants; the units of ΔH_{rxn} are kilojoules per mole. Reversing a chemical reaction reverses the sign of ΔH_{rxn}.

The magnitude of ΔH_{rxn} also depends on the physical state of the reactants and the products because processes such as melting solids or vaporizing liquids are also accompanied by enthalpy changes: the **enthalpy of fusion** (ΔH_{fus}) and the **enthalpy of vaporization** (ΔH_{vap}), respectively. The overall enthalpy change for a series of reactions is the sum of the enthalpy changes for the individual reactions, which is **Hess's law**. The **enthalpy of combustion** (ΔH_{comb}) is the enthalpy change that occurs when a substance is burned in excess oxygen.

7.7.3 CONTRIBUTORS AND ATTRIBUTIONS

- Modified by Joshua Halpern (Howard University)

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7.8: INDIRECT DETERMINATION OF ΔH - HESS'S LAW

LEARNING OBJECTIVES

- To use Hess's law and thermochemical cycles to calculate enthalpy changes of chemical reactions.

Because enthalpy is a state function, the enthalpy change for a reaction depends on only two things:

1. the masses of the reacting substances and
2. the physical states of the reactants and products.

It does **not** depend on the path by which reactants are converted to products. If you climbed a mountain, for example, the altitude change would not depend on whether you climbed the entire way without stopping or you stopped many times to take a break. If you stopped often, the overall change in altitude would be the sum of the changes in altitude for each short stretch climbed. Similarly, when we add two or more balanced chemical equations to obtain a net chemical equation, ΔH for the net reaction is the sum of the ΔH values for the individual reactions. This principle is called Hess's law, after the Swiss-born Russian chemist Germain Hess (1802–1850), a pioneer in the study of thermochemistry. Hess's law allows us to calculate ΔH values for reactions that are difficult to carry out directly by adding together the known ΔH values for individual steps that give the overall reaction, even though the overall reaction may not actually occur via those steps.

We can illustrate Hess's law using the thermite reaction. The overall reaction shown in Equation 7.8.1 can be viewed as occurring in three distinct steps with known ΔH values. As shown in Figure 7.8.1:

1. The first reaction produces 1 mol of solid aluminum oxide (Al_2O_3) and 2 mol of liquid iron at its melting point of 1758°C (Equation 7.8.1 a); the enthalpy change for this reaction is −732.5 kJ/mol of Fe_2O_3.
2. The second reaction is the conversion of 2 mol of liquid iron at 1758°C to 2 mol of solid iron at 1758°C (Equation 7.8.1b); the enthalpy change for this reaction is −13.8 kJ/mol of Fe (−27.6 kJ per 2 mol Fe).
3. In the third reaction, 2 mol of solid iron at 1758°C is converted to 2 mol of solid iron at 25°C (Equation 7.8.1c); the enthalpy change for this reaction is −45.5 kJ/mol of Fe (−91.0 kJ per 2 mol Fe).

As you can see in Figure 7.8.1, the overall reaction is given by the longest arrow (shown on the left), which is the sum of the three shorter arrows (shown on the right). Adding Equations 7.8.1a-7.8.1c} gives the overall reaction, shown Equation 7.8.1d:

$$\begin{array}{lcll}
2Al\,(s,\ 25°C) + Fe_2O_3\,(s,\ 25°C) & \rightarrow & 2Fe\,(l,\ 1758°C) + Al_2O_3\,(s,\ 1758°C) & \Delta H = -732.5\ kJ \quad (reaction\ a) \\
2Fe\,(l,\ 1758°C) & \rightarrow & 2Fe\,(s,\ 1758°C) & \Delta H = -\ 27.6\ kJ \quad (reaction\ b) \\
2Fe\,(s,\ 1758°C) + 2Al\,(s,\ 1758°C) & \rightarrow & 2Fe\,(s,\ 25°C) + 2Al\,(s,\ 25°C) & \Delta H = -\ 91.0\ kJ \quad (reaction\ c) \\
\hline
2Al\,(s,\ 25°C) + Fe_2O_3\,(s,\ 25°C) & \rightarrow & 2Al\,(s,\ 25°C) + 2Fe_2O_3\,(s,\ 25°C) & \Delta H = -852.2\ kJ \quad (total\ reaction\ d)
\end{array} \tag{7.8.1}$$

By Hess's law, the enthalpy change for part (d) is the sum of the enthalpy changes for parts (a), (b), and (c). In essence, Hess's law enables us to calculate the enthalpy change for the sum of a series of reactions without having to draw a diagram like that in Figure 7.8.1.

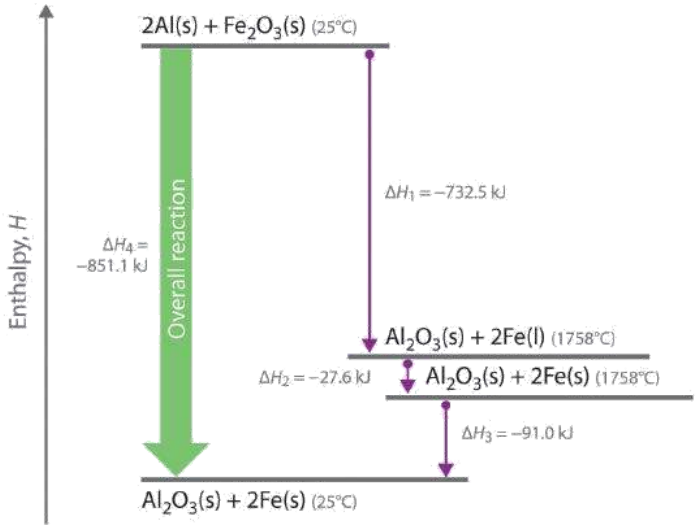


Figure **7.8.1**: Energy Changes Accompanying the Thermite Reaction. Because enthalpy is a state function, the overall enthalpy change for the reaction of 2 mol of Al(s) with 1 mol of Fe_2O_3(s) is −851.1 kJ, whether the reaction occurs in a single step (ΔH_4, shown on the left) or in three hypothetical steps (shown on the right) that involve the successive formation of solid Al_2O_3 and liquid iron (ΔH_1), solid iron at 1758°C (ΔH_2), and solid iron at 25°C (ΔH_3). Thus $\Delta H_4 = \Delta H_1 + \Delta H_2 + \Delta H_3$, as stated by Hess's law.

Comparing parts (a) and (d) in Equation 7.8.1 also illustrates an important point: The magnitude of ΔH for a reaction depends on the physical states of the reactants and the products (gas, liquid, solid, or solution). When the product is liquid iron at its melting point (part (a) in Equation 7.8.1), only 732.5 kJ of heat are released to the surroundings compared with 852 kJ when the product is solid iron at 25°C (part (d) in Equation 7.8.1). The difference, 120 kJ, is the amount of energy that is released when 2 mol of liquid iron solidifies and cools to 25°C. It is important to specify the physical state of all reactants and products when writing a thermochemical equation.

When using Hess's law to calculate the value of ΔH for a reaction, follow this procedure:

1. Identify the equation whose ΔH value is unknown and write individual reactions with known ΔH values that, when added together, will give the desired equation. We illustrate how to use this procedure in Example **7.8.1**.
2. Arrange the chemical equations so that the reaction of interest is the sum of the individual reactions.
3. If a reaction must be reversed, change the sign of ΔH for that reaction. Additionally, if a reaction must be multiplied by a factor to obtain the correct number of moles of a substance, multiply its ΔH value by that same factor.
4. Add together the individual reactions and their corresponding ΔH values to obtain the reaction of interest and the unknown ΔH.

✔ EXAMPLE 7.8.1

When carbon is burned with limited amounts of oxygen gas (O_2), carbon monoxide (CO) is the main product:

$$2\,C(s) + O_2(g) \longrightarrow 2\,CO(g) \qquad \Delta H = -221.0\ kJ \qquad \textbf{(reaction 1)}$$

When carbon is burned in excess O_2, carbon dioxide (CO_2) is produced:

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H = -393.5\ kJ \qquad \textbf{(reaction 2)}$$

Use this information to calculate the enthalpy change per mole of CO for the reaction of CO with O_2 to give CO_2.

Given: two balanced chemical equations and their ΔH values

Asked for: enthalpy change for a third reaction

Strategy:

A. After balancing the chemical equation for the overall reaction, write two equations whose ΔH values are known and that, when added together, give the equation for the overall reaction. (Reverse the direction of one or more of the equations as necessary, making sure to also reverse the sign of ΔH.)

B. Multiply the equations by appropriate factors to ensure that they give the desired overall chemical equation when added together. To obtain the enthalpy change per mole of CO, write the resulting equations as a sum, along with the enthalpy change for each.

Solution:

A We begin by writing the balanced chemical equation for the reaction of interest:

$$\mathrm{CO\,(g) + \tfrac{1}{2}\,O_2\,(g) \longrightarrow CO_2\,(g)} \qquad \Delta H_{rxn} = ? \qquad \text{(reaction 3)}$$

There are at least two ways to solve this problem using Hess's law and the data provided. The simplest is to write two equations that can be added together to give the desired equation and for which the enthalpy changes are known. Observing that CO, a reactant in reaction 2 and a product in Equation reaction 1, we can reverse reaction 1 to give

$$2CO\,(g) \rightarrow 2C\,(s) + O_2\,(g) \qquad \Delta H = +221.0\ kJ$$

Because we have reversed the direction of the reaction, the sign of ΔH is changed. We can use reaction 2, as written because its product, CO_2, is the product we want in reaction 3,:

$$\mathrm{C\,(s) + O_2\,(g) \longrightarrow CO_2\,(s)} \qquad \Delta H = -393.5\ kJ \qquad (7.8.2)$$

B Adding these two equations together does not give the desired reaction, however, because the numbers of C(s) on the left and right sides do not cancel. According to our strategy, we can multiply the second equation by 2 to obtain 2 mol of C(s) as the reactant:

$$\mathrm{2\,C\,(s) + 2\,O_2\,(g) \longrightarrow 2\,CO_2\,(s)} \qquad \Delta H = -787.0\ kJ \qquad (7.8.3)$$

Writing the resulting equations as a sum, along with the enthalpy change for each, gives

$$\begin{array}{rcl} 2CO\,(g) & \rightarrow & \cancel{2C\,(s)} + \cancel{O_2\,(g)} \quad \Delta H = -\Delta H_1 = +221.0\ kJ \\ \cancel{2C\,(s)} + \cancel{2}\,O_2\,(g) & \rightarrow & 2CO_2\,(g) \quad \Delta H = -\Delta 2H_2 = -787.0\ kJ \\ 2CO\,(g) + O_2\,(g) & \rightarrow & 2CO_2\,(g) \quad \Delta H = -566.0\ kJ \end{array} \qquad (7.8.4)$$

Note that the overall chemical equation and the enthalpy change for the reaction are both for the reaction of 2 mol of CO with O_2, and the problem asks for the amount per mole of CO. Consequently, we must divide both sides of the final equation and the magnitude of ΔH by 2:

$$CO\,(g) + \tfrac{1}{2}O_2\,(g) \rightarrow CO_2\,(g) \quad \Delta H = -283.0\ kJ$$

An alternative and equally valid way to solve this problem is to write the two given equations as occurring in steps. Note that we have multiplied the equations by the appropriate factors to allow us to cancel terms:

$$\begin{array}{lrcl} (A) & 2C\,(s) + O_2\,(g) & \rightarrow & \cancel{2CO\,(g)} \quad \Delta H_A = \Delta H_1 = +221.0\ kJ \\ (B) & \cancel{2CO\,(g)} + O_2\,(g) & \rightarrow & 2CO_2\,(g) \quad \Delta H_B = ? \\ (C) & 2C\,(s) + 2O_2\,(g) & \rightarrow & 2CO_2\,(g) \quad \Delta H = 2\Delta H_2 = 2 \times (-393.5\ kJ) = -787.0\ kJ \end{array} \qquad (7.8.5)$$

The sum of reactions A and B is reaction C, which corresponds to the combustion of 2 mol of carbon to give CO_2. From Hess's law, $\Delta H_A + \Delta H_B = \Delta H_C$, and we are given ΔH for reactions A and C. Substituting the appropriate values gives

$$-221.0\ kJ + \Delta H_B = -787.0\ kJ$$
$$\Delta H_B = -566.0$$

This is again the enthalpy change for the conversion of 2 mol of CO to CO_2. The enthalpy change for the conversion of 1 mol of CO to CO_2 is therefore −566.0 ÷ 2 = −283.0 kJ/mol of CO, which is the same result we obtained earlier. As you can see, there may be more than one correct way to solve a problem.

? EXERCISE 7.8.1

The reaction of acetylene (C_2H_2) with hydrogen (H_2) can produce either ethylene (C_2H_4) or ethane (C_2H_6):

$$C_2H_2\,(g) + H_2\,(g) \rightarrow C_2H_4\,(g) \quad \Delta H = -175.7\ kJ/mol\ C_2H_2$$
$$C_2H_2\,(g) + 2H_2\,(g) \rightarrow C_2H_6\,(g) \quad \Delta H = -312.0\ kJ/mol\ C_2H_2$$

What is ΔH for the reaction of C_2H_4 with H_2 to form C_2H_6?

Answer

−136.3 kJ/mol of C_2H_4

7.8.1 SUMMARY

Hess's law is that the overall enthalpy change for a series of reactions is the sum of the enthalpy changes for the individual reactions. For a chemical reaction, the **enthalpy of reaction** (ΔH_{rxn}) is the difference in enthalpy between products and reactants; the units of ΔH_{rxn} are kilojoules per mole. Reversing a chemical reaction reverses the sign of ΔH_{rxn}.

7.8.2 CONTRIBUTORS AND ATTRIBUTIONS

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7.9: STANDARD ENTHALPIES OF FORMATION

LEARNING OBJECTIVES

- To understand Enthalpies of Formation and be able to use them to calculate Enthalpies of Reaction

One way to report the heat absorbed or released by chemical reactions would be to compile a massive set of reference tables that list the enthalpy changes for all possible chemical reactions, which would require an incredible amount of effort. Fortunately, Hess's law allows us to calculate the enthalpy change for virtually any conceivable chemical reaction using a relatively small set of tabulated data, starting from the elemental forms of each atom at 25 °C and 1 atm pressure.

Enthalpy of formation (ΔH_f) is the enthalpy change for the formation of 1 mol of a compound from its component elements, such as the formation of carbon dioxide from carbon and oxygen. The formation of any chemical can be as a reaction from the corresponding elements:

$$\text{elements} \rightarrow \text{compound}$$

which in terms of the the Enthalpy of formation becomes

$$\Delta H_{rxn} = \Delta H_f \tag{7.9.1}$$

For example, consider the combustion of carbon:

$$\mathrm{C(s) + O_2(g) \longrightarrow CO_2(g)}$$

then

$$\Delta H_{rxn} = \Delta H_f\,[CO_2\,(g)]$$

The sign convention for ΔH_f is the same as for any enthalpy change: $\Delta H_f < 0$ if heat is released when elements combine to form a compound and $\Delta H_f > 0$ if heat is absorbed.

> The sign convention is the same for all enthalpy changes: negative if heat is released by the system and positive if heat is absorbed by the system.

7.9.1 STANDARD ENTHALPIES OF FORMATION

The magnitude of ΔH for a reaction depends on the physical states of the reactants and the products (gas, liquid, solid, or solution), the pressure of any gases present, and the temperature at which the reaction is carried out. To avoid confusion caused by differences in reaction conditions and ensure uniformity of data, the scientific community has selected a specific set of conditions under which enthalpy changes are measured. These standard conditions serve as a reference point for measuring differences in enthalpy, much as sea level is the reference point for measuring the height of a mountain or for reporting the altitude of an airplane.

The standard conditions for which most thermochemical data are tabulated are a *pressure* of 1 atmosphere (atm) for all gases and a *concentration* of 1 M for all species in solution (1 mol/L). In addition, each pure substance must be in its standard state, which is usually its most stable form at a pressure of 1 atm at a specified temperature. We assume a temperature of 25°C (298 K) for all enthalpy changes given in this text, unless otherwise indicated. Enthalpies of formation measured under these conditions are called **standard enthalpies of formation** (ΔH_f°) The enthalpy change for the formation of 1 mol of a compound from its component elements when the component elements are each in their standard states. The standard enthalpy of formation of any element in its most stable form is zero by definition.

> *The standard enthalpy of formation of any element in its standard state is zero by definition.*

For example, although oxygen can exist as ozone (O_3), atomic oxygen (O), and molecular oxygen (O_2), O_2 is the most stable form at 1 atm pressure and 25°C. Similarly, hydrogen is H_2(g), not atomic hydrogen (H). Graphite and diamond are both forms of elemental carbon, but because graphite is more stable at 1 atm pressure and 25°C, the standard state of carbon is graphite (Figure **7.9.1**). Therefore, $\mathrm{O_2(g)}$, $\mathrm{H_2(g)}$, and graphite have ΔH_f° values of zero.

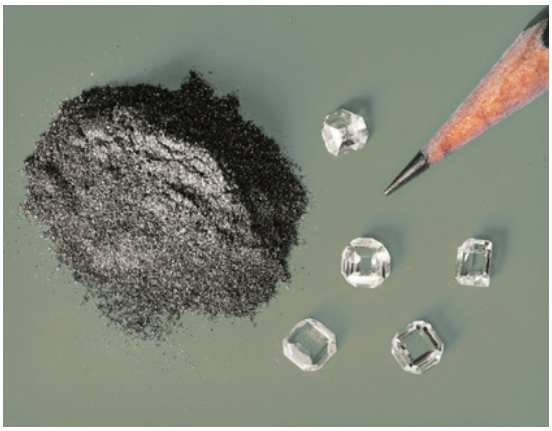


Figure 7.9.1: Elemental Carbon. Although graphite and diamond are both forms of elemental carbon, graphite is slightly more stable at 1 atm pressure and 25°C than diamond is. Given enough time, diamond will revert to graphite under these conditions. Hence graphite is the standard state of carbon.

The standard enthalpy of formation of glucose from the elements at 25°C is the enthalpy change for the following reaction:

$$6C\,(s, graphite) + 6H_2\,(g) + 3O_2\,(g) \rightarrow C_6H_{12}O_6\,(s) \quad \Delta H_f^\circ = -1273.3\ kJ \tag{7.9.2}$$

It is not possible to measure the value of $\Delta H^\circ{}_{of}$ for glucose, −1273.3 kJ/mol, by simply mixing appropriate amounts of graphite, $\mathbf{O_2}$, and $\mathbf{H_2}$ and measuring the heat evolved as glucose is formed since the reaction shown in Equation 7.9.2 does not occur at a measurable rate under any known conditions. Glucose is not unique; most compounds cannot be prepared by the chemical equations that define their standard enthalpies of formation. Instead, values of $\Delta H^\circ{}_{of}$ are obtained using **Hess's law** and standard enthalpy changes that have been measured for other reactions, such as combustion reactions. Values of ΔH_f° for an extensive list of compounds are given in Table T1. Note that ΔH_f° values are always reported in kilojoules per mole of the substance of interest. Also notice in Table T1 that the standard enthalpy of formation of O_2(g) is zero because it is the most stable form of oxygen in its standard state.

✔ EXAMPLE 7.9.1: ENTHALPY OF FORMATION

For the formation of each compound, write a balanced chemical equation corresponding to the standard enthalpy of formation of each compound.

a. $\mathbf{HCl\,(g)}$
b. $\mathbf{MgCO_3\,(s)}$
c. $\mathbf{CH_3(CH_2)_{14}CO_2H\,(s)}$ (*palmitic acid*)

Given:

compound formula and phase.

Asked for:

balanced chemical equation for its formation from elements in standard states

Strategy:

Use Table T1 to identify the standard state for each element. Write a chemical equation that describes the formation of the compound from the elements in their standard states and then balance it so that 1 mol of product is made.

Solution:

To calculate the standard enthalpy of formation of a compound, we must start with the elements in their standard states. The standard state of an element can be identified in Table T1: by a ΔH_f° value of 0 kJ/mol.

Hydrogen chloride contains one atom of hydrogen and one atom of chlorine. Because the standard states of elemental hydrogen and elemental chlorine are $\mathbf{H_2\,(g)}$ and $\mathbf{Cl_2\,(g)}$, respectively, the unbalanced chemical equation is

$$\mathbf{H_2\,(g) + Cl_2\,(g) \rightarrow HCl\,(g)}$$

Fractional coefficients are required in this case because ΔH°_f values are reported for *1 mol* of the product, $\mathbf{HCl}$. Multiplying both $\mathbf{H_2\,(g)}$ and $\mathbf{Cl_2\,(g)}$ by 1/2 balances the equation:

$$\mathbf{\tfrac{1}{2}\,H_2\,(g) + \tfrac{1}{2}\,Cl_2\,(g) \rightarrow HCl\,(g)}$$

The standard states of the elements in this compound are $\mathrm{Mg(s)}$, $\mathrm{C(s, graphite)}$, and $\mathrm{O_2(g)}$. The unbalanced chemical equation is thus

$$\mathrm{Mg(s) + C(s, graphite) + O_2(g) \rightarrow MgCO_3(s)}$$

This equation can be balanced by inspection to give

$$\mathrm{Mg(s) + C(s, graphite) + \tfrac{3}{2}\, O_2\ (g) \rightarrow MgCO_3(s)}$$

Palmitic acid, the major fat in meat and dairy products, contains hydrogen, carbon, and oxygen, so the unbalanced chemical equation for its formation from the elements in their standard states is as follows:

$$\mathrm{C(s, graphite) + H_2(g) + O_2(g) \rightarrow CH_3(CH_2)_{14}CO_2H(s)}$$

There are 16 carbon atoms and 32 hydrogen atoms in 1 mol of palmitic acid, so the balanced chemical equation is

$$\mathrm{16\,C(s, graphite) + 16\,H_2(g) + O_2(g) \longrightarrow CH_3(CH_2)_{14}CO_2H(s)}$$

? EXERCISE 7.9.1

For the formation of each compound, write a balanced chemical equation corresponding to the standard enthalpy of formation of each compound.

a. $\mathrm{NaCl(s)}$
b. $\mathrm{H_2SO_4(l)}$
c. $\mathrm{CH_3CO_2H(l)}$ (*acetic acid*)

Answer a

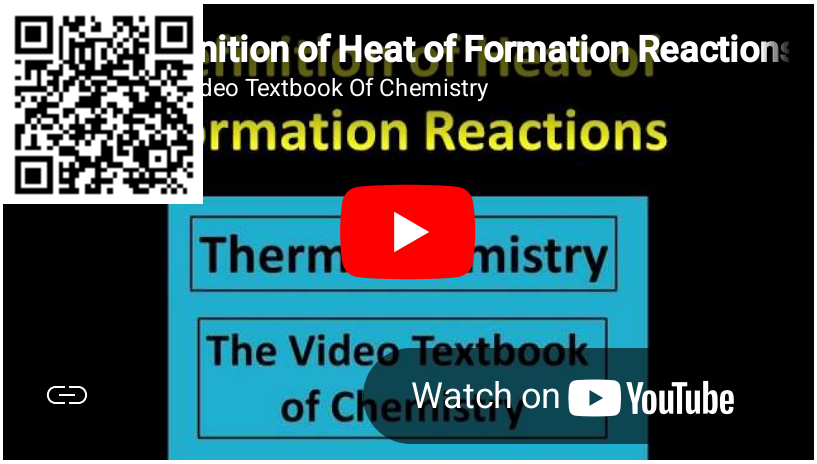
$$\mathrm{Na(s) + \tfrac{1}{2}\, Cl_2(g) \rightarrow NaCl(s)}$$

Answer b

$$\mathrm{H_2(g) + \tfrac{1}{8}\, S_8(s) + 2\,O_2\ (g) \rightarrow H_2\ SO_4(\ l)}$$

Answer c

$$\mathrm{2\,C(s) + O_2(g) + 2\,H_2(g) \longrightarrow CH_3CO_2H(l)}$$



Definition of Heat of Formation Reactions: https://youtu.be/A20k0CK4doI

7.9.2 STANDARD ENTHALPIES OF REACTION

Tabulated values of standard enthalpies of formation can be used to calculate enthalpy changes for *any* reaction involving substances whose ΔH_f° values are known. The standard enthalpy of reaction ΔH_{rxn}° is the enthalpy change that occurs when a reaction is carried out with all reactants and products in their standard states. Consider the general reaction

$$aA + bB \rightarrow cC + dD \tag{7.9.3}$$

where A, B, C, and D are chemical substances and a, b, c, and d are their stoichiometric coefficients. The magnitude of ΔH° is the sum of the standard enthalpies of formation of the products, each multiplied by its appropriate coefficient, minus the sum of the standard enthalpies

of formation of the reactants, also multiplied by their coefficients:

$$\Delta H^o_{rxn} = \underbrace{\left[c\Delta H^o_f(C)+d\Delta H^o_f(D)\right]}_{\text{products}} - \underbrace{\left[a\Delta H^o_f(A)+b\Delta H^o_f(B)\right]}_{\text{reactants}} \tag{7.9.4}$$

More generally, we can write

$$\Delta H^o_{rxn} = \sum m\Delta H^o_f\,(products) - \sum n\Delta H^o_f\,(reactants) \tag{7.9.5}$$

where the symbol $\sum$ means "sum of" and m and n are the stoichiometric coefficients of each of the products and the reactants, respectively. "Products minus reactants" summations such as Equation 7.9.5 arise from the fact that enthalpy is a state function. Because many other thermochemical quantities are also state functions, "products minus reactants" summations are very common in chemistry; we will encounter many others in subsequent chapters.

> "Products minus reactants" summations are typical of state functions.

To demonstrate the use of tabulated ΔH^o values, we will use them to calculate ΔH_{rxn} for the combustion of glucose, the reaction that provides energy for your brain:

$$C_6H_{12}O_6\,(s) + 6\,O_2\,(g) \;\rightarrow 6\,CO_2\,(g) + 6\,H_2O\,(l) \tag{7.9.6}$$

Using Equation 7.9.5, we write

$$\begin{aligned}\Delta H^o_f \\ = \left\{6\Delta H^o_f\,[CO_2\,(g)] + 6\Delta H^o_f\,[H_2O\,(g)]\right\} - \left\{\Delta H^o_f\,[C_6H_{12}O_6\,(s)] + 6\Delta H^o_f\,[O_2\,(g)]\right\}\end{aligned} \tag{7.9.7}$$

From Table T1, the relevant ΔH^o_f values are $\Delta H^o_f\,[CO_2(g)]$ = -393.5 kJ/mol, $\Delta H^o_f\,[H_2O(l)]$ = -285.8 kJ/mol, and $\Delta H^o_f\,[C_6H_{12}O_6(s)]$ = -1273.3 kJ/mol. Because $O_2(g)$ is a pure element in its standard state, $\Delta H^o_f\,[O_2(g)]$ = 0 kJ/mol. Inserting these values into Equation 7.9.7 and changing the subscript to indicate that this is a combustion reaction, we obtain

$$\Delta H^o_{comb} = [6\,(-393.5\ kJ/mol) + 6\,(-285.8\ kJ/mol)] - [-1273.3 + 6\,(0\ kJ\ mol)] \tag{7.9.8}$$

$$= -2802.5\ kJ/mol \tag{7.9.9}$$

As illustrated in Figure 7.9.2, we can use Equation 7.9.8 to calculate ΔH^o_f for glucose because enthalpy is a state function. The figure shows two pathways from reactants (middle left) to products (bottom). The more direct pathway is the downward green arrow labeled ΔH^o_{comb}. The alternative hypothetical pathway consists of **four separate reactions** that convert the reactants to the elements in their standard states (upward purple arrow at left) and then convert the elements into the desired products (downward purple arrows at right). The reactions that convert the reactants to the elements are the reverse of the equations that define the ΔH^o_f values of the reactants. Consequently, the enthalpy changes are

$$\begin{aligned}\Delta H^o_1 &= \Delta H^o_f\,[glucose\,(s)] \\ &= -1\ \cancel{mol\ glucose}\left(\frac{1273.3\ kJ}{1\ \cancel{mol\ glucose}}\right) \\ &= +1273.3\ kJ \\ \Delta H^o_2 &= 6\Delta H^o_f\,[O_2\,(g)] \\ &= 6\ \cancel{mol\ O_2}\left(\frac{0\ kJ}{1\ \cancel{mol\ O_2}}\right) \\ &= 0\ kJ\end{aligned} \tag{7.9.10}$$

> *Recall that when we reverse a reaction, we must also reverse the **sign** of the accompanying enthalpy change (Equation 7.9.4 since the products are now reactants and vice versa.*

The overall enthalpy change for conversion of the reactants (1 mol of glucose and 6 mol of O_2) to the elements is therefore +1273.3 kJ.

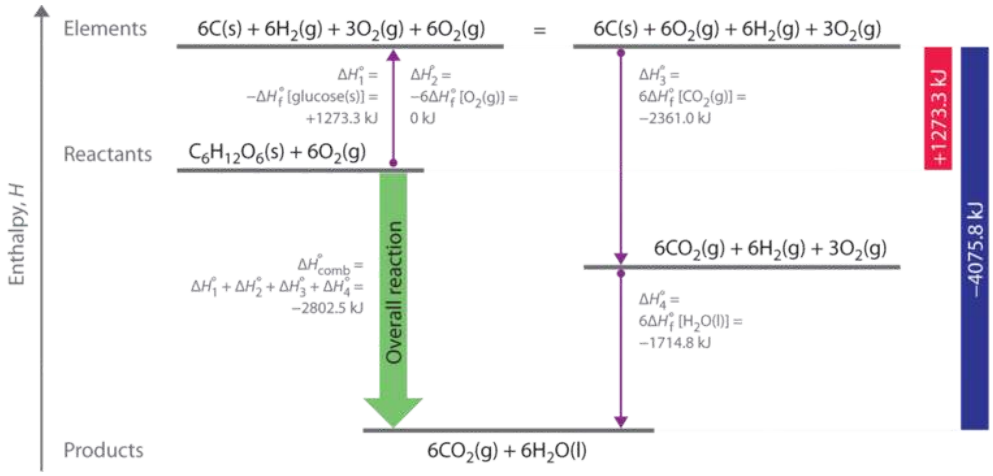


Figure **7.9.1**: A Thermochemical Cycle for the Combustion of Glucose. Two hypothetical pathways are shown from the reactants to the products. The green arrow labeled ΔH^o_{comb} indicates the combustion reaction. Alternatively, we could first convert the reactants to the elements via the reverse of the equations that define their standard enthalpies of formation (the upward arrow, labeled ΔH^o_1 and ΔH^o_2). Then we could convert the elements to the products via the equations used to define their standard enthalpies of formation (the downward arrows, labeled ΔH^o_3 and ΔH^o_4). Because enthalpy is a state function, ΔH^o_{comb} is equal to the sum of the enthalpy changes $\Delta H^o_1 + \Delta H^o_2 + \Delta H^o_3 + \Delta H^o_4$.

The reactions that convert the elements to final products (downward purple arrows in Figure **7.9.2**) are identical to those used to define the ΔH^o_f values of the products. Consequently, the enthalpy changes (from Table T1) are

$$\Delta H^o_3 = \Delta H^o_f\,[CO_2\,(g)] = 6\ \cancel{mol\ CO_2}\left(\frac{393.5\ kJ}{1\ \cancel{mol\ CO_2}}\right) = -2361.0\ kJ$$
$$\Delta H^o_4 = 6\Delta H^o_f\,[H_2O\,(l)] = 6\ \cancel{mol\ H_2O}\left(\frac{-285.8\ kJ}{1\ \cancel{mol\ H_2O}}\right) = -1714.8\ kJ \tag{7.9.11}$$

The overall enthalpy change for the conversion of the elements to products (6 mol of carbon dioxide and 6 mol of liquid water) is therefore −4075.8 kJ. Because enthalpy is a state function, the difference in enthalpy between an initial state and a final state can be computed using *any* pathway that connects the two. Thus the enthalpy change for the combustion of glucose to carbon dioxide and water is the sum of the enthalpy changes for the conversion of glucose and oxygen to the elements (+1273.3 kJ) and for the conversion of the elements to carbon dioxide and water (−4075.8 kJ):

$$\Delta H^o_{comb} = +1273.3\ kJ + (-4075.8\ kJ) = -2802.5\ kJ \tag{7.9.12}$$

This is the same result we obtained using the "products minus reactants" rule (Equation 7.9.5) and ΔH^o_f values. The two results must be the same because Equation 7.9.12 is just a more compact way of describing the thermochemical cycle shown in Figure **7.9.1**.

✔ EXAMPLE 7.9.2: HEAT OF COMBUSTION

Long-chain fatty acids such as palmitic acid ($CH_3(CH_2)_{14}CO_2H$) are one of the two major sources of energy in our diet (ΔH^o_f =−891.5 kJ/mol). Use the data in Table T1 to calculate ΔH^o_{comb} for the combustion of palmitic acid. Based on the energy released in combustion *per gram*, which is the better fuel — glucose or palmitic acid?

Given: compound and ΔH^o_f values

Asked for: ΔH^o_{comb} per mole and per gram

Strategy:

A. After writing the balanced chemical equation for the reaction, use Equation 7.9.5 and the values from Table T1 to calculate ΔH^o_{comb} the energy released by the combustion of 1 mol of palmitic acid.

B. Divide this value by the molar mass of palmitic acid to find the energy released from the combustion of 1 g of palmitic acid. Compare this value with the value calculated in Equation 7.9.8 for the combustion of glucose to determine which is the better fuel.

Solution:

A To determine the energy released by the combustion of palmitic acid, we need to calculate its ΔH^o_f. As always, the first requirement is a balanced chemical equation:

$$C_{16}H_{32}O_{2(s)} + 23O_{2(g)} \rightarrow 16CO_{2(g)} + 16H_2O_{(l)}$$

Using Equation 7.9.5 ("products minus reactants") with ΔH^{o}_{f} values from Table T1 (and omitting the physical states of the reactants and products to save space) gives

$$\begin{aligned}\Delta H^{o}_{comb} &= \sum m\Delta H^{o}_{f}\,(products) - \sum n\Delta H^{o}_{f}\,(reactants)\\ &= [16\,(-393.5\ kJ/mol\ CO_2) + 16\,(-285.8\ kJ/mol\ H_2O\,)]\\ &\quad - [-891.5\ kJ/mol\ C_{16}H_{32}O_2 + 23\,(0\ kJ/mol\ O_2\,)]\\ &= -9977.3\ kJ/mol\end{aligned}$$

This is the energy released by the combustion of 1 mol of palmitic acid.

B The energy released by the combustion of 1 g of palmitic acid is

$$\Delta H^{o}_{comb}\ per\ gram = \left(\frac{9977.3\ kJ}{\cancel{1\ mol}}\right)\left(\frac{\cancel{1\ mol}}{256.42\ g}\right) = -38.910\ kJ/g$$

As calculated in Equation 7.9.8, \(ΔH^o_f\) of glucose is −2802.5 kJ/mol. The energy released by the combustion of 1 g of glucose is therefore

$$\Delta H^{o}_{comb}\ per\ gram = \left(\frac{-2802.5\ kJ}{\cancel{1\ mol}}\right)\left(\frac{\cancel{1\ mol}}{180.16\ g}\right) = -15.556\ kJ/g$$

The combustion of fats such as palmitic acid releases more than twice as much energy per gram as the combustion of sugars such as glucose. This is one reason many people try to minimize the fat content in their diets to lose weight.

? EXERCISE 7.9.2: WATER–GAS SHIFT REACTION

Use Table T1 to calculate ΔH^{o}_{rxn} for the *water–gas shift reaction*, which is used industrially on an enormous scale to obtain H_2(g):

$$\mathrm{CO\ (g) + H_2O\ (g) \longrightarrow CO_2\,(g) + H_2\ (g)}$$

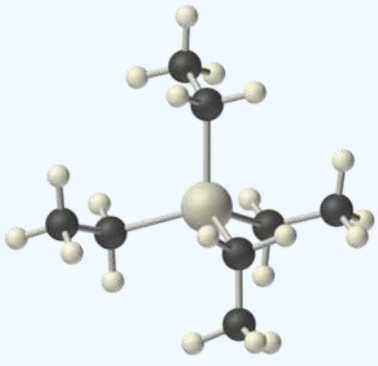
Answer

−41.2 kJ/mol

We can also measure the enthalpy change for another reaction, such as a combustion reaction, and then use it to calculate a compound's ΔH^{o}_{f} which we cannot obtain otherwise. This procedure is illustrated in Example 7.9.3.

✓ EXAMPLE 7.9.3: TETRAETHYLLEAD

Beginning in 1923, tetraethyllead [$(C_2H_5)_4Pb$] was used as an antiknock additive in gasoline in the United States. Its use was completely phased out in 1986 because of the health risks associated with chronic lead exposure. Tetraethyllead is a highly poisonous, colorless liquid that burns in air to give an orange flame with a green halo. The combustion products are CO_2(g), H_2O(l), and red PbO(s). What is the standard enthalpy of formation of tetraethyllead, given that ΔH^{o}_{f} is −19.29 kJ/g for the combustion of tetraethyllead and ΔH^{o}_{f} of red PbO(s) is −219.0 kJ/mol?



Tetraethyllead

Given: reactant, products, and ΔH^{o}_{comb} values

Asked for: ΔH^{o}_{f} of the reactants

Strategy:

A. Write the balanced chemical equation for the combustion of tetraethyl lead. Then insert the appropriate quantities into Equation 7.9.5 to get the equation for ΔH^{o}_{f} of tetraethyl lead.

B. Convert ΔH^{o}_{comb} per gram given in the problem to ΔH^{o}_{comb} per mole by multiplying ΔH^{o}_{comb} per gram by the molar mass of tetraethyllead.

C. Use Table T1 to obtain values of ΔH^{o}_{f} for the other reactants and products. Insert these values into the equation for ΔH^{o}_{f} of tetraethyl lead and solve the equation.

Solution:

A The balanced chemical equation for the combustion reaction is as follows:

$$2\,(C_2H_5)_4Pb\,(l) + 27\,O_2\,(g) \longrightarrow 2\,PbO\,(s) + 16\,CO_2\,(g) + 20\,H_2O\,(l)$$

Using Equation 7.9.5 gives

$$\Delta H^{o}_{comb} = \left[2\Delta H^{o}_{f}\,(PbO) + 16\Delta H^{o}_{f}\,(CO_2) + 20\Delta H^{o}_{f}\,(H_2O)\right] - \left[2\Delta H^{o}_{f}\,((C_2H_5)_4\,Pb) + 27\Delta H^{o}_{f}\,(O_2)\right]$$

Solving for $\Delta H^{o}_{f}[(C_2H_5)_4Pb]$ gives

$$\Delta H^{o}_{f}\,((C_2H_5)_4\,Pb) = \Delta H^{o}_{f}\,(PbO) + 8\Delta H^{o}_{f}\,(CO_2) + 10\Delta H^{o}_{f}\,(H_2O) - \frac{27}{2}\Delta H^{o}_{f}\,(O_2) - \frac{\Delta H^{o}_{comb}}{2}$$

The values of all terms other than $\Delta H^{o}_{f}[(C_2H_5)_4Pb]$ are given in Table T1.

B The magnitude of ΔH^{o}_{comb} is given in the problem in kilojoules per *gram* of tetraethyl lead. We must therefore multiply this value by the molar mass of tetraethyl lead (323.44 g/mol) to get ΔH^{o}_{comb} for 1 mol of tetraethyl lead:

$$\Delta H^{o}_{comb} = \left(\frac{-19.29\ kJ}{\cancel{g}}\right)\left(\frac{323.44\ \cancel{g}}{mol}\right) = -6329\ kJ/mol$$

Because the balanced chemical equation contains 2 mol of tetraethyllead, ΔH^{o}_{rxn} is

$$\Delta H^{o}_{rxn} = 2\ \cancel{mol\ (C_2H5)_4\,Pb}\left(\frac{-6329\ kJ}{1\ \cancel{mol\ (C_2H5)_4\,Pb}}\right) = -12,480\ kJ$$

C Inserting the appropriate values into the equation for $\Delta H^{o}_{f}[(C_2H_5)_4Pb]$ gives

$$\begin{aligned}\Delta H^{o}_{f}[(C_2H_4)_4Pb] &= [1\ mol\ PbO\ \times 219.0\ kJ/mol] + [8\ mol\ CO_2 \times (-393.5\ kJ/mol)] \\ &\quad + [10\ mol\ H_2O \times (-285.8\ kJ/mol)] \\ &\quad + [-27/2\ mol\ O_2) \times 0\ kJ/mol\ O_2]\,[12,480.2\ kJ/mol\ \ (C_2H_5)_4\,Pb] \\ &= -219.0\ kJ - 3148\ kJ - 2858kJ - 0kJ + 6240\ kJ = 15kJ/mol\end{aligned}$$

? EXERCISE 7.9.3

Ammonium sulfate, $(NH_4)_2SO_4$, is used as a fire retardant and wood preservative; it is prepared industrially by the highly exothermic reaction of gaseous ammonia with sulfuric acid:

$$2\,NH_3\,(g) + H_2SO_4\,(aq) \rightarrow (NH_4)_2SO_4\,(s)$$

The value of ΔH^{o}_{rxn} is -179.4 kJ/mole H_2SO_4. Use the data in Table T1 to calculate the standard enthalpy of formation of ammonium sulfate (in kilojoules per mole).

Answer

−1181 kJ/mol



Calculating DH° using DHf°: https://youtu.be/Y3aJJno9W2c

7.9.3 SUMMARY

- The standard state for measuring and reporting enthalpies of formation or reaction is 25 ^{o}C and 1 atm.
- The elemental form of each atom is that with the lowest enthalpy in the standard state.
- The standard state heat of formation for the elemental form of each atom is zero.

The **enthalpy of formation** (ΔH_f) is the enthalpy change that accompanies the formation of a compound from its elements. **Standard enthalpies of formation** (ΔH_f^o) are determined under **standard conditions**: a pressure of 1 atm for gases and a concentration of 1 M for species in solution, with all pure substances present in their **standard states** (their most stable forms at 1 atm pressure and the temperature of the measurement). The standard heat of formation of any element in its most stable form is defined to be zero. The **standard enthalpy of reaction** (ΔH_{rxn}^o) can be calculated from the sum of the **standard enthalpies of formation** of the products (each multiplied by its stoichiometric coefficient) minus the sum of the standard enthalpies of formation of the reactants (each multiplied by its stoichiometric coefficient)—the "products minus reactants" rule. The **enthalpy of solution** (ΔH_{soln}) is the heat released or absorbed when a specified amount of a solute dissolves in a certain quantity of solvent at constant pressure.

7.9.4 CONTRIBUTORS AND ATTRIBUTIONS

- Modified by Joshua Halpern (Howard University)

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7.E: FUNDAMENTALS OF THERMOCHEMISTRY (EXERCISES)

These are homework exercises to accompany the Textmap created for "Principles of Modern Chemistry" by Oxtoby et al. Complementary General Chemistry question banks can be found for other Textmaps and can be accessed here.

7.E.1 Q1A

A sample of $\mathbf{O_2}$ gas is under an external pressure of 17 atm and contained in a cylinder with a volume of 50 L. The gas is cooled and the resulting volume is 25 L. Calculate the amount of work done **on** the $\mathbf{O_2}$ gas.

7.E.2 Q1B

A system containing oxygen gas is heated at a constant pressure of 40.0 atm so that its volume increases 177 L to 458 L. Express the amount of work that the system did in kilo-joules.

7.E.3 Q2

The gas mixture inside one of the cylinders of an airplane expands against a constant external pressure of 5.00 atm because of the growing altitude, from an initial volume of 500 mL (at the end of the compression stroke) to the final volume of 1200 mL. Calculate the work done on the gas mixture during this process and express it in Joules.

7.E.4 Q3

The following events are based on a true story. A butcher for the local Chinese restaurant needs to defrost a large chunk of beef, which weights $\mathbf{50\ lb}$ and is currently at $\mathbf{0°C}$. He wants to accomplish this by is going out onto the street and repeatedly drop it onto the ground. Suppose the potential energy of the meat completely transforms into heat each time it hits the ground, and that energy can be calculated from

$$V = mg\Delta h$$

where m is mass of the object, g is the acceleration of gravity, and Δh is change in height. If the man is $\mathbf{5\ ft}$ tall and he wants to get the meat to room temperature ($\mathbf{25°C}$), how many times does he have to drop the piece of meat? Assume the environment has no effect on the meat, and that it does not lose any heat. (Specific Heat of the Meat: $\mathbf{0.25}\frac{\mathbf{J}}{\mathbf{g\,°C}}$).

7.E.5 Q4

Suppose you have a ball ($C_p = 0.85\frac{J}{g°C}$) at 25°C, what will its final temperature be if the amount of work equal to dropping it down from a height of 86.6m is done to it ? ($g = 9.81\frac{m}{s^2}$)

7.E.6 Q7A

The rule of Dulong and Petit shows that the molar heat capacities of most metallic elements group around a certain value “X” $\frac{J}{K\ mol}$ at 25°C. By first calculating and showing the molar heat capacities of metals rhenium, silver, lead, tungsten, copper, molybdenum and hafnium (given that the respective specific heat capacities of these metals are $0.14\frac{J}{K\ g}$, $0.23\frac{J}{K\ g}$, $0.13\frac{J}{K\ g}$, $0.13\frac{J}{K\ g}$, $0.39\frac{J}{K\ g}$, $0.25\frac{J}{K\ g}$ and $0.14\frac{J}{K\ g}$), find the value of “X”. (hint: take the average value of the calculated molar heat capacities and round off value to nearest whole number).

7.E.7 Q7B

The specific heat capacities of metals aluminum, bismuth, copper, lead, and silver at 25°C are 0.900, 0.123, 0.386, 0.128, and $0.233\frac{J}{g\ K}$. Calculate the molar heat capacities of these metals. According to the rule of Dulong and Petit, the molar heat capacities of metallic elements, like these, are approximately $25\frac{J}{K\ mol}$.

7.E.8 Q9

An undisclosed volume of water is tightly sealed in a microwave-safe container at room temperature before it is placed in an ice bath where it is cooled by a student.

a. During the cooling process within the ice bath, state whether (ΔU), Q, and W of the system are negative, zero, or positive. Explain your reasoning.

b. After being cooled, the student decides that the water seems too cold so it is placed in the microwave where the container of water is heated back to room temperature. What are the new signs of (ΔU), Q, and W during the heating process? Explain your reasoning.

c. Now determine the signs of ($\Delta U_1 + \Delta U_2$), ($Q_1 + Q_2$) , and ($W_1 + W_2$), where possible, assuming that the cooling process was step 1 and the heating process was step 2.

7.E.9 Q11A

Your lab partner slipped a sample of unknown hot metal that is 40.0g, which is initially at 130.0°C into a 100.0 g water that is initially at 50.0°C. A temperature probe indicates that equilibrium is reached at 60.15°C. Using the specific heat capacity of water $4.18\frac{J}{K}$, calculate the specific heat capacity of the unknown metal.

7.E.10 Q11B

Let's say you 34.5 grams of some hot metal that is initially at 75°C and you put that metal into 64.0 grams of water that is initially at 25°C. If the the two objects reach thermal equilibrium at 39°C, what is the specific heat capacity of the metal when the specific heat capacity of water is $4.18\frac{J}{K\ g}$.

7.E.11 Q12

A 10.00 g sample of Aluminum at 60.0 °C and a 30.0 g sample of copper at a temperature of -20.0 °C were thrown simultaneously into a 50.0 g of water at a temperature of 25.0 °C. What will be the final temperature of the system consisting of the two metal samples and the water? Assuming that this system is completely isolated from the surroundings. Use the information below for your calculations.

- $c_{s(\mathrm{Al})} = 0.900 J/(K \cdot g)$
- $c_{s(\mathrm{Cu})} = 0.385 J/(K \cdot g)$
- $c_{s(\mathrm{H_2O})} = 4.184 J/(K \cdot g)$

7.E.12 Q15A

Calculated the heat required to melt 3.00 g of ice and the heat required to change the temperature of water from 0°C to 100°C. What is the proportionality of the heat necessary to melt ice compared to the heat required to change the temperature of water from 0°C to 100°C? Use values from Table S2 and assume ΔH_f =334 J g^{-1} for calculations? Why is the heat positive instead of negative?

7.E.13 Q15B

An observation in the 18th century stated that the heat that raised a certain mass of water from its freezing point to boiling point is equal to four-thirds of the heat required to melt the same mass of ice. Using the theory behind the observation, estimate the heat required to melt 10 g of ice, know that the heat capacity of water is 4.18 J/ºC.

7.E.14 Q17

For his birthday, his John's parents have given him a compressible oven filled with 0.250 mol argon. If he sets this compressible oven at 1.00 atm and 273 K and let it contract from a constant external pressure of 0.100 atm until the gas pressure reaches 10.00 atm and the temperature reaches 400 K, what is the work done on the gas, the internal energy change, and the heat absorbed by the gas?

7.E.15 Q19

Take 4 moles of ideal, monatomic gas going through expansion processes. The gas was initially put at a pressure of 5.00 atm and a temperature of 30°C. The gas first goes through isothermal expansion until the volume doubled. An isochoric process follows as the pressure is halved. $C_v = \frac{3}{2}R$

a. Build ΔU, W, and Q table for each process.

b. Find the final temperature.

7.E.16 Q20

An apparatus is set up such that an ideal gas is released into vacuum by opening a stopcock, hence allowing it to freely expand (i.e., no external force is applied). Calculate ΔU of the system, and prove that the free expansion process is adiabatic i.e no heat transfer.

7.E.17 Q21

A 150 L vessel contains 8.00 moles of neon at 270 K is compressed adiabatically, so that there is no gain nor loss of any heat, and irreversibly until the final temperature is 470 K. Calculate the change in internal energy, the heat added to the gas, and the work done on the gas.

7.E.18 Q22

A gas expands at constant external pressure of 3.00 atm until its volume has increased by 9.00 to 15.00 L. During this process, it absorbs 800J of heat from the surroundings.

a. Calculate the energy change of the gas, ΔU
b. Calculate the work, w, done on the gas in an irreversible adiabatic (q = 0) process connecting the same initial and final state.

7.E.19 Q23

Using the theorem of equipartition of energy, calculate the specific heat capacity at constant pressure C_p at 25ºC and 1 atm for O_2 and CO. Compare the calculated values to the experimental data ($O_2 = 29.36, CO = 29.1$) and thus calculate the percent of the experimental value that results from vibrational motions. Answer: The percent of C_p due to vibrational motions is 0.897% for O_2 and 0.141% for CO.

7.E.20 Q23B

Using the classical equipartition theorem, calculate the value of C_p at 298 K and 1 atm for $HF(g)$ and $F_2(g)$, assuming that their pressure is constant. Then compare your calculation with the experiment values of $29.13 \frac{J}{K\ mol}$ and $31.30 \frac{J}{K\ mol}$ respectively. What is the per cent of the measured value that arises from vibrational motions?

7.E.21 Q25

a. Calculate the change of enthalpy when a 69-grams sample of zinc is heated from 753 K to 927 K at a constant pressure of 1 atm.
b. Calculate the change of enthalpy when 3 moles of butane are heated from 204 K to 258 K at a constant pressure of 1 atm.

7.E.22 Q31

What is the change in enthalpy when 8.19 grams of ethane (C_2H_6) vaporizes, assuming a normal boiling point and $\Delta H_{vap} = 14.72 \frac{kJ}{mol}$.

7.E.23 Q33

The heat capacity C_p of ice is $38 \frac{J}{K\ mol}$ and C_p of water is $75 \frac{J}{K\ mol}$. A 24.0 g ice cube at -15 ºC is placed into 120 g of water at room temperature (25ºC). What is the temperature of the water when it reaches equilibrium?

7.E.24 Q35

Determine the change in enthalpy (ΔH) for the following chemical reaction

$$4\,NH_{3(g)} + 5\,O_{2(g)} \longrightarrow 4\,NO_{(g)} + 6\,H_2O_{(g)}$$

given that:

$$O_{2(g)} + N_{2(g)} \longrightarrow 2\,NO_{(g)}\ \Delta H = +180.5 \frac{kJ}{mol}$$

$$2\,H_2O_{(g)} \longrightarrow 2\,H_{2\,(g)} + O_{2\,(g)}\ \Delta H = +483.64 \frac{kJ}{mol}$$

$$3\,H_{2(g)} + N_{2(g)} \longrightarrow 2\,NH_{3(g)}\ \Delta H = -92.22 \frac{kJ}{mol}.$$

7.E.25 Q37

ΔH of $C_6H_6(g)$ from $C_6H_6(l)$ to its gaseous form is +33.9 kJ/mol. Which of these two substances absorbs off more heat when 10 lbs of the substance is burned? Which of these two substances require less energy when condensed to solid form?

7.E.26 Q39

Calculate the enthalpy change under standard conditions for the reaction:

$$C_3H_6O\,(l) + 4\,O_2\,(g) \longrightarrow 3\,CO_2\,(g) + 3\,H_2O\,(l)$$

given information below:

- $\Delta H°_{f,\ O_2(g)}$: 0 kJ/mol
- $\Delta H°_{f,\ CO_2\,(g)}$: -393.5 kJ/mol
- $\Delta H°_{f,\ H_2O(l)}$: -285.83 kJ/mol
- $\Delta H°_{f,\ C_3H_6O(l)}$: -248 kJ/mol

7.E.27 Q47

A 10 gram sample of pure hydrogen is burned completely with excess oxygen to generate liquid water in a constant volume calorimeter at 25 °C. The amount of heat evolved is 1,420 kJ.

a. Write and balance the chemical equation for the combustion reaction.
b. Calculate the standard change in internal energy for the combustion of 1.00 mole hydrogen to liquid water.
c. Calculate the standard enthalpy change per mole of hydrogen for the same reaction as in part (a).
d. Calculate the standard enthalpy of formation per mole of hydrogen, using data for the standard enthalpies of formation of liquid water (Table T1).

A consequence of the constant-volume condition is that the heat released corresponds to q_v and thus to the internal energy change ΔU_{sys} rather than to ΔH_{sys} under constant pressure conditions.

$$\Delta U_{sys} = q_v$$

This comes from the definition of enthalpy

$$H_{sys} = U_{sys} + PV$$

and associated change

$$\Delta H_{sys} = \Delta U_{sys} + \Delta(PV)$$

or using the chain rule

$$\Delta H_{sys} = \Delta U_{sys} + \cancelto{0}{P\Delta V} + V\Delta P$$

which simplifies to

$$\Delta H_{sys} = \Delta U_{sys} + V\Delta P$$

If we assuming ideal gas law for the gases

$$PV = nRT$$

or

$$\Delta P = \frac{\Delta nRT}{V}$$

substituting this into the equation for enthalpy change gives the enthalpy change under *constant volume* conditions in terms of changing number of moles

$$\Delta H_{sys} = \Delta U_{sys} + \Delta n_g RT$$

or

$$\Delta H_{sys} = q_v + \Delta n_g RT$$

where Δn_g is the change in the number of moles of gases in the reaction.

7.E.28 Q49

Carbon dioxide (CO_2) is a common byproduct of the combustion of fossil fuels. Estimate the standard enthalpy of formation (ΔH_f) of carbon dioxide at 25°C, use Table T1.

7.E.29 Q51

Given the table of average bond enthalpies shown below, estimate the enthalpy change $\Delta H°$ for the following reaction:

$$2\,H_2\,(g) + O_2\,(g) \longrightarrow 2\,H_2O\,(l)$$

Bond	Bond Enthalpy (kJ/mol)
H–H	436
H–O	463
O=O	498

7.E.30 Q59

Two quantum states are separated by an energy of 0.6×10^{-21}J. Calculate the relative populations of the two quantum states at a temperature of 33°C.

7.E.31 Q63

By utilizing the Harmonic Oscillator Model, calculate the relative population of the first energy state and the ground state, both at $\mathbf{278.15\,K}$, for $\mathbf{H_2}$. The force constant for $\mathbf{H_2}$ is $\mathbf{510\frac{N}{m}}$

7.E.32 Q69

A container holds 2 L of gas under 5.00 atm and a ball floating in 10 L of NaOH. As the volume of the gas expands to 20 L, the ball is turned upside down. This turn is caused by the temperature increase of the NaOH after the gas expands. Assuming that no heat is lost, the density of NaOH is 2.13 g/cm^3 and the specific heat is 4.184 J/g K, calculate the increase in temperature of the NaOH.

7.E.33 Q69

Some gas in a piston expands against a constant pressure of 1.2 atm from a volume of 3 L to 18 L. The piston turns an egg beater submerged in 150 g of water. If the water was originally at 25°C, what is its temperature once the gas stops expanding? Assume that all of heat goes into the water and the specific heat capacity of water is 4.184 J K^{-1} g^{-1}.

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CHAPTER OVERVIEW

8: Principles of Thermodynamics (Entropy and Gibbs Energy)

The name "thermodynamics" is really a silly name. Think about it; the field deals primarily with the condition of equilibrium, that is, no change or a "static" situation. The actual field that describes non-equilibration properties is "kinetics" or "dynamics," hence the more apt term for this field is really "thermostatics." However, since we cannot change a name that has been in use for 150 years, we will stick with it and pretend otherwise.

8.1: The Nature of Spontaneous Processes
8.2: Entropy and Spontaneity - A Molecular Statistical Interpretation
8.3: Entropy and Heat - Experimental Basis of the Second Law of Thermodynamics
8.4: Entropy Changes and Spontaneity
8.5: Entropy Changes in Reversible Processes
8.6: Quantum States, Microstates, and Energy Spreading
8.7: The Third Law of Thermodynamics
8.8: Gibbs Energy
8.E: Principles of Thermodynamics (Exercises)

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8.1: The Nature of Spontaneous Processes

Learning Objectives

- Distinguish between spontaneous and nonspontaneous processes
- Describe the dispersal of matter and energy that accompanies certain spontaneous processes

In this section, consider the differences between two types of changes in a system: Those that occur spontaneously and those that occur only with the continuous input of energy. In doing so, we'll gain an understanding as to why some systems are naturally inclined to change in one direction under certain conditions. We'll also gain insight into how the spontaneity of a process affects the distribution of energy and matter within the system.

Spontaneous and Nonspontaneous Processes

Processes have a natural tendency to occur in one direction under a given set of conditions. Water will naturally flow downhill, but uphill flow requires outside intervention such as the use of a pump. A spontaneous process is one that occurs naturally under certain conditions. A nonspontaneous process, on the other hand, will not take place unless it is "driven" by the continual input of energy from an external source. A process that is spontaneous in one direction under a particular set of conditions is nonspontaneous in the reverse direction. At room temperature and typical atmospheric pressure, for example, ice will spontaneously melt, but water will not spontaneously freeze.

The spontaneity of a process is *not* correlated to the speed of the process. A spontaneous change may be so rapid that it is essentially instantaneous or so slow that it cannot be observed over any practical period of time. To illustrate this concept, consider the decay of radioactive isotopes, a topic more thoroughly treated in the chapter on nuclear chemistry. Radioactive decay is by definition a spontaneous process in which the nuclei of unstable isotopes emit radiation as they are converted to more stable nuclei. All the decay processes occur spontaneously, but the rates at which different isotopes decay vary widely. Technetium-99m is a popular radioisotope for medical imaging studies that undergoes relatively rapid decay and exhibits a half-life of about six hours. Uranium-238 is the most abundant isotope of uranium, and its decay occurs much more slowly, exhibiting a half-life of more than four billion years (Figure **8.1.1**).

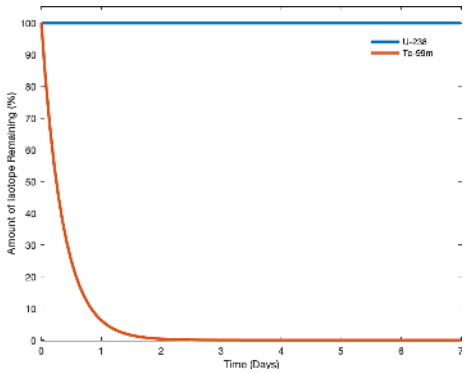


Figure **8.1.1**: Both U-238 and Tc-99m undergo spontaneous radioactive decay, but at drastically different rates. Over the course of one week, essentially all of a Tc-99m sample and none of a U-238 sample will have decayed. (CC by 4.0; Morgan Johnson via LibreTexts)

Two curves are shown to represent U-238 and Tc-99m respectively. The vertical axes represents the percentage of isotope remaining and the horizontal axes is the time that has elapsed in days.

As another example, consider the conversion of diamond into graphite (Figure **8.1.2**).

$$\mathrm{C(s,\,diamond)} \longrightarrow \mathrm{C(s,\,graphite)} \tag{8.1.1}$$

The phase diagram for carbon indicates that graphite is the stable form of this element under ambient atmospheric pressure, while diamond is the stable allotrope at very high pressures, such as those present during its geologic formation. Thermodynamic calculations of the sort described in the last section of this chapter indicate that the conversion of diamond to graphite at ambient pressure occurs spontaneously, yet diamonds are observed to exist, and persist, under these conditions. Though the process is spontaneous under typical ambient conditions, its rate is extremely slow, and so for all practical purposes diamonds are indeed "forever." Situations such as these emphasize the important distinction between the thermodynamic and the kinetic aspects of a process. In this particular case, diamonds are said to be *thermodynamically unstable* but *kinetically stable* under ambient conditions.

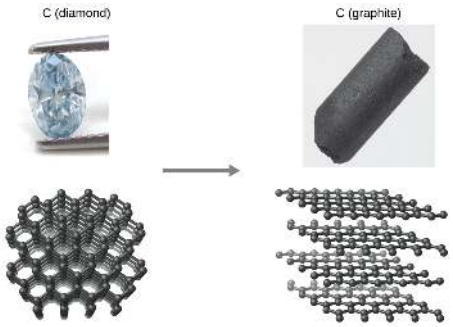


Figure **8.1.2**: The conversion of carbon from the diamond allotrope to the graphite allotrope is spontaneous at ambient pressure, but its rate is immeasurably slow at low to moderate temperatures. This process is known as graphitization, and its rate can be increased to easily measurable values at temperatures in the 1000–2000 K range. (credit "diamond" photo: modification of work by "Fancy Diamonds"/Flickr; credit "graphite" photo: modification of work by images-of-elements.com/carbon.php)

Comparison of diamond and graphite shown in its physical form as well as its molecular arrangement respectively.

Dispersal of Matter and Energy

As we extend our discussion of thermodynamic concepts toward the objective of predicting spontaneity, consider now an isolated system consisting of two flasks connected with a closed valve. Initially there is an ideal gas on the left and a vacuum on the right (Figure **8.1.3**). When the valve is opened, the gas spontaneously expands to fill both flasks. Recalling the definition of pressure-volume work from the chapter on thermochemistry, note that no work has been done because the pressure in a vacuum is zero.

$$w = -P\Delta V \tag{8.1.2}$$

$$= 0 \;\; (\mathrm{P} = 0 \,\mathrm{in\ a\ vaccum}) \tag{8.1.3}$$

Note as well that since the system is isolated, no heat has been exchanged with the surroundings (q = 0). The first law of thermodynamics confirms that there has been no change in the system's internal energy as a result of this process.

$$\Delta U = q + w \qquad \text{(First Law of Thermodynamics)}$$
$$= 0 + 0 = 0 \qquad (8.1.4)$$

The spontaneity of this process is therefore not a consequence of any change in energy that accompanies the process. Instead, the movement of the gas appears to be related to the greater, more *uniform dispersal of matter* that results when the gas is allowed to expand. Initially, the system was comprised of one flask containing matter and another flask containing nothing. After the spontaneous process took place, the matter was distributed both more widely (occupying twice its original volume) and more uniformly (present in equal amounts in each flask).

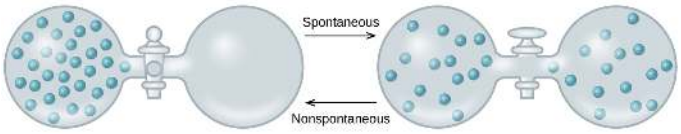


Figure **8.1.3**: An isolated system consists of an ideal gas in one flask that is connected by a closed valve to a second flask containing a vacuum. Once the valve is opened, the gas spontaneously becomes evenly distributed between the flasks.

When the valve is closed, all of the gas molecules 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 **8.1.4**). When these objects come into contact, heat spontaneously flows from the hotter object (X) to the colder one (Y). This corresponds to a loss of thermal energy by X and a gain of thermal energy by Y.

$$q_X < 0 \quad \text{and} \quad q_Y = -q_X > 0 \qquad (8.1.5)$$

From the perspective of this two-object system, there was no net gain or loss of thermal energy, rather the available thermal energy was redistributed among the two objects. This spontaneous process resulted in a *more uniform dispersal of energy*.



Figure **8.1.4**:When two objects at different temperatures come in contact, heat spontaneously flows from the hotter to the colder object.

Two separated blocks. One is labeled X and the other labeled Y. The diagram next to it shows the two blocks in contact with one another.

As illustrated by the two processes described, an important factor in determining the spontaneity of a process is the extent to which it changes the dispersal or distribution of matter and/or energy. In each case, a spontaneous process took place that resulted in a more uniform distribution of matter or energy.

✔ Example 8.1.1: Redistribution of Matter during a Spontaneous Process

Describe how matter and energy are redistributed when the following spontaneous processes take place:

a. A solid sublimes.
b. A gas condenses.
c. A drop of food coloring added to a glass of water forms a solution with uniform color.

Solution



Figure **8.1.5**:(credit a: modification of work by Jenny Downing; credit b: modification of work by "Fuzzy Gerdes"/Flickr; credit c: modification of work by Sahar Atwa)

This figure has three photos labeled, "a," "b," and "c." Photo a shows a glass with dry ice in water. There is a thick vapor coming from the top of the glass. Photo b shows water forming outside of a glass containing cold beverage. Photo c shows a sealed container that holds a red liquid.

a. *Sublimation* is the conversion of a solid (relatively high density) to a gas (much lesser density). This process yields a much greater dispersal of matter, since the molecules will occupy a much greater volume after the solid-to-gas transition. However, an input of energy from the surroundings ss required for the molecules to leave the solid phase and enter the gas phase.
b. *Condensation* is the conversion of a gas (relatively low density) to a liquid (much greater density). This process yields a much lesser dispersal of matter, since the molecules will occupy a much lesser volume after the gas-to-liquid transition. As the gas molecules move together to form the droplets of liquid, they form intermolecular forces and thus release energy to the surroundings.
c. The process in question is *dilution*. The food dye molecules initially occupy a much smaller volume (the drop of dye solution) than they occupy once the process is complete (in the full glass of water). The process therefore entails a greater dispersal of matter. The process may also yield a more uniform dispersal of matter, since the initial state of the system involves two regions of different dye concentrations (high in the drop, zero in the water), and the final state of the system contains a single dye concentration throughout. This process can occur with out a change in energy because the molecules have kinetic energy relative to the temperature of the water, and so will be constantly in motion.

? Exercise 8.1.1

Describe how matter and energy are redistributed when you empty a canister of compressed air into a room.

Answer

This process entails both a greater and more uniform dispersal of matter as the compressed air in the canister is permitted to expand into the lower-pressure air of the room. The process also requires an input of energy to disrupt the intermolecular forces between the closely-spaced gas molecules that are originally compressed into the container. If you were to touch the nozzle of the canister, you would notice that it is cold because the exiting molecules are taking energy away from their surroundings, and the canister is part of the surroundings.

Summary

Chemical and physical processes have a natural tendency to occur in one direction under certain conditions. A spontaneous process occurs without the need for a continual input of energy from some external source, while a nonspontaneous process requires such. Systems undergoing a spontaneous process may or may not experience a gain or loss of energy, but they will experience a change in the way matter and/or energy is distributed within the system. In this section we have only discussed nuclear decay, physical changes of pure substances, and macroscopic events such as water flowing downhill. In the following sections we will discuss mixtures and chemical reactions, situations in which the description of sponteneity becomes more challenging.

Glossary

nonspontaneous process
: process that requires continual input of energy from an external source

spontaneous change
: process that takes place without a continuous input of energy from an external source

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8.2: ENTROPY AND SPONTANEITY - A MOLECULAR STATISTICAL INTERPRETATION

LEARNING OBJECTIVES

- The Learning Objective of this Module is to understand the relationship between internal energy and entropy.

We know that the first law of thermodynamics governs changes in the state function we called internal energy (U) and that changes in the internal energy (ΔU) are closely related to changes in the enthalpy (ΔH), which is a measure of the heat flow between a system and its surroundings at constant pressure. You also learned previously that the enthalpy change for a chemical reaction can be calculated using tabulated values of enthalpies of formation. This information, however, does not tell us whether a particular process or reaction will occur spontaneously.

8.2.1 SPONTANEOUS REACTIONS

Let's consider a familiar example of spontaneous change. If a hot frying pan that has just been removed from the stove is allowed to come into contact with a cooler object, such as cold water in a sink, heat will flow from the hotter object to the cooler one, in this case usually releasing steam. Eventually both objects will reach the same temperature, at a value between the initial temperatures of the two objects. This transfer of heat from a hot object to a cooler one obeys the first law of thermodynamics: energy is conserved.

Now consider the same process in reverse. Suppose that a hot frying pan in a sink of cold water were to become hotter while the water became cooler. As long as the same amount of thermal energy was gained by the frying pan and lost by the water, the first law of thermodynamics would be satisfied. Yet we all know that such a process cannot occur: heat always flows from a hot object to a cold one, never in the reverse direction. That is, by itself the magnitude of the heat flow associated with a process does not predict whether the process will occur spontaneously.

For many years, chemists and physicists tried to identify a single measurable quantity that would enable them to predict whether a particular process or reaction would occur spontaneously. Initially, many of them focused on enthalpy changes and hypothesized that an exothermic process would always be spontaneous. But although it is true that many, if not most, spontaneous processes are exothermic, there are also many spontaneous processes that are not exothermic. For example, at a pressure of 1 atm, ice melts spontaneously at temperatures greater than 0°C, yet this is an endothermic process because heat is absorbed. Similarly, many salts (such as NH_4NO_3, NaCl, and KBr) dissolve spontaneously in water even though they absorb heat from the surroundings as they dissolve (i.e., $\Delta H_{soln} > 0$). Reactions can also be both spontaneous and highly endothermic, like the reaction of barium hydroxide with ammonium thiocyanate shown in Figure **8.2.1**.



Figure **8.2.1**: An Endothermic Reaction. The reaction of barium hydroxide with ammonium thiocyanate is spontaneous but highly endothermic, so water, one product of the reaction, quickly freezes into slush. When water is placed on a block of wood under the flask, the highly endothermic reaction that takes place in the flask freezes water that has been placed under the beaker, so the flask becomes frozen to the wood. For a full video: see www.youtube.com/watch?v=GQkJI-Nq3Os.

Thus enthalpy is not the only factor that determines whether a process is spontaneous. For example, after a cube of sugar has dissolved in a glass of water so that the sucrose molecules are uniformly dispersed in a dilute solution, they never spontaneously come back together in solution to form a sugar cube. Moreover, the molecules of a gas remain evenly distributed throughout the entire volume of a glass bulb and never spontaneously assemble in only one portion of the available volume. To help explain why these phenomena proceed spontaneously in

only one direction requires an additional state function called entropy (S), a thermodynamic property of all substances that is proportional to their degree of disorder.

> The direction of a spontaneous process is not governed by the internal energy change nor enthalpy change and thus the First Law of Thermodynamics cannot predict the direction of a natural process

8.2.2 PROBABILITIES AND MICROSTATES

Chemical and physical changes in a system may be accompanied by either an increase or a decrease in the disorder of the system, corresponding to an increase in entropy ($\Delta S > 0$) or a decrease in entropy ($\Delta S < 0$), respectively. As with any other state function, the change in entropy is defined as the difference between the entropies of the final and initial states:

$$\Delta S = S_f - S_i \tag{8.2.1}$$

When a gas expands into a vacuum, its entropy increases because the increased volume allows for greater atomic or molecular disorder. The greater the number of atoms or molecules in the gas, the greater the disorder. The magnitude of the entropy of a system depends on the number of microscopic states, or microstates, associated with it (in this case, the number of atoms or molecules); that is, the greater the number of microstates, the greater the entropy.

How can we express disorder quantitatively? From the example of coins, you can probably see that simple statistics plays a role: the probability of obtaining three heads and seven tails after tossing ten coins is just the ratio of the number of ways that ten different coins can be arranged in this way, to the number of all possible arrangements of ten coins.



Using the language of molecular statistics, we say that a collection of coins in which a given fraction of its members are heads-up constitutes a *macroscopic state* of the system. Since we do not care which coins are heads-up, there are clearly numerous configurations of the individual coins which can result in this "macrostate". Each of these configurations specifies a *microscopic state* of the system. The greater the number of microstates that correspond to a given macrostate (or configuration), the greater the probability of that macrostate. To see what this means, consider the possible outcomes of a toss of four coins (Table **8.2.1**):

Table **8.2.1**: Coin Toss Results

macrostate (Configuration)	ways	probability	microstates
0 heads	1	1/16	TTTT
1 head	4	4/16 = 1/4	HTTT THTT TTHT TTTH
2 heads	6	6/16 = 3/8	HHTT HTHT HTTH THHT TTHH THTH
3 heads	4	4/16 = 1/4	HHHT HTHH HHTH THHH
4 heads	1	1/16	HHHH

A toss of four coins will yield one of the five outcomes (macrostates) listed in the leftmost column of the table. The second column gives the number of "ways"— that is, the number of head/tail configurations of the set of coins (the number of microstates)— that can result in the macrostate. The probability of a toss resulting in a particular macrostate is proportional to the number of microstates corresponding to the macrostate, and is equal to this number, divided by the total number of possible microstates (in this example, 2^4 =16). An important assumption here is that all microstates are equally probable; that is, the toss is a "fair" one in which the many factors that determine the trajectory of each coin operate in an entirely random way.

> The greater the number of **microstates** that correspond to a given **macrostate**, the greater the probability of that **macrostate**.

8.2.3 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:

$$S = k \ln \Omega \tag{8.2.2}$$

Here k is the Boltzmann constant and has a value of 1.38×10^{-23} J/K.

As for other state functions, the change in entropy for a process is the difference between its final (S_f) and initial (S_i) values:

$$\Delta S = S_f - S_i \tag{8.2.3}$$

$$= k \ln \Omega_f - k \ln \Omega_i \tag{8.2.4}$$

$$= k \ln \frac{\Omega_f}{\Omega_i} \tag{8.2.5}$$

For processes involving an increase in the number of microstates, $\Omega_f > \Omega_i$, the entropy of the system increases, $\Delta S > 0$. Conversely, processes that reduce the number of microstates, $\Omega_f < \Omega_i$, yield a decrease in system entropy, $\Delta S < 0$. This molecular-scale interpretation of entropy provides a link to the probability that a process will occur as illustrated in the next paragraphs.

Consider the general case of a system comprised of N particles distributed among n boxes. The number of microstates possible for such a system is n^N. For example, distributing four particles among two boxes will result in $2^4 = 16$ different microstates as illustrated in Figure 8.2.2. Microstates with equivalent particle arrangements (not considering individual particle identities) are grouped together and are called *distributions*. The probability that a system will exist with its components in a given distribution is proportional to the number of microstates within the distribution. Since entropy increases logarithmically with the number of microstates (Equation 8.2.2), *the most probable distribution is therefore the one of greatest entropy*.

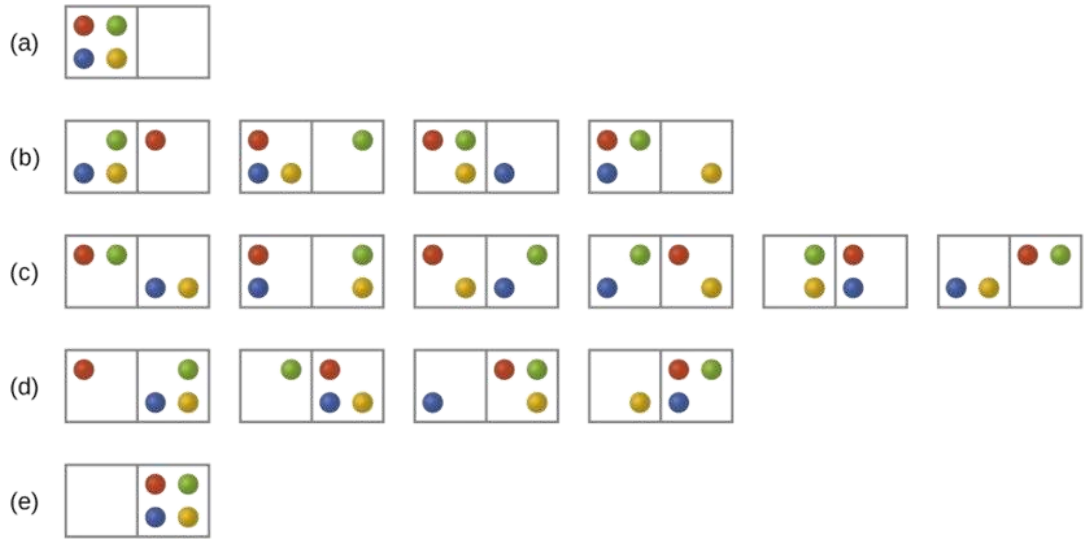


Figure 8.2.2: The sixteen microstates associated with placing four particles in two boxes are shown. The microstates are collected into five distributions—(a), (b), (c), (d), and (e)—based on the numbers of particles in each box.

For this system, the most probable configuration is one of the six microstates associated with distribution (c) where the particles are evenly distributed between the boxes, that is, a configuration of two particles in each box. The probability of finding the system in this configuration is

$$\frac{6}{16} = \frac{3}{8}$$

The least probable configuration of the system is one in which all four particles are in one box, corresponding to distributions (a) and (e), each with a probability of

$$\frac{1}{16}$$

The probability of finding all particles in only one box (either the left box or right box) is then

$$\left(\frac{1}{16}+\frac{1}{16}\right)=\frac{2}{16}=\frac{1}{8}$$

As you add more particles to the system, the number of possible microstates increases exponentially (2^N). A macroscopic (laboratory-sized) system would typically consist of moles of particles ($N \sim 10^{23}$), and the corresponding number of microstates would be staggeringly huge. Regardless of the number of particles in the system, however, the distributions in which roughly equal numbers of particles are found in each box are always the most probable configurations.

The previous description of an ideal gas expanding into a vacuum is a macroscopic example of this particle-in-a-box model. For this system, the most probable distribution is confirmed to be the one in which the matter is most uniformly dispersed or distributed between the two flasks. The spontaneous process whereby the gas contained initially in one flask expands to fill both flasks equally therefore yields an increase in entropy for the system.

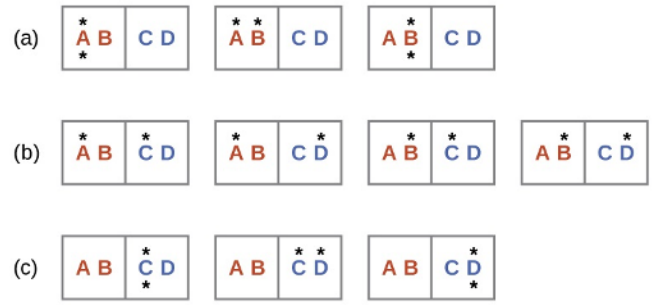
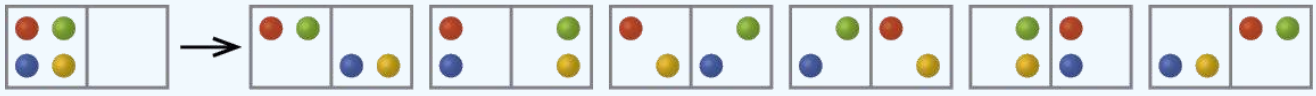


Figure **8.2.3**: This shows a microstate model describing the flow of heat from a hot object to a cold object. (a) Before the heat flow occurs, the object comprised of particles A and B contains both units of energy and as represented by a distribution of three microstates. (b) If the heat flow results in an even dispersal of energy (one energy unit transferred), a distribution of four microstates results. (c) If both energy units are transferred, the resulting distribution has three microstates.

A similar approach may be used to describe the spontaneous flow of heat. Consider a system consisting of two objects, each containing two particles, and two units of energy (represented as "*") in Figure **8.2.3**. The hot object is comprised of particles **A** and **B** and initially contains both energy units. The cold object is comprised of particles **C** and **D**, which initially has no energy units. Distribution (a) shows the three microstates possible for the initial state of the system, with both units of energy contained within the hot object. If one of the two energy units is transferred, the result is distribution (b) consisting of four microstates. If both energy units are transferred, the result is distribution (c) consisting of three microstates. And so, we may describe this system by a total of ten microstates. The probability that the heat does not flow when the two objects are brought into contact, that is, that the system remains in distribution (a), is $\frac{3}{10}$. More likely is the flow of heat to yield one of the other two distribution, the combined probability being $\frac{7}{10}$. The most likely result is the flow of heat to yield the uniform dispersal of energy represented by distribution (b), the probability of this configuration being $\frac{4}{10}$. As for the previous example of matter dispersal, extrapolating this treatment to macroscopic collections of particles dramatically increases the probability of the uniform distribution relative to the other distributions. This supports the common observation that placing hot and cold objects in contact results in spontaneous heat flow that ultimately equalizes the objects' temperatures. And, again, this spontaneous process is also characterized by an increase in system entropy.

✔ EXAMPLE 8.2.1: DETERMINATION OF ΔS

Consider the system shown here. What is the change in entropy for a process that converts the system from distribution (a) to (c)?



Solution

We are interested in the following change:

The initial number of microstates is one, the final six:

$$\begin{aligned}\Delta S &= k\ln\frac{\Omega_c}{\Omega_a}\\ &= 1.38\times10^{-23}\,J/K\times\ln\frac{6}{1}\\ &= 2.47\times10^{-23}\,J/K\end{aligned}$$

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 8.2.1

Consider the system shown in Figure **8.2.3**. What is the change in entropy for the process where *all* the energy is transferred from the hot object (**AB**) to the cold object (**CD**)?

Answer

0 J/K

A disordered system has a greater number of possible microstates than does an ordered system, so it has a higher entropy. This is most clearly seen in the entropy changes that accompany phase transitions, such as solid to liquid or liquid to gas. As you know, a crystalline solid is composed of an ordered array of molecules, ions, or atoms that occupy fixed positions in a lattice, whereas the molecules in a liquid are free to move and tumble within the volume of the liquid; molecules in a gas have even more freedom to move than those in a liquid. Each degree of motion increases the number of available microstates, resulting in a higher entropy. Thus the entropy of a system must increase during melting ($\Delta S_{fus} > 0$). Similarly, when a liquid is converted to a vapor, the greater freedom of motion of the molecules in the gas phase means that $\Delta S_{vap} > 0$. Conversely, the reverse processes (condensing a vapor to form a liquid or freezing a liquid to form a solid) must be accompanied by a decrease in the entropy of the system: $\Delta S < 0$.

DEFINITION: ENTROPY

Entropy (S) is a thermodynamic property of all substances that is proportional to their degree of disorder. The greater the number of possible microstates for a system, the greater the disorder and the higher the entropy.

Disorder is more probable than order because there are so many more ways of achieving it. Thus coins and cards tend to assume random configurations when tossed or shuffled, and socks and books tend to become more scattered about a teenager's room during the course of daily living. But there are some important differences between these large-scale mechanical, or macro systems, and the collections of sub-microscopic particles that constitute the stuff of chemistry, and which we will refer to here generically as **molecules**. Molecules, unlike macro objects, are capable of accepting, storing, and giving up energy in tiny amounts (quanta), and act as highly efficient carriers and spreaders of thermal energy as they move around. Thus, **in chemical systems**,

1. **We are dealing with huge numbers of particles**. This is important because statistical predictions are always more accurate for larger samples. Thus although for the four tosses there is a good chance (62%) that the H/T ratio will fall outside the range of 0.45 - 0.55, this probability becomes almost zero for 1000 tosses. To express this in a different way, the chances that 1000 gas molecules moving about randomly in a container would at any instant be distributed in a sufficiently non-uniform manner to produce a detectable pressure difference between the two halves of a container will be extremely small. If we increase the number of molecules to a chemically significant number (around 10^{20}, say), then the same probability becomes indistinguishable from zero.
2. **Once the change begins, it proceeds spontaneously.** That is, no external agent (a tosser, shuffler, or teenager) is needed to keep the process going. Gases will spontaneously expand if they are allowed to, and reactions, once started, will proceed toward equilibrium.
3. **Thermal energy is continually being exchanged between the particles of the system, and between the system and the surroundings.** Collisions between molecules result in exchanges of momentum (and thus of kinetic energy) amongst the particles of the system, and (through collisions with the walls of a container, for example) with the surroundings.
4. **Thermal energy spreads rapidly and randomly throughout the various energetically accessible microstates of the system.** The **direction** of spontaneous change is that which results in the maximum possible spreading and sharing of thermal energy.

The importance of these last two points is far greater than you might at first think, but to fully appreciate this, you must recall the various ways in which thermal energy is stored in molecules.

8.2.4 SIGN OF ENTROPY CHANGE

The relationships between entropy, microstates, and matter/energy dispersal described previously allow us to make generalizations regarding the relative entropies of substances and to predict the sign of entropy changes for chemical and physical processes. Consider the phase changes illustrated in Figure **8.2.4**. In the solid phase, the atoms or molecules are restricted to nearly fixed positions with respect to each other and are capable of only modest oscillations about these positions. With essentially fixed locations for the system's component particles, the number of microstates is relatively small. In the liquid phase, the atoms or molecules are free to move over and around each

other, though they remain in relatively close proximity to one another. This increased freedom of motion results in a greater variation in possible particle locations, so the number of microstates is correspondingly greater than for the solid. As a result, $S_{liquid} > S_{solid}$ and the process of converting a substance from solid to liquid (melting) is characterized by an increase in entropy, $\Delta S > 0$. By the same logic, the reciprocal process (freezing) exhibits a decrease in entropy, $\Delta S < 0$.

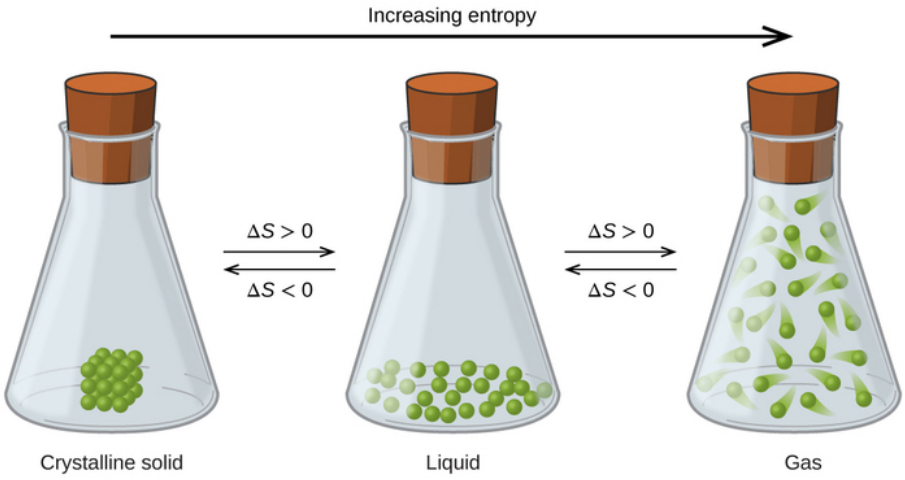


Figure 8.2.4: The entropy of a substance increases ($\Delta S > 0$) as it transforms from a relatively ordered solid, to a less-ordered liquid, and then to a still less-ordered gas. The entropy decreases ($\Delta S < 0$) as the substance transforms from a gas to a liquid and then to a solid.

Now consider the vapor or gas phase. The atoms or molecules occupy a *much* greater volume than in the liquid phase; therefore each atom or molecule can be found in many more locations than in the liquid (or solid) phase. Consequently, for any substance,

$$S_{gas} \gg S_{liquid} > S_{solid} \tag{8.2.6}$$

and the processes of vaporization and sublimation likewise involve increases in entropy, $\Delta S > 0$. Likewise, the reciprocal phase transitions, condensation and deposition, involve decreases in entropy, $\Delta S < 0$.

According to kinetic-molecular theory, the temperature of a substance is proportional to the average kinetic energy of its particles. Raising the temperature of a substance will result in more extensive vibrations of the particles in solids and more rapid translations of the particles in liquids and gases. At higher temperatures, the distribution of kinetic energies among the atoms or molecules of the substance is also broader (more dispersed) than at lower temperatures. Thus, the entropy for any substance increases with temperature (Figure 8.2.5).

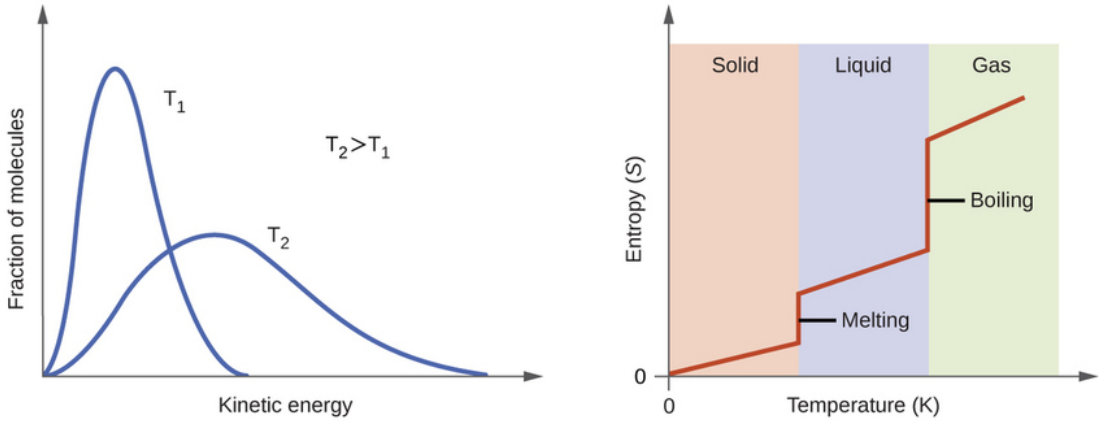


Figure 8.2.5: Entropy increases as the temperature of a substance is raised, which corresponds to the greater spread of kinetic energies. When a substance melts or vaporizes, it experiences a significant increase in entropy.

The entropy of a substance is influenced by structure of the particles (atoms or molecules) that comprise the substance. With regard to atomic substances, heavier atoms possess greater entropy at a given temperature than lighter atoms, which is a consequence of the relation between a particle's mass and the spacing of quantized translational energy levels (which is a topic beyond the scope of our treatment). For molecules, greater numbers of atoms (regardless of their masses) increase the ways in which the molecules can vibrate and thus the number of possible microstates and the system entropy.

Finally, variations in the types of particles affect the entropy of a system. Compared to a pure substance, in which all particles are identical, the entropy of a mixture of two or more different particle types is greater. This is because of the additional orientations and interactions that

are possible in a system comprised of nonidentical components. For example, when a solid dissolves in a liquid, the particles of the solid experience both a greater freedom of motion and additional interactions with the solvent particles. This corresponds to a more uniform dispersal of matter and energy and a greater number of microstates. The process of dissolution therefore involves an increase in entropy, $\Delta S > 0$.

Considering the various factors that affect entropy allows us to make informed predictions of the sign of ΔS for various chemical and physical processes as illustrated in Example **8.2.2**.

EXAMPLE 8.2.2: PREDICTING THE SIGN OF ΔS

Predict the sign of the entropy change for the following processes. Indicate the reason for each of your predictions.

a. One mole liquid water at room temperature $\longrightarrow$ one mole liquid water at 50 °C
b. $\mathrm{Ag^+}(aq) + \mathrm{Cl^-}(aq) \longrightarrow \mathrm{AgCl}(s)$
c. $\mathrm{C_6H_6\,(l)} + \frac{15}{2}\,\mathrm{O_2\,(g)} \longrightarrow 6\,\mathrm{CO_2\,(g)} + 3\,\mathrm{H_2O\,(l)}$
d. $\mathrm{NH_3}(s) \longrightarrow \mathrm{NH_3}(l)$

Solution

a. positive, temperature increases
b. negative, reduction in the number of ions (particles) in solution, decreased dispersal of matter
c. negative, net decrease in the amount of gaseous species
d. positive, phase transition from solid to liquid, net increase in dispersal of matter

EXERCISE 8.2.2

Predict the sign of the enthalpy change for the following processes. Give a reason for your prediction.

a. $\mathrm{NaNO_3}(s) \longrightarrow \mathrm{Na^+}(aq) + \mathrm{NO_3^-}(aq)$
b. the freezing of liquid water
c. $\mathrm{CO_2}(s) \longrightarrow \mathrm{CO_2}(g)$
d. $\mathrm{CaCO}(s) \longrightarrow \mathrm{CaO}(s) + \mathrm{CO_2}(g)$

Answer a

Positive; The solid dissolves to give an increase of mobile ions in solution.

Answer b

Negative; The liquid becomes a more ordered solid.

Answer c

Positive; The relatively ordered solid becomes a gas.

Answer d

Positive; There is a net production of one mole of gas.

8.2.5 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.

8.2.6 CONTRIBUTORS AND ATTRIBUTIONS

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8.3: Entropy and Heat - Experimental Basis of the Second Law of Thermodynamics

Learning Objectives

- The Learning Objective of this Module is to understand the relationship between internal energy and entropy.

Thermodynamic Definition of Entropy

Experiments show that the magnitude of ΔS_{vap} is 80–90 J/(mol•K) for a wide variety of liquids with different boiling points. However, liquids that have highly ordered structures due to hydrogen bonding or other intermolecular interactions tend to have significantly higher values of ΔS_{vap}. For instance, ΔS_{vap} for water is 102 J/(mol•K). Another process that is accompanied by entropy changes is the formation of a solution. As illustrated in Figure **8.3.1**, the formation of a liquid solution from a crystalline solid (the solute) and a liquid solvent is expected to result in an increase in the number of available microstates of the system and hence its entropy. Indeed, dissolving a substance such as NaCl in water disrupts both the ordered crystal lattice of **NaCl** and the ordered hydrogen-bonded structure of water, leading to an increase in the entropy of the system. At the same time, however, each dissolved $\mathbf{Na^+}$ ion becomes hydrated by an ordered arrangement of at least six water molecules, and the Cl^- ions also cause the water to adopt a particular local structure. Both of these effects increase the order of the system, leading to a decrease in entropy. The overall entropy change for the formation of a solution therefore depends on the relative magnitudes of these opposing factors. In the case of an **NaCl** solution, disruption of the crystalline **NaCl** structure and the hydrogen-bonded interactions in water is quantitatively more important, so $\Delta S_{soln} > 0$.

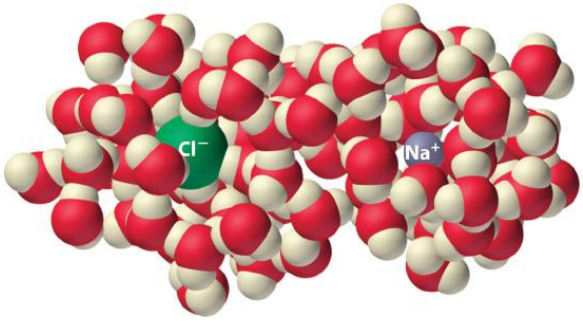


Figure **8.3.1**: The Effect of Solution Formation on Entropy

Dissolving **NaCl** in water results in an increase in the entropy of the system. Each hydrated ion, however, forms an ordered arrangement with water molecules, which decreases the entropy of the system. The magnitude of the increase is greater than the magnitude of the decrease, so the overall entropy change for the formation of an NaCl solution is positive.

Example 8.3.1

Predict which substance in each pair has the higher entropy and justify your answer.

a. 1 mol of $NH_3(g)$ or 1 mol of He(g), both at 25°C
b. 1 mol of Pb(s) at 25°C or 1 mol of Pb(l) at 800°C

Given: amounts of substances and temperature

Asked for: higher entropy

Strategy:

From the number of atoms present and the phase of each substance, predict which has the greater number of available microstates and hence the higher entropy.

Solution:

a. Both substances are gases at 25°C, but one consists of He atoms and the other consists of NH_3 molecules. With four atoms instead of one, the NH_3 molecules have more motions available, leading to a greater number of microstates. Hence we predict that the NH_3 sample will have the higher entropy.

b. The nature of the atomic species is the same in both cases, but the phase is different: one sample is a solid, and one is a liquid. Based on the greater freedom of motion available to atoms in a liquid, we predict that the liquid sample will have the higher entropy.

? Exercise 8.3.1

Predict which substance in each pair has the higher entropy and justify your answer.

a. 1 mol of He(g) at 10 K and 1 atm pressure or 1 mol of He(g) at 250°C and 0.2 atm
b. a mixture of 3 mol of $H_2(g)$ and 1 mol of $N_2(g)$ at 25°C and 1 atm or a sample of 2 mol of $NH_3(g)$ at 25°C and 1 atm

Answer a

1 mol of He(g) at 250°C and 0.2 atm (higher temperature and lower pressure indicate greater volume and more microstates)

Answer b

a mixture of 3 mol of $H_2(g)$ and 1 mol of $N_2(g)$ at 25°C and 1 atm (more molecules of gas are present)

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8.4: Entropy Changes and Spontaneity

Learning Objectives

- State and explain the second and third laws of thermodynamics
- Calculate entropy changes for phase transitions and chemical reactions under standard conditions

Connecting Entropy and Heat to Spontaneity

In the quest to identify a property that may reliably predict the spontaneity of a process, we have identified a very promising candidate: entropy. Processes that involve an increase in entropy *of the system* ($\Delta S_{sys} > 0$) are very often spontaneous; however, examples to the contrary are plentiful. By expanding consideration of entropy changes to include *the surroundings*, we may reach a significant conclusion regarding the relation between this property and spontaneity. In thermodynamic models, the system and surroundings comprise everything, that is, the universe, and so the following is true:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \tag{8.4.1}$$

To illustrate this relation, consider again the process of heat flow between two objects, one identified as the system and the other as the surroundings. There are three possibilities for such a process:

1. The objects are at different temperatures, and heat flows from the hotter to the cooler object. *This is always observed to occur spontaneously.* Designating the hotter object as the system and invoking the definition of entropy yields the following:

   $$\Delta S_{\text{sys}} = \frac{-q_{\text{rev}}}{T_{\text{sys}}} \tag{8.4.2}$$

   and

   $$\Delta S_{\text{surr}} = \frac{q_{\text{rev}}}{T_{\text{surr}}} \tag{8.4.3}$$

   The arithmetic signs of q_{rev} denote the loss of heat by the system and the gain of heat by the surroundings. Since $T_{\text{sys}} > T_{\text{surr}}$ in this scenario, the magnitude of the entropy change for the surroundings will be greater than that for the system, and so the sum of ΔS_{sys} and ΔS_{surr} will yield a positive value for ΔS_{univ}. *This process involves an increase in the entropy of the universe.*
2. The objects are at different temperatures, and heat flows from the cooler to the hotter object. *This is never observed to occur spontaneously.* Again designating the hotter object as the system and invoking the definition of entropy yields the following:

   $$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T_{\text{sys}}} \tag{8.4.4}$$

   and

   $$\Delta S_{\text{surr}} = \frac{-q_{\text{rev}}}{T_{\text{surr}}} \tag{8.4.5}$$

   The arithmetic signs of q_{rev} denote the gain of heat by the system and the loss of heat by the surroundings. The magnitude of the entropy change for the surroundings will again be greater than that for the system, but in this case, the signs of the heat changes will yield a negative value for ΔS_{univ}. *This process involves a decrease in the entropy of the universe.*
3. The temperature difference between the objects is infinitesimally small, $T_{sys} \approx T_{surr}$, and so the heat flow is thermodynamically *reversible*. See the previous section's discussion). In this case, the system and surroundings experience entropy changes that are equal in magnitude and therefore sum to yield a value of zero for ΔS_{univ}. *This process involves no change in the entropy of the universe.*

These results lead to a profound statement regarding the relation between entropy and spontaneity known as the second law of thermodynamics: *all spontaneous changes cause an increase in the entropy of the universe.* A summary of these three relations is provided in Table **8.4.1**.

Table **8.4.1**: The Second Law of Thermodynamics

$\Delta S_{univ} > 0$	spontaneous
$\Delta S_{univ} < 0$	nonspontaneous (spontaneous in opposite direction)
$\Delta S_{univ} = 0$	reversible (system is at equilibrium)

Definition: The Second Law of Thermodynamics

All spontaneous changes cause an increase in the entropy of the universe, i.e.,

$$\Delta S_{\text{univ}} > 0. \tag{8.4.6}$$

For many realistic applications, the surroundings are vast in comparison to the system. In such cases, the heat gained or lost by the surroundings as a result of some process represents a very small, nearly infinitesimal, fraction of its total thermal energy. For example, combustion of a fuel in air involves transfer of heat from a system (the fuel and oxygen molecules undergoing reaction) to surroundings that are infinitely more massive (the earth's atmosphere). As a result, q_{surr} is a good approximation of q_{rev}, and the second law may be stated as the following:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \tag{8.4.7}$$

$$= \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} \tag{8.4.8}$$

We may use this equation to predict the spontaneity of a process as illustrated in Example 8.4.1.

Example 8.4.1: Will Ice Spontaneously Melt?

The entropy change for the process

$$\mathrm{H_2O}(s) \longrightarrow \mathrm{H_2O}(l)$$

is 22.1 J/K and requires that the surroundings transfer 6.00 kJ of heat to the system. Is the process spontaneous at −10.00 °C? Is it spontaneous at +10.00 °C?

Solution

We can assess the spontaneity of the process by calculating the entropy change of the universe. If ΔS_{univ} is positive, then the process is spontaneous. At both temperatures, ΔS_{sys} = 22.1 J/K and q_{surr} = −6.00 kJ.

At −10.00 °C (263.15 K), the following is true:

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \\ &= \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} \\ &= 22.1\ \text{J/K} + \frac{-6.00 \times 10^3\ \text{J}}{263.15\ \text{K}} \\ &= -0.7\ J/K\end{aligned}$$

S_{univ} < 0, so melting is nonspontaneous (*not* spontaneous) at −10.0 °C.

At 10.00 °C (283.15 K), the following is true:

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} \\ &= 22.1\ J/K + \frac{-6.00 \times 10^3\ J}{283.15\ K} \\ &= +0.9\ J/K\end{aligned}$$

$\Delta S_{univ} > 0$, so melting *is* spontaneous at 10.00 °C.

? Exercise 8.4.1

Using this information, determine if liquid water will spontaneously freeze at the same temperatures. What can you say about the values of ΔS_{univ}?

Answer

Entropy is a state function, and freezing is the opposite of melting. At −10.00 °C spontaneous, +0.7 J/K; at +10.00 °C nonspontaneous, −0.9 J/K.

Summary

The second law of thermodynamics states that a *spontaneous* process increases the entropy of the universe, $S_{univ} > 0$. If $\Delta S_{univ} < 0$, the process is *nonspontaneous*, and if $\Delta S_{univ} = 0$, the system is at equilibrium.

Key Equations

- $\Delta S^\circ = \Delta S^\circ_{298} = \sum \nu S^\circ_{298}(\text{products}) - \sum \nu S^\circ_{298}(\text{reactants})$
- $\Delta S = \frac{q_{\text{rev}}}{T}$
- $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$
- $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T}$

Contributors and Attributions

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8.5: Entropy Changes in Reversible Processes

Learning Objectives

You are expected to be able to define and explain the significance of terms identified in ***bold***.

- A ***reversible*** *process* is one carried out in infinitesimal steps after which, when undone, both the system and surroundings (that is, the world) remain unchanged (see the example of gas expansion-compression below). Although true reversible change cannot be realized in practice, it can always be approximated.
- As a process is carried out in a more reversible manner, the value of *w* approaches its maximum possible value, and *q* approaches its minimum possible value.
- Although *q* is not a state function, the quotient q_{rev}/T is, and is known as the *entropy*.

A change is said to occur reversibly when it can be carried out in a series of infinitesimal steps, each one of which can be undone by making a similarly minute change to the conditions that bring the change about. For example, the reversible expansion of a gas can be achieved by reducing the external pressure in a series of infinitesimal steps; reversing any step will restore the system and the surroundings to their previous state. Similarly, heat can be transferred reversibly between two bodies by changing the temperature difference between them in infinitesimal steps each of which can be undone by reversing the temperature difference.

The most widely cited example of an **irreversible** change is the free expansion of a gas into a vacuum. Although the system can always be restored to its original state by recompressing the gas, this would require that the surroundings perform work on the gas. Since the gas does no work on the surrounding in a free expansion (the external pressure is zero, so $P\Delta V = 0$,) there will be a permanent change in the surroundings. Another example of irreversible change is the conversion of mechanical work into frictional heat; there is no way, by reversing the motion of a weight along a surface, that the heat released due to friction can be restored to the system.

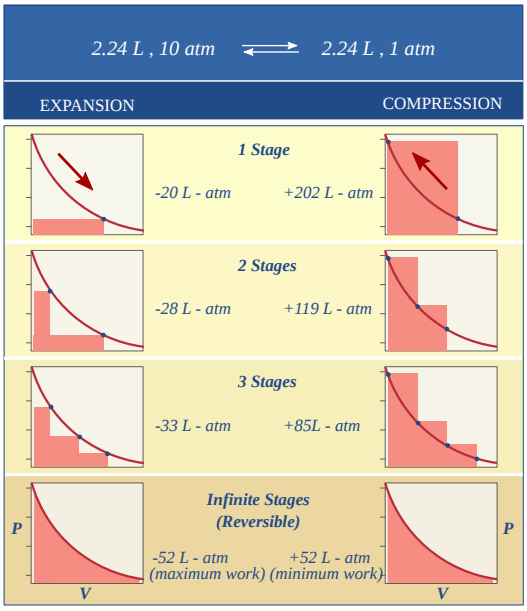


Figure 8.5.1: Reversible vs. Irreversible Expansions and Compressions. (CC BY-NC; Ümit Kaya)

These diagrams show the same expansion and compression ±ΔV carried out in different numbers of steps ranging from a single step at the top to an "infinite" number of steps at the bottom. As the number of steps increases, the processes become less irreversible; that is, the difference between the work done in expansion and that required to re-compress the gas diminishes. In the limit of an ”infinite” number of steps (bottom), these work terms are identical, and both the system and surroundings (the “world”) are unchanged by the expansion-compression cycle. In all other cases the system (the gas) is restored to its initial state, **but the *surroundings* are forever changed.**

Definition: Reversible Changes

A reversible change is one carried out in such as way that, when undone, both the system and surroundings (that is, the world) remain unchanged.

It should go without saying, of course, that any process that proceeds in infinitesimal steps would take infinitely long to occur, so thermodynamic reversibility is an idealization that is never achieved in real processes, except when the system is already at equilibrium, in which case no change will occur anyway! So why is the concept of a reversible process so important?

The answer can be seen by recalling that the change in the internal energy that characterizes any process can be distributed in an infinity of ways between heat flow across the boundaries of the system and work done on or by the system, as expressed by the First Law of thermodynamics

$$\Delta U = q + w. \tag{8.5.1}$$

Each combination of q and w represents a different pathway between the initial and final states. It can be shown that as a process such as the expansion of a gas is carried out in successively longer series of smaller steps, the absolute value of q approaches a minimum, and that of w approaches a maximum that is characteristic of the particular process. Thus when a process is carried out reversibly, the w-term in Equation 8.5.1 has its greatest possible value, and the q-term is at its smallest. These special quantities w_{max} and q_{min} (which we denote as q_{rev} and pronounce "q-reversible") have unique values for any given process and are therefore state functions.

Work and Reversibility

Changes in entropy (ΔS), together with changes in enthalpy (ΔH), enable us to predict in which direction a chemical or physical change will occur spontaneously. Before discussing how to do so, however, we must understand the difference between a reversible process and an irreversible one. In a reversible process, every intermediate state between the extremes is an equilibrium state, regardless of the direction of the change. In contrast, an irreversible process is one in which the intermediate states are not equilibrium states, so change occurs spontaneously in only one direction. As a result, a reversible process can change direction at any time, whereas an irreversible process cannot. When a gas expands reversibly against an external pressure such as a piston, for example, the expansion can be reversed at any time by reversing the motion of the piston; once the gas is compressed, it can be allowed to expand again, and the process can continue indefinitely. In contrast, the expansion of a gas into a vacuum ($P_{ext} = 0$) is irreversible because the external pressure is measurably less than the internal pressure of the gas. No equilibrium states exist, and the gas expands irreversibly. When gas escapes from a microscopic hole in a balloon into a vacuum, for example, the process is irreversible; the direction of airflow cannot change.

Because work done during the expansion of a gas depends on the opposing external pressure ($w = P_{ext}\Delta V$), work done in a reversible process is always equal to or greater than work done in a corresponding irreversible process: $w_{rev} \geq w_{irrev}$. Whether a process is reversible or irreversible, the first law of thermodynamics holds (Equation 8.5.1). Because U is a state function, the magnitude of ΔU does not depend on reversibility and is independent of the path taken. So

$$\Delta U = q_{rev} + w_{rev} \tag{8.5.2}$$

$$= q_{irrev} + w_{irrev} \tag{8.5.3}$$

Work done in a reversible process is always equal to or greater than work done in a corresponding irreversible process:

$$w_{rev} \geq w_{irrev} \tag{8.5.4}$$

In other words, ΔU for a process is the same whether that process is carried out in a reversible manner or an irreversible one. We now return to our earlier definition of entropy, using the magnitude of the heat flow for a reversible process (q_{rev}) to define entropy quantitatively.

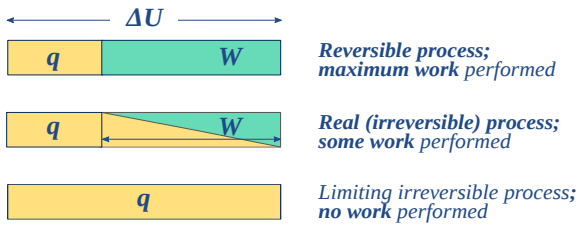


Figure 8.5.2: Note that the reversible condition implies w_{max} and q_{min}. The impossibility of extracting all of the internal energy as work is essentially a statement of the Second Law. (CC BY-NC; Ümit Kaya)

For a process that reversibly exchanges a quantity of heat q_{rev} with the surroundings, the entropy change is defined as

$$\Delta S = \frac{q_{rev}}{T} \tag{8.5.5}$$

This is the basic way of evaluating ΔS for *constant-temperature processes* such as phase changes, or the isothermal expansion of a gas. For processes in which the temperature is not constant such as heating or cooling of a substance, the equation must be integrated over the required temperature range, as discussed below.

Q&A: If no real process can take place reversibly, what use is an expression involving q_{rev}?

This is a rather fine point that you should understand: although transfer of heat between the system and surroundings is impossible to achieve in a truly reversible manner, this idealized pathway is only crucial for the definition of ΔS; by virtue of its being a state function, the same value of ΔS will apply when the system undergoes the same net change via any pathway. For example, the entropy change a gas undergoes when its volume is doubled at constant temperature will be the same regardless of whether the expansion is carried out in 1000 tiny steps (as reversible as patience is likely to allow) or by a single-step (as irreversible a pathway as you can get!) expansion into a vacuum (Figure 8.5.1).

Entropy is an *extensive* quantity; that is, it is proportional to the quantity of matter in a system; thus 100 g of metallic copper has twice the entropy of 50 g at the same temperature. This makes sense because the larger piece of copper contains twice as many quantized energy levels able to contain the thermal energy.

Entropy and "disorder"

Entropy is still described, particularly in older textbooks, as a measure of disorder. In a narrow technical sense this is correct, since the spreading and sharing of thermal energy does have the effect of randomizing the disposition of thermal energy within a system. But to simply equate entropy with “disorder” without further qualification is extremely misleading because it is far too easy to forget that entropy (and thermodynamics in general) applies only to molecular-level systems capable of exchanging thermal energy with the surroundings. Carrying these concepts over to macro systems may yield compelling analogies, but it is no longer science. It is far better to avoid the term “disorder” altogether in discussing entropy.



ΔS_{sys} for an Isothermal Expansion (or Compression)

As a substance becomes more dispersed in space, the thermal energy it carries is also spread over a larger volume, leading to an increase in its entropy. Because entropy, like energy, is an extensive property, a dilute solution of a given substance may well possess a smaller entropy than the same volume of a more concentrated solution, but the entropy *per mole* of solute (the *molar* entropy) will of course always increase as the solution becomes more dilute.

For gaseous substances, the volume and pressure are respectively direct and inverse measures of concentration. For an ideal gas that expands at a constant temperature (meaning that it absorbs heat from the surroundings to compensate for the work it does during the expansion), the increase in entropy is given by

$$\Delta S = R \ln \left(\frac{V_2}{V_1} \right) \tag{8.5.6}$$

Note: If the gas is allowed to cool during the expansion, the relation becomes more complicated and will best be discussed in a more advanced course.

Because the pressure of an ideal gas is *inversely proportional* to its volume, i.e.,

$$P = \frac{nRT}{V} \tag{8.5.7}$$

we can easily alter Equation 8.5.6 to express the entropy change associated with a change in the pressure of an ideal gas:

$$\Delta S = R \ln \left(\frac{P_1}{P_2} \right) \tag{8.5.8}$$

Also the concentration $c = n/V$ for an ideal gas is *proportional* to pressure

$$P = cRT \tag{8.5.9}$$

we can expressing the entropy change directly in concentrations, we have the similar relation

$$\Delta S = R \ln \left(\frac{c_1}{c_2} \right) \tag{8.5.10}$$

Although these equations strictly apply only to perfect gases and cannot be used at all for liquids and solids, it turns out that in a dilute solution, the solute can often be treated as a gas dispersed in the volume of the solution, so the last equation can actually give a fairly accurate value for the entropy of dilution of a solution. We will see later that this has important consequences in determining the equilibrium concentrations in a homogeneous reaction mixture.

The Relationship between Internal Energy and Entropy

Because the quantity of heat transferred (q_{rev}) is directly proportional to the absolute temperature of an object (T) ($q_{rev} \propto T$), the hotter the object, the greater the amount of heat transferred. Moreover, adding heat to a system increases the kinetic energy of the component atoms and molecules and hence their disorder ($\Delta S \propto q_{rev}$). Combining these relationships for any reversible process,

$$q_{\text{rev}} = T\Delta S \tag{8.5.11}$$

and

$$\Delta S = \frac{q_{\text{rev}}}{T} \tag{8.5.12}$$

Because the numerator (q_{rev}) is expressed in units of energy (joules), the units of ΔS are joules/kelvin (J/K). Recognizing that the work done in a reversible process at constant pressure is

$$w_{rev} = -P\Delta V, \tag{8.5.13}$$

we can express Equation 8.5.3 as follows:

$$\Delta U = q_{rev} + w_{rev} \tag{8.5.14}$$

$$= T\Delta S - P\Delta V \tag{8.5.15}$$

Thus the change in the internal energy of the system is related to the change in entropy, the absolute temperature, and the PV work done.

To illustrate the use of Equation 8.5.12 and Equation 8.5.15, we consider two reversible processes before turning to an irreversible process. When a sample of an ideal gas is allowed to expand reversibly at constant temperature, heat must be added to the gas during expansion to keep its T constant (Figure 8.5.5). The internal energy of the gas does not change because the temperature of the gas does not change; that is, $\Delta U = 0$ and $q_{rev} = -w_{rev}$. During expansion, $\Delta V > 0$, so the gas performs work on its surroundings:

$$w_{rev} = -P\Delta V < 0. \tag{8.5.16}$$

According to Equation 8.5.15, this means that q_{rev} must increase during expansion; that is, the gas must absorb heat from the surroundings during expansion, and the surroundings must give up that same amount of heat. The entropy change of the *system* is therefore

$$\Delta S_{sys} = +\frac{q_{rev}}{T} \tag{8.5.17}$$

and the entropy change of the *surroundings* is

$$\Delta S_{surr} = -\frac{q_{rev}}{T}. \tag{8.5.18}$$

The corresponding change in entropy of the universe is then as follows:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} \tag{8.5.19}$$

$$= \frac{q_{rev}}{T} + \left(-\frac{q_{rev}}{T}\right) \tag{8.5.20}$$

$$= 0 \tag{8.5.21}$$

Thus no change in ΔS_{univ} has occurred.

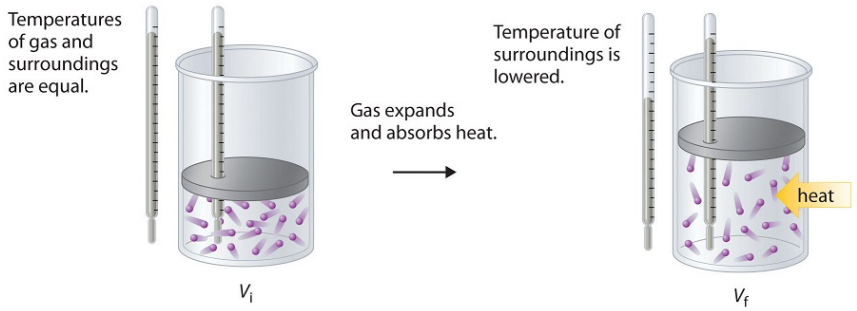


Figure 8.5.5: Expansion of Gas at Constant Temperature. (CC BY-SA-NC; Anonymous by request)

In the initial state (top), the temperatures of a gas and the surroundings are the same. During the reversible expansion of the gas, heat must be added to the gas to maintain a constant temperature. Thus the internal energy of the gas does not change, but work is performed on the surroundings. In the final state (bottom), the temperature of the surroundings is lower because the gas has absorbed heat from the surroundings during expansion.

Now consider the reversible melting of a sample of ice at 0°C and 1 atm. The enthalpy of fusion of ice is 6.01 kJ/mol, which means that 6.01 kJ of heat are absorbed reversibly from the surroundings when 1 mol of ice melts at 0°C, as illustrated in Figure 8.5.6. The surroundings constitute a sample of low-density carbon foam that is thermally conductive, and the system is the ice cube that has been placed on it. The direction of heat flow along the resulting temperature gradient is indicated with an arrow. From Equation 8.5.12, we see that the entropy of fusion of ice can be written as follows:

$$\Delta S_{fus} = \frac{q_{rev}}{T} = \frac{\Delta H_{fus}}{T} \tag{8.5.22}$$

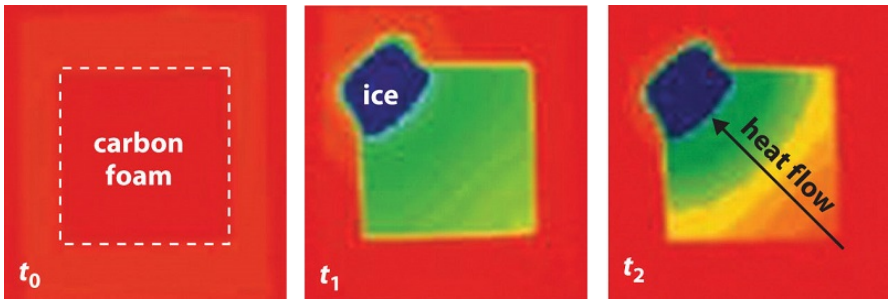


Figure 8.5.6: Thermograms Showing That Heat Is Absorbed from the Surroundings When Ice Melts at 0°C

By convention, a thermogram shows cold regions in blue, warm regions in red, and thermally intermediate regions in green. When an ice cube (the system, dark blue) is placed on the corner of a square sample of low-density carbon foam with very high thermal conductivity, the temperature of the foam is lowered (going from red to green). As the ice melts, a temperature gradient appears, ranging from warm to very cold. An arrow indicates the direction of heat flow from the surroundings (red and green) to the ice cube. The amount of heat lost by the surroundings is the same as the amount gained by the ice, so the entropy of the universe does not change.

In this case,

$$\Delta S_{fus} = \frac{6.01\,kJ/mol}{273\,K} \tag{8.5.23}$$

$$= 22.0\,J/(mol \bullet K) \tag{8.5.24}$$

$$= \Delta S_{sys}. \tag{8.5.25}$$

The amount of heat lost by the surroundings is the same as the amount gained by the ice, so

$$\Delta S_{surr} = \frac{q_{rev}}{T} \tag{8.5.26}$$

$$= \frac{-6.01\,kJ/mol}{273\,K} \tag{8.5.27}$$

$$= -22.0\,J/(mol \bullet K). \tag{8.5.28}$$

Once again, we see that the entropy of the universe does not change:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} \tag{8.5.29}$$

$$= 22.0\,J/(mol \bullet K) - 22.0\,J/(mol \bullet K) \tag{8.5.30}$$

$$= 0 \tag{8.5.31}$$

In these two examples of reversible processes, the entropy of the universe is unchanged. This is true of all reversible processes and constitutes part of the second law of thermodynamics: the entropy of the universe remains constant in a reversible process, whereas the entropy of the universe increases in an irreversible (spontaneous) process.

The Second Law of Thermodynamics

The entropy of the universe **increases** during a spontaneous process. It also **increases** during an observable non-spontaneous process.

As an example of an irreversible process, consider the entropy changes that accompany the spontaneous and irreversible transfer of heat from a hot object to a cold one, as occurs when lava spewed from a volcano flows into cold ocean water. The cold substance, the water, gains heat ($q > 0$), so the change in the entropy of the water can be written as $\Delta S_{cold} = q/T_{cold}$. Similarly, the hot substance, the lava, loses heat ($q < 0$), so its entropy change can be written as $\Delta S_{hot} = -q/T_{hot}$, where T_{cold} and T_{hot} are the temperatures of the cold and hot substances, respectively. The total entropy change of the universe accompanying this process is therefore

$$\Delta S_{\text{univ}} = \Delta S_{\text{cold}} + \Delta S_{\text{hot}} \tag{8.5.32}$$

$$= \frac{q}{T_{\text{cold}}} + \left(-\frac{q}{T_{\text{hot}}}\right) \tag{8.5.33}$$

The numerators on the right side of Equation 8.5.33 are the same in magnitude but opposite in sign. Whether ΔS_{univ} is positive or negative depends on the relative magnitudes of the denominators. By definition, $T_{hot} > T_{cold}$, so $-q/T_{hot}$ must be less than q/T_{cold}, and ΔS_{univ} must be positive. As predicted by the second law of thermodynamics, the entropy of the universe increases during this irreversible process. Any process for which ΔS_{univ} is positive is, by definition, a spontaneous one that will occur as written. Conversely, any process for which ΔS_{univ} approaches zero will not occur spontaneously as written but will occur spontaneously in the reverse direction. We see, therefore, that heat is spontaneously transferred from a hot substance, the lava, to a cold substance, the ocean water. In fact, if the lava is hot enough (e.g., if it is molten), so much heat can be transferred that the water is converted to steam (Figure **8.5.7**).



Figure **8.5.7**: Spontaneous Transfer of Heat from a Hot Substance to a Cold Substance

When molten lava flows into cold ocean water, so much heat is spontaneously transferred to the water that steam is produced.

Example 8.5.1: Tin Pest

Tin has two allotropes with different structures. Gray tin (α-tin) has a structure similar to that of diamond, whereas white tin (β-tin) is denser, with a unit cell structure that is based on a rectangular prism. At temperatures greater than 13.2°C, white tin is the more stable phase, but below that temperature, it slowly converts reversibly to the less dense, powdery gray phase. This phenomenon was argued to plagued Napoleon's army during his ill-fated invasion of Russia in 1812: the buttons on his soldiers' uniforms were made of tin and disintegrated during the Russian winter, adversely affecting the soldiers' health (and morale). The conversion of white tin to gray tin is exothermic, with ΔH = −2.1 kJ/mol at 13.2°C.

a. What is ΔS for this process?
b. Which is the more highly ordered form of tin—white or gray?

Given: ΔH and temperature

Asked for: ΔS and relative degree of order

Strategy:

Use Equation 8.5.12 to calculate the change in entropy for the reversible phase transition. From the calculated value of ΔS, predict which allotrope has the more highly ordered structure.

Solution

a. We know from Equation 8.5.12 that the entropy change for any reversible process is the heat transferred (in joules) divided by the temperature at which the process occurs. Because the conversion occurs at constant pressure, and ΔH and ΔU are essentially equal for reactions that involve only solids, we can calculate the change in entropy for the reversible phase transition where $q_{rev} = \Delta H$. Substituting the given values for ΔH and temperature in kelvins (in this case, T = 13.2°C = 286.4 K),

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{(-2.1\ \text{kJ/mol})(1000\ \text{J/kJ})}{286.4\ \text{K}} = -7.3\ \text{J/(mol}\cdot\text{K)}$$

b. The fact that $\Delta S < 0$ means that entropy decreases when white tin is converted to gray tin. Thus gray tin must be the more highly ordered structure.

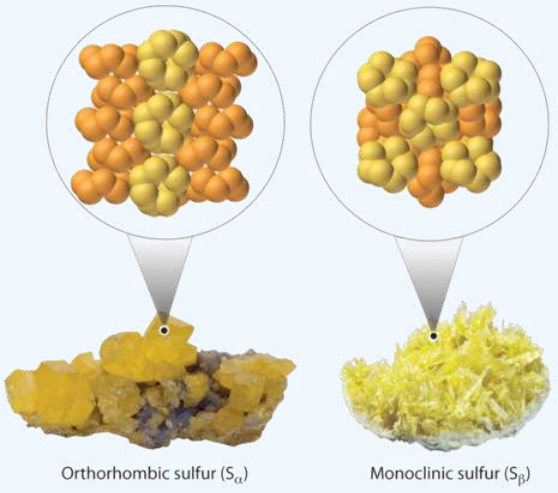


Video **8.5.1**: Time lapse tin pest reaction. Beta tin to alpha tin transformation, time lapse video of sample maintained at -40 C. 20 shots per hour.

Note: Whether failing buttons were indeed a contributing factor in the failure of the invasion remains disputed; critics of the theory point out that the tin used would have been quite impure and thus more tolerant of low temperatures. Laboratory tests provide evidence that the time required for unalloyed tin to develop significant tin pest damage at lowered temperatures is about 18 months, which is more than twice the length of Napoleon's Russian campaign. It is clear though that some of the regiments employed in the campaign had tin buttons and that the temperature reached sufficiently low values (at least -40 °C) to facilitate tin pest.

? Exercise 8.5.1: Sulfur

Elemental sulfur exists in two forms: an orthorhombic form (S_α), which is stable below 95.3°C, and a monoclinic form (S_β), which is stable above 95.3°C. The conversion of orthorhombic sulfur to monoclinic sulfur is endothermic, with $\Delta H = 0.401\ kJ/mol$ at 1 atm.



a. What is ΔS for this process?
b. Which is the more highly ordered form of sulfur—S_α or S_β?

Answer a

1.09 J/(mol•K)

Answer b

S_α

Summary

During a spontaneous process, the entropy of the universe increases.

$$\Delta S = \frac{q_{rev}}{T}$$

A reversible process is one for which all intermediate states between extremes are *equilibrium states*; it can change direction at any time. In contrast, an irreversible process occurs in one direction only. The change in entropy of the system or the surroundings is the quantity of heat transferred divided by the temperature. The second law of thermodynamics states that in a reversible process, the entropy of the universe is constant, whereas in an irreversible process, such as the transfer of heat from a hot object to a cold object, the entropy of the universe increases.

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8.6: Quantum States, Microstates, and Energy Spreading

Learning Objectives

- Explain how entropy is a measure of the degree of the spreading and sharing of thermal energy within a system.
- Explain why the entropy of a substance increases with its molecular weight and complexity and with temperature.
- Explain why entropy increases as the pressure or concentration becomes smaller.
- Explain why entropies of gases are much larger than those of condensed phases.

Entropy is a measure of the degree of spreading and sharing of thermal energy within a system. This "spreading and sharing" can be spreading of the thermal energy into a larger volume of *space* or its sharing amongst previously inaccessible microstates of the system. Entropy is an ***extensive* quantity**; that is, it is proportional to the quantity of matter in a system; thus 100 g of metallic copper has twice the entropy of 50 g at the same temperature. This makes sense because the larger piece of copper contains twice as many quantized energy levels able to contain the thermal energy.

Thermal energy is the portion of a molecule's energy that is proportional to its *temperature*, and thus relates to motion at the molecular scale. What kinds of molecular motions are possible? For monatomic molecules, there is only one: actual movement from one location to another, which we call *translation*. Since there are three directions in space, all molecules possess three modes of *translational motion*.

For polyatomic molecules, two additional kinds of motions are possible. One of these is *rotation*; a linear molecule such as CO_2 in which the atoms are all laid out along the x-axis can rotate along the y- and z-axes, while molecules having less symmetry can rotate about all three axes. Thus linear molecules possess two modes of rotational motion, while non-linear ones have three rotational modes. Finally, molecules consisting of two or more atoms can undergo internal *vibrations*. For freely moving molecules in a gas, the number of vibrational modes or patterns depends on both the number of atoms and the shape of the molecule, and it increases rapidly as the molecule becomes more complicated.

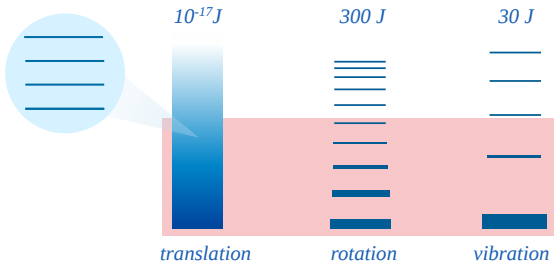


Figure **8.6.1**: Relative Energy levels for translation (left), rotation (middle) and vibration (right). (CC BY-NC; Ümit Kaya based off of figure by Stephen Lower)

The relative populations of the quantized translational, rotational, and vibrational energy states of a typical diatomic molecule are depicted by the thickness of the lines in this schematic (not-to-scale!) diagram. The colored shading indicates the total thermal energy available at a given temperature. The numbers at the top show order-of-magnitude spacings between adjacent levels. It is readily apparent that virtually all the thermal energy resides in translational states.

Notice the greatly different spacing of the three kinds of energy levels in Figure **8.6.1**. This is extremely important because it determines the number of energy quanta that a molecule can accept, and, as Figure **8.6.2** demonstrates, the number of different ways this energy can be distributed amongst the molecules.

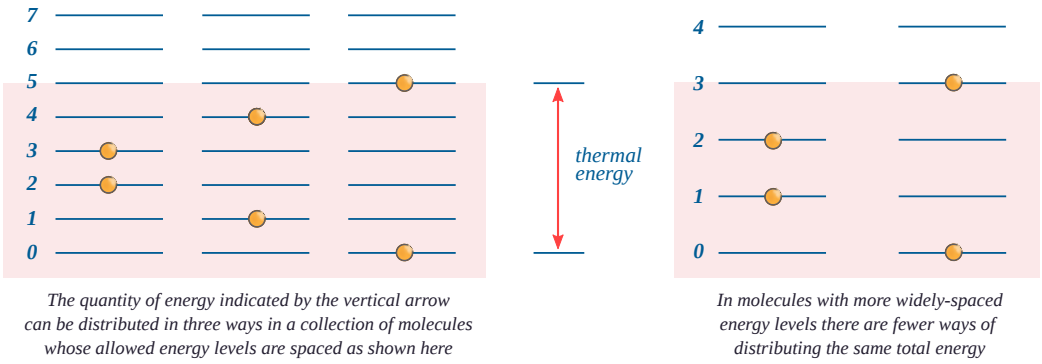


Figure **8.6.2**: The more closely spaced the quantized energy states of a molecule, the greater will be the number of ways in which a given quantity of thermal energy can be shared amongst a collection of these molecules. (CC BY-NC; Ümit Kaya based off of figure by Stephen Lower)

> The spacing of molecular energy states becomes closer as the mass and number of bonds in the molecule increases, so we can generally say that the more complex the molecule, the greater the density of its energy states.

At the atomic and molecular level, all energy is *quantized*; each particle possesses discrete states of kinetic energy and is able to accept thermal energy only in packets whose values correspond to the energies of one or more of these states. Polyatomic molecules can store energy in rotational and vibrational motions, and all molecules (even monatomic ones) will possess translational kinetic energy (thermal energy) at all temperatures above absolute zero. The energy difference between adjacent translational states is so minute that translational kinetic energy can be regarded as *continuous* (non-quantized) for most practical purposes.

The number of ways in which thermal energy can be distributed amongst the allowed states within a collection of molecules is easily calculated from simple statistics, but we will confine ourselves to an example here. Suppose that we have a system consisting of three molecules and three quanta of energy to share among them. We can give all the kinetic energy to any one molecule, leaving the others with none, we can give two units to one molecule and one unit to another, or we can share out the energy equally and give one unit to each molecule. All told, there are ten possible ways of distributing three units of energy among three identical molecules as shown here:

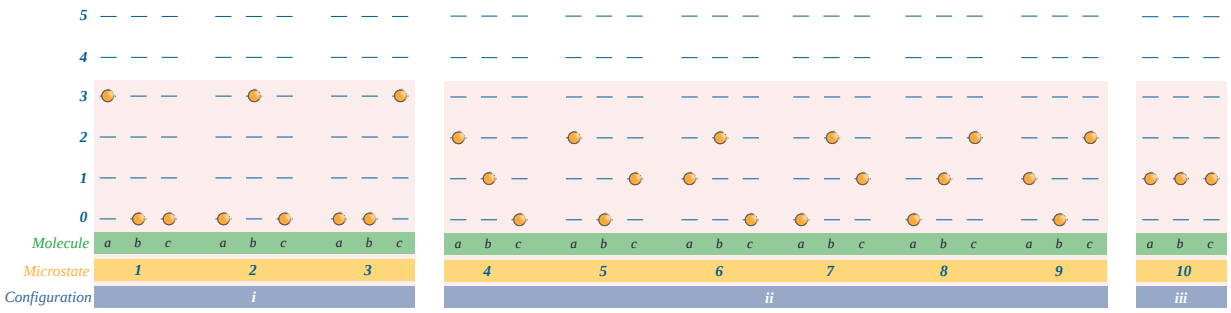


Figure **8.6.3**. (CC BY-NC; Ümit Kaya based off of figure by Stephen Lower)

Each of these ten possibilities represents a distinct *microstate* that will describe the system at any instant in time. Those microstates that possess identical distributions of energy among the accessible quantum levels (and differ only in which particular molecules occupy the levels) are known as **configurations**. Because all microstates are equally probable, the probability of any one configuration is proportional to the number of microstates that can produce it. Thus in the system shown above, the configuration labeled *ii* will be observed 60% of the time, while *iii* will occur only 10% of the time.

As the number of molecules and the number of quanta increases, the number of accessible microstates grows explosively; if 1000 quanta of energy are shared by 1000 molecules, the number of available microstates will be around 10^{600}— a number that greatly exceeds the number of atoms in the observable universe! The number of possible configurations (as defined above) also increases, but in such a way as to greatly reduce the probability of all but the most probable configurations. Thus for a sample of a gas large enough to be observable under normal conditions, **only a single configuration (energy distribution amongst the quantum states) need be considered**; even the second-most-probable configuration can be neglected.

The bottom line: any collection of molecules large enough in numbers to have chemical significance will have its thermal energy distributed over an unimaginably large number of microstates. The number of microstates increases exponentially as more energy states ("configurations" as defined above) become accessible owing to

- Addition of energy quanta (higher temperature),
- Increase in the number of molecules (resulting from dissociation, for example).
- the volume of the system increases (which decreases the spacing between energy states, allowing more of them to be populated at a given temperature.)

Spontaneous Process: Heat Death

Energy is *conserved*; if you lift a book off the table, and let it fall, the total amount of energy in the world remains unchanged. All you have done is transferred it from the form in which it was stored within the glucose in your body to your muscles, and then to the book (that is, you did work on the book by moving it up against the earth's gravitational field). After the book has fallen, this same quantity of energy exists as thermal energy (heat) in the book and table top.

What *has* changed, however, is the availability of this energy. Once the energy has spread into the huge number of thermal microstates in the warmed objects, the probability of its spontaneously (that is, by chance) becoming un-dispersed is essentially zero. Thus although the energy is still "there", it is forever beyond utilization or recovery. The profundity of this conclusion was recognized around 1900, when it was first described at the "heat death" of the world. This refers to the fact that every spontaneous process (essentially every change that occurs) is accompanied by the "dilution" of energy. The obvious implication is that all of the molecular-level kinetic energy will be spread out completely, and nothing more will ever happen.

Spontaneous Process: Gases Expansions

Everybody knows that a gas, if left to itself, will tend to expand and fill the volume within which it is confined completely and uniformly. What "drives" this expansion? At the simplest level it is clear that with more space available, random motions of the individual molecules will inevitably disperse them throughout the space. But as we mentioned above, the allowed energy states that molecules can occupy are spaced more closely in a larger volume than in a smaller one. The larger the volume available to the gas, the greater the number of microstates its thermal energy can occupy. Since all such states within the thermally accessible range of energies are equally probable, the expansion of the gas can be viewed as a consequence of the tendency of thermal energy to be spread and shared as widely as possible. Once this has happened, the probability that this sharing of energy will reverse itself (that is, that the gas will spontaneously contract) is so minute as to be unthinkable.

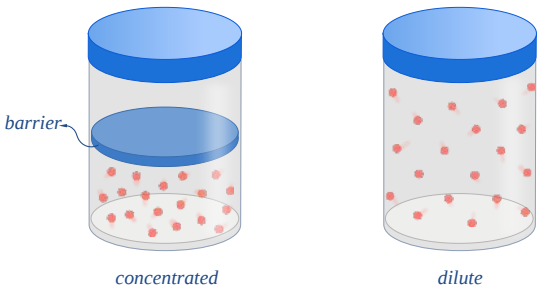


Figure 8.6.4: (CC BY-NC; Ümit Kaya based off of figure by Stephen Lower)

Imagine a gas initially confined to one half of a box (Figure 8.6.4). The barrier is then removed so that it can expand into the full volume of the container. We know that the entropy of the gas will increase as the thermal energy of its molecules spreads into the

enlarged space. In terms of the spreading of thermal energy, Figure Figure **8.6.5** may be helpful. The tendency of a gas to expand is due to the more closely-spaced thermal energy states in the larger volume ②.

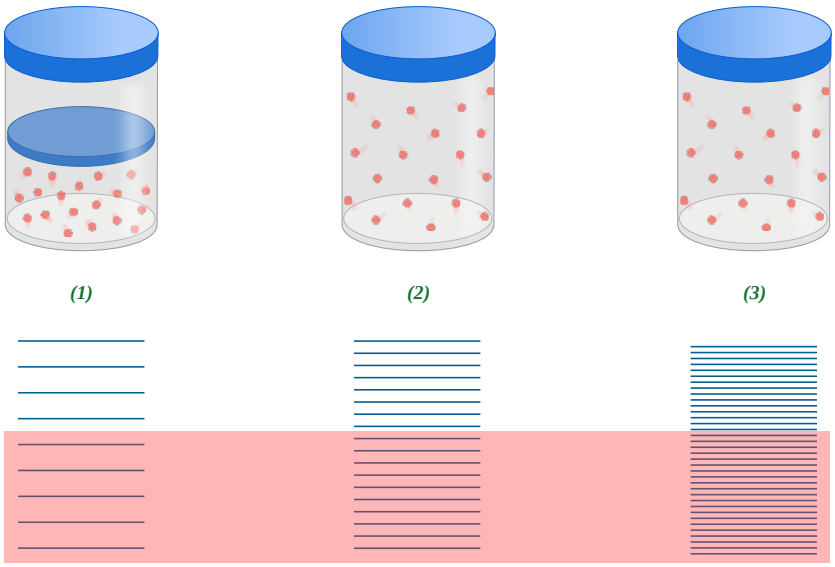


Figure **8.6.5**: The pink shading represents the thermally-accessible range of microstates for a given temperature. (CC BY-NC; Ümit Kaya based off of figure by Stephen Lower)

Spontaneous Process: Mixing and dilution

Mixing and dilution really amount to the same thing, especially for ideal gases. Replace the pair of containers shown above with one containing two kinds of molecules in the separate sections (Figure **8.6.6**). When we remove the barrier, the "red" and "blue" molecules will each expand into the space of the other. (Recall Dalton's Law that "each gas is a vacuum to the other gas"). However, notice that although each gas underwent an expansion, the overall process amounts to what we call "mixing".

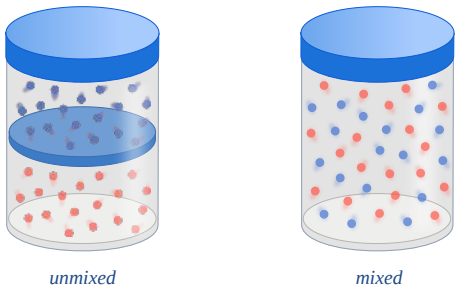


Figure **8.6.6**: Mixing of a gas. (CC BY-NC; Ümit Kaya based off of figure by Stephen Lower)

What is true for gaseous molecules can, in principle, apply also to solute molecules dissolved in a solvent. But bear in mind that whereas the enthalpy associated with the expansion of a perfect gas is by definition zero, ΔH's of mixing of two liquids or of dissolving a solute in a solvent have finite values which may limit the miscibility of liquids or the solubility of a solute.

But what's really dramatic is that when just *one molecule* of a second gas is introduced into the container (③ in Figure **8.6.5**), an unimaginably huge number of new configurations become possible, greatly increasing the number of microstates that are thermally accessible (as indicated by the pink shading above).

Spontaneous Process: Thermal Equilibrium

Just as gases spontaneously change their volumes from “smaller-to-larger”, the flow of heat from a warmer body to a cooler one always operates in the direction “warmer-to-cooler” because this allows thermal energy to populate a larger number of energy

microstates as new ones are made available by bringing the cooler body into contact with the warmer one; in effect, the thermal energy becomes more “diluted”.

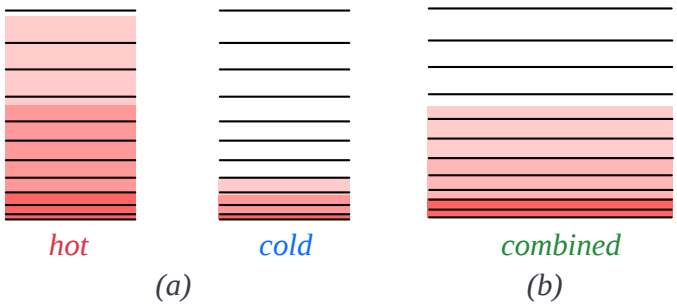


Figure 8.6.7: Part a of the figure is a schematic depiction of the thermal energy states in two separated identical bodies at different temperatures indicated by shading. (CC BY-NC; Ümit Kaya based off of figure by Stephen Lower)

When the bodies are brought into thermal contact (*b*), thermal energy flows from the higher occupied levels in the warmer object into the unoccupied levels of the cooler one until equal numbers are occupied in both bodies, bringing them to the same temperature. As you might expect, the increase in the amount of energy spreading and sharing is proportional to the amount of heat transferred *q*, but there is one other factor involved, and that is the *temperature* at which the transfer occurs. When a quantity of heat *q* passes into a system at temperature *T*, the degree of dilution of the thermal energy is given by

$$\frac{q}{T} \tag{8.6.1}$$

To understand why we have to divide by the temperature, consider the effect of very large and very small values of T in the denominator of Equation 8.6.1. If the body receiving the heat is initially at a very low temperature, relatively few thermal energy states are initially occupied, so the amount of energy spreading into vacant states can be very great. Conversely, if the temperature is initially large, more thermal energy is already spread around within it, and absorption of the additional energy will have a relatively small effect on the degree of thermal disorder within the body.

Summary

Entropy is a measure of the degree of spreading and sharing of thermal energy within a system. This “spreading and sharing” can be spreading of the thermal energy into a larger volume of *space* or its sharing amongst previously inaccessible microstates of the system. The following box shows how this concept applies to a number of common processes.

Observations and Explanations in terms of Entropy changes

A deck of cards is shuffled, or 100 coins, initially heads up, are randomly tossed.

Source of Entropy Increase of System

This has nothing to do with entropy because macro objects are unable to exchange thermal energy with the surroundings within the time scale of the process

Two identical blocks of copper, one at 20°C and the other at 40°C, are placed in contact.

Source of Entropy Increase of System

The cooler block contains more unoccupied microstates, so heat flows from the warmer block until equal numbers of microstates are populated in the two blocks.

A gas expands isothermally to twice its initial volume.

Source of Entropy Increase of System

A constant amount of thermal energy spreads over a larger volume of space

1 mole of water is heated by 1C°.

Source of Entropy Increase of System

The increased thermal energy makes additional microstates accessible. (The increase is by a factor of about $10^{20,000,000,000,000,\,000,000,000}$.)

Equal volumes of two gases are allowed to mix.

Source of Entropy Increase of System

The effect is the same as allowing each gas to expand to twice its volume; the thermal energy in each is now spread over a larger volume.

One mole of dihydrogen, H_2, is placed in a container and heated to 3000K.

Source of Entropy Increase of System

Some of the $\mathbf{H_2}$ dissociates to $\mathbf{H}$ atoms because at this temperature there are more thermally accessible microstates in the 2 moles of $\mathbf{H}$ atoms.

The above reaction mixture is cooled to 300 K.

Source of Entropy Increase of System

The composition shifts back to virtually all $\mathbf{H_2}$ because this molecule contains more thermally accessible microstates at low temperatures.

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8.7: The Third Law of Thermodynamics

Learning Objectives

- The *absolute entropy* of a pure substance at a given temperature is the sum of all the entropy it would acquire on warming from absolute zero (where $S = 0$) to the particular temperature.
- Calculate entropy changes for phase transitions and chemical reactions under standard conditions

The atoms, molecules, or ions that compose a chemical system can undergo several types of molecular motion, including translation, rotation, and vibration (Figure 8.7.1). The greater the molecular motion of a system, the greater the number of possible microstates and the higher the entropy. A perfectly ordered system with only a single microstate available to it would have an entropy of zero. The only system that meets this criterion is a perfect crystal at a temperature of absolute zero (0 K), in which each component atom, molecule, or ion is fixed in place within a crystal lattice and exhibits no motion (ignoring quantum *zero point motion*).

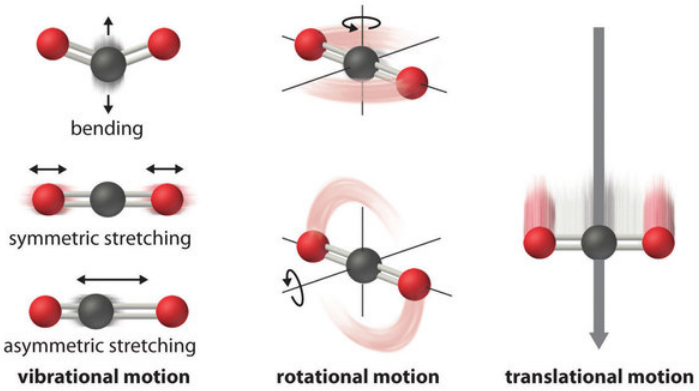


Figure 8.7.1: Molecular Motions. Vibrational, rotational, and translational motions of a carbon dioxide molecule are illustrated here. Only a perfectly ordered, crystalline substance at absolute zero would exhibit no molecular motion (classically; there will always be motion quantum mechanically) and have zero entropy. In practice, this is an unattainable ideal. (CC BY-SA-NC; Anonymous by request)

This system may be described by a single microstate, as its purity, perfect crystallinity and complete lack of motion (at least classically, quantum mechanics argues for constant motion) means there is but one possible location for each identical atom or molecule comprising the crystal ($\Omega = 1$). According to the Boltzmann equation, the entropy of this system is zero.

$$\begin{aligned} S &= k \ln \Omega \\ &= k \ln(1) \\ &= 0 \end{aligned}$$

In practice, absolute zero is an ideal temperature that is unobtainable, and a perfect single crystal is also an ideal that cannot be achieved. Nonetheless, the combination of these two ideals constitutes the basis for the third law of thermodynamics: the entropy of any perfectly ordered, crystalline substance at absolute zero is zero.

Definition: Third Law of Thermodynamics

The entropy of a pure, perfect crystalline substance at 0 K is zero.

The third law of thermodynamics has two important consequences: it defines the sign of the entropy of any substance at temperatures above absolute zero as positive, and it provides a fixed reference point that allows us to measure the absolute entropy of any substance at any temperature. In this section, we examine two different ways to calculate ΔS for a reaction or a physical change. The first, based on the definition of absolute entropy provided by the third law of thermodynamics, uses tabulated values of absolute entropies of substances. The second, based on the fact that entropy is a state function, uses a thermodynamic cycle similar to those discussed previously.

Standard-State Entropies

One way of calculating ΔS for a reaction is to use tabulated values of the standard molar entropy (S^o), which is the entropy of 1 mol of a substance under standard pressure (1 bar). Often the standard molar entropy is given at 298 K and is often demarked as ΔS^o_{298}. The units of S^o are J/(mol•K). Unlike enthalpy or internal energy, it is possible to obtain absolute entropy values by measuring the entropy change that occurs between the reference point of 0 K (corresponding to $S = 0$) and 298 K (Tables T1 and T2).

As shown in Table 8.7.1, for substances with approximately the same molar mass and number of atoms, S^o values fall in the order

$$S^o(\text{gas}) \gg S^o(\text{liquid}) > S^o(\text{solid}). \tag{8.7.1}$$

For instance, S^o for liquid water is 70.0 J/(mol•K), whereas S^o for water vapor is 188.8 J/(mol•K). Likewise, S^o is 260.7 J/(mol•K) for gaseous I_2 and 116.1 J/(mol•K) for solid I_2. This order makes qualitative sense based on the kinds and extents of motion available to atoms and molecules in the three phases (Figure 8.7.1). The correlation between physical state and absolute entropy is illustrated in Figure 8.7.2, which is a generalized plot of the entropy of a substance versus temperature.

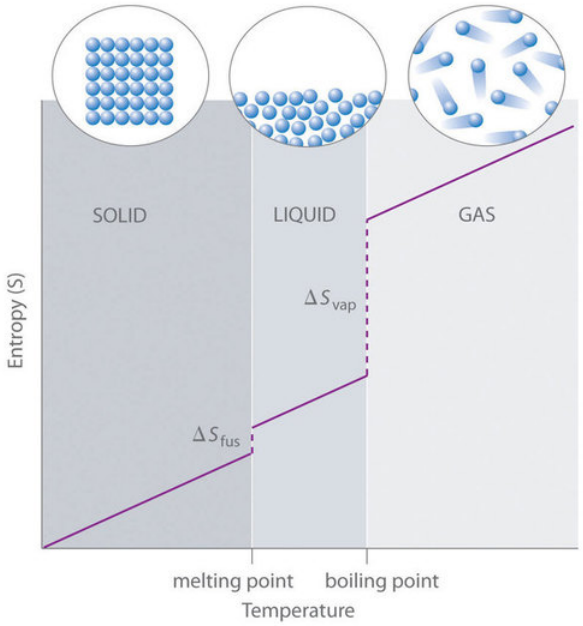


Figure 8.7.2: A Generalized Plot of Entropy versus Temperature for a Single Substance. Absolute entropy increases steadily with increasing temperature until the melting point is reached, where it jumps suddenly as the substance undergoes a phase change from a highly ordered solid to a disordered liquid (ΔS_{fus}). The entropy again increases steadily with increasing temperature until the boiling point is reached, where it jumps suddenly as the liquid undergoes a phase change to a highly disordered gas (ΔS_{vap}). (CC BY-SA-NC; anonymous).

The Third Law Lets us Calculate Absolute Entropies

The *absolute entropy* of a substance at any temperature above 0 K must be determined by calculating the increments of heat q required to bring the substance from 0 K to the temperature of interest, and then summing the ratios q/T. Two kinds of experimental measurements are needed:

1. The enthalpies associated with any **phase changes** the substance may undergo within the temperature range of interest. Melting of a solid and vaporization of a liquid correspond to sizeable increases in the number of microstates available to accept thermal energy, so as these processes occur, energy will flow into a system, filling these new microstates to the extent required to maintain a constant temperature (the freezing or boiling point); these inflows of thermal energy correspond to the heats of fusion and vaporization. The entropy increase associated with transition at temperature T is

$$\frac{\Delta H_{fusion}}{T}. \tag{8.7.2}$$

2. The **heat capacity** C of a phase expresses the quantity of heat required to change the temperature by a small amount ΔT, or more precisely, by an infinitesimal amount dT. Thus the entropy increase brought about by warming a substance over a range of temperatures that does not encompass a phase transition is given by the sum of the quantities $C\frac{dT}{T}$ for each increment of temperature dT. This is of course just the integral

$$S_{0\rightarrow T} = \int_0^T \frac{C_p}{T} dt \tag{8.7.3}$$

Because the heat capacity is itself slightly temperature dependent, the most precise determinations of absolute entropies require that the functional dependence of C on T be used in the integral in Equation 8.7.3, i.e.,:

$$S_{0\rightarrow T} = \int_0^T \frac{C_p(T)}{T} dt. \tag{8.7.4}$$

When this is not known, one can take a series of heat capacity measurements over narrow temperature increments ΔT and measure the area under each section of the curve. The area under each section of the plot represents the entropy change associated with heating the substance through an interval ΔT. To this must be added the enthalpies of melting, vaporization, and of any solid-solid phase changes.

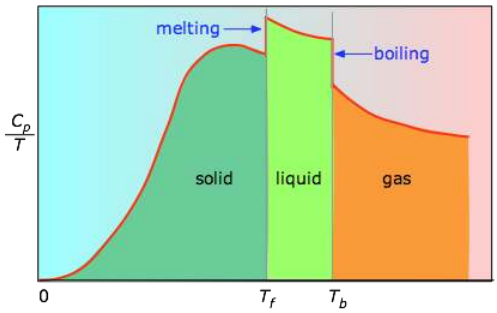


Figure 8.7.3: Heat capacity/temperature as a function of temperature. (CC BY; Stephan Lower)

Values of C_p for temperatures near zero are not measured directly, but can be estimated from quantum theory. The cumulative areas from 0 K to any given temperature (Figure 8.7.3) are then plotted as a function of T, and any phase-change entropies such as

$$S_{vap} = \frac{H_{vap}}{T_b} \tag{8.7.5}$$

are added to obtain the absolute entropy at temperature T. As shown in Figure 8.7.2 above, the entropy of a substance increases with temperature, and it does so for two reasons:

- As the temperature rises, more microstates become accessible, allowing thermal energy to be more widely dispersed. This is reflected in the gradual increase of entropy with temperature.
- The molecules of solids, liquids, and gases have increasingly greater freedom to move around, facilitating the spreading and sharing of thermal energy. Phase changes are therefore accompanied by massive and discontinuous increase in the entropy.

Calculating ΔS_{sys}

We can make careful calorimetric measurements to determine the temperature dependence of a substance's entropy and to derive absolute entropy values under specific conditions. Standard entropies are given the label S^o_{298} for values determined for one mole of substance at a pressure of 1 bar and a temperature of 298 K. The standard entropy change (ΔS^o) for any process may be computed from the standard entropies of its reactant and product species like the following:

$$\Delta S^o = \sum \nu S^o_{298}(\text{products}) - \sum \nu S^o_{298}(\text{reactants}) \tag{8.7.6}$$

Here, ν represents stoichiometric coefficients in the balanced equation representing the process. For example, ΔS^o for the following reaction at room temperature

$$m\text{A} + n\text{B} \longrightarrow x\text{C} + y\text{D} \tag{8.7.7}$$

is computed as the following:

$$\Delta S^o = [xS^o_{298}(\mathrm{C}) + yS^o_{298}(\mathrm{D})] - [mS^o_{298}(\mathrm{A}) + nS^o_{298}(\mathrm{B})] \tag{8.7.8}$$

Table 8.7.1 lists some standard entropies at 298.15 K. You can find additional standard entropies in Tables T1 and T2

Table 8.7.1: Standard Molar Entropy Values of Selected Substances at 25°C

Gases		Liquids		Solids	
Substance	S^o *[J/(mol•K)]*	*Substance*	S^o *[J/(mol•K)]*	*Substance*	S^o *[J/(mol•K)]*
He	126.2	H_2O	70.0	C (diamond)	2.4
H_2	130.7	CH_3OH	126.8	C (graphite)	5.7
Ne	146.3	Br_2	152.2	LiF	35.7
Ar	154.8	CH_3CH_2OH	160.7	SiO_2 (quartz)	41.5
Kr	164.1	C_6H_6	173.4	Ca	41.6
Xe	169.7	CH_3COCl	200.8	Na	51.3
H_2O	188.8	C_6H_{12} (cyclohexane)	204.4	MgF_2	57.2
N_2	191.6	C_8H_{18} (isooctane)	329.3	K	64.7
O_2	205.2			NaCl	72.1
CO_2	213.8			KCl	82.6
I_2	260.7			I_2	116.1

A closer examination of Table 8.7.1 also reveals that substances with similar molecular structures tend to have similar S^o values. Among crystalline materials, those with the lowest entropies tend to be rigid crystals composed of small atoms linked by strong, highly directional bonds, such as diamond ($S^o = 2.4\ J/(mol \bullet K)$). In contrast, graphite, the softer, less rigid allotrope of carbon, has a higher S^o (5.7 J/(mol•K)) due to more ~~disorder~~ (microstates) in the crystal. Soft crystalline substances and those with larger atoms tend to have higher entropies because of increased molecular motion and disorder. Similarly, the absolute entropy of a substance tends to increase with increasing molecular complexity because the number of available microstates increases with molecular complexity. For example, compare the S^o values for $CH_3OH(l)$ and $CH_3CH_2OH(l)$. Finally, substances with strong hydrogen bonds have lower values of S^o, which reflects a more ordered structure.

> *Entropy increases with softer, less rigid solids, solids that contain larger atoms, and solids with complex molecular structures.*

To calculate ΔS^o for a chemical reaction from standard molar entropies, we use the familiar "products minus reactants" rule, in which the absolute entropy of each reactant and product is multiplied by its stoichiometric coefficient in the balanced chemical equation. Example 8.7.1 illustrates this procedure for the combustion of the liquid hydrocarbon isooctane (C_8H_{18}; 2,2,4-trimethylpentane).

Example 8.7.1

Use the data in Table 8.7.1 to calculate ΔS^o for the reaction of liquid isooctane with $O_2(g)$ to give $CO_2(g)$ and $H_2O(g)$ at 298 K.

Given: standard molar entropies, reactants, and products

Asked for: ΔS°

Strategy:

Write the balanced chemical equation for the reaction and identify the appropriate quantities in Table 8.7.1. Subtract the sum of the absolute entropies of the reactants from the sum of the absolute entropies of the products, each multiplied by their

appropriate stoichiometric coefficients, to obtain ΔS^o for the reaction.

Solution:

The balanced chemical equation for the complete combustion of isooctane (C_8H_{18}) is as follows:

$$C_8H_{18}\,(l) + \tfrac{25}{2}\,O_2\,(g) \longrightarrow 8\,CO_2\,(g) + 9\,H_2O\,(g)$$

We calculate ΔS^o for the reaction using the "products minus reactants" rule, where m and n are the stoichiometric coefficients of each product and each reactant:

$$\begin{aligned}\Delta S^o_{rxn} &= \sum mS^o(\text{products}) - \sum nS^o(\text{reactants})\\ &= [8S^o(CO_2) + 9S^o(H_2O)] - [S^o(C_8H_{18}) + \frac{25}{2}S^o(O_2)]\\ &= \{[8\text{ mol } CO_2 \times 213.8\text{ J/(mol}\cdot\text{K)}] + [9\text{ mol } H_2O \times 188.8\text{ J/(mol}\cdot\text{K)}]\}\\ &\quad - \left\{[1\text{ mol } C_8H_{18} \times 329.3\text{ J/(mol}\cdot\text{K)}] + \left[\frac{25}{2}\text{ mol } O_2 \times 205.2\text{ J/(mol}\cdot\text{K)}\right]\right\}\\ &= 515.3\text{ J/K}\end{aligned}$$

ΔS^o is positive, as expected for a combustion reaction in which one large hydrocarbon molecule is converted to many molecules of gaseous products.

Exercise 8.7.1

Use the data in Table 8.7.1 to calculate ΔS^o for the reaction of $H_2\,(g)$ with liquid benzene (C_6H_6) to give cyclohexane (C_6H_{12}) at 298 K.

Answer

-361.1 J/K

Example 8.7.2: Determination of ΔS°

Calculate the standard entropy change for the following process at 298 K:

$$H_2O(g) \longrightarrow H_2O(l)$$

Solution

The value of the standard entropy change at room temperature, ΔS^o_{298}, is the difference between the standard entropy of the product, $H_2O(l)$, and the standard entropy of the reactant, $H_2O(g)$.

$$\begin{aligned}\Delta S^o_{298} &= S^o_{298}(H_2O\,(l)) - S^o_{298}(H_2O\,(g))\\ &= (70.0\ J\ mol^{-1}K^{-1}) - (188.8\ J mol^{-1}K^{-1})\\ &= -118.8\ J\ mol^{-1}K^{-1}\end{aligned}$$

The value for ΔS^o_{298} is negative, as expected for this phase transition (condensation), which the previous section discussed.

Exercise 8.7.2

Calculate the standard entropy change for the following process at 298 K:

$$H_2(g) + C_2H_4(g) \longrightarrow C_2H_6(g)$$

Answer

$-120.6\text{ J mol}^{-1}\text{ K}^{-1}$

Example 8.7.3: Determination of ΔS°

Calculate the standard entropy change for the combustion of methanol, CH_3OH at 298 K:

$$2\,CH_3OH(l) + 3\,O_2(g) \longrightarrow 2\,CO_2(g) + 4\,H_2O(l)$$

Solution

The value of the standard entropy change is equal to the difference between the standard entropies of the products and the entropies of the reactants scaled by their stoichiometric coefficients. The standard entropy of formations are found in Table 8.7.1.

$$\begin{aligned}\Delta S^o &= \Delta S^o_{298} \\ &= \sum \nu S^o_{298}(\text{products}) - \sum \nu S^o_{298}(\text{reactants}) \\ &= 2S^o_{298}(CO_2(g)) + 4S^o_{298}(H_2O(l))] - [2S^o_{298}(CH_3OH(l)) + 3S^o_{298}(O_2(g))] \\ &= [(2 \times 213.8) + (4 \times 70.0)] - [(2 \times 126.8) + (3 \times 205.03)] \\ &= -161.6\ J/mol \cdot K\end{aligned}$$

Exercise 8.7.3

Calculate the standard entropy change for the following reaction at 298 K:

$$Ca(OH)_2(s) \longrightarrow CaO(s) + H_2O(l)$$

Answer

24.7 J/mol•K

Summary

Energy values, as you know, are all relative, and must be defined on a scale that is completely arbitrary; there is no such thing as the absolute energy of a substance, so we can arbitrarily define the enthalpy or internal energy of an element in its most stable form at 298 K and 1 atm pressure as zero. The same is *not* true of the entropy; since entropy is a measure of the "dilution" of thermal energy, it follows that the less thermal energy available to spread through a system (that is, the lower the temperature), the smaller will be its entropy. In other words, as the absolute temperature of a substance approaches zero, so does its entropy. This principle is the basis of the *Third law of thermodynamics*, which states that the entropy of a perfectly-ordered solid at 0 K is zero.

In practice, chemists determine the absolute entropy of a substance by measuring the molar heat capacity (C_p) as a function of temperature and then plotting the quantity C_p/T versus T. The area under the curve between 0 K and any temperature T is the absolute entropy of the substance at T. In contrast, other thermodynamic properties, such as internal energy and enthalpy, can be evaluated in only relative terms, not absolute terms.

The second law of thermodynamics states that a spontaneous process increases the entropy of the universe, $S_{univ} > 0$. If $\Delta S_{univ} < 0$, the process is nonspontaneous, and if $\Delta S_{univ} = 0$, the system is at equilibrium. The third law of thermodynamics establishes the zero for entropy as that of a perfect, pure crystalline solid at 0 K. With only one possible microstate, the entropy is zero. We may compute the standard entropy change for a process by using standard entropy values for the reactants and products involved in the process.

Contributors and Attributions

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- Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook

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8.8: Gibbs Energy

Learning Objectives

- To understand the relationship between Gibbs free energy and work.

One of the major goals of chemical thermodynamics is to establish criteria for predicting whether a particular reaction or process will occur spontaneously. We have developed one such criterion, the change in entropy of the universe: if $\Delta S_{univ} > 0$ for a process or a reaction, then the process will occur spontaneously as written. Conversely, if $\Delta S_{univ} < 0$, a process cannot occur spontaneously; if $\Delta S_{univ} = 0$, the system is at equilibrium. The sign of ΔS_{univ} is a universally applicable and infallible indicator of the spontaneity of a reaction. Unfortunately, using ΔS_{univ} requires that we calculate ΔS for **both a system and its surroundings**. This is not particularly useful for two reasons: we are normally much more interested in the system than in the surroundings, and it is difficult to make quantitative measurements of the surroundings (i.e., the rest of the universe). A criterion of spontaneity that is based solely on the state functions of a system would be much more convenient and is provided by a new state function: the Gibbs free energy.

Gibbs Energy and Spontaneity

The Gibbs energy (also known as the *Gibbs function*) is defined as

$$G_{sys} = H_{sys} - TS_{sys} \tag{8.8.1}$$

in which S refers to the entropy of the *system*. Since H, T and S are all state functions, so is G. Thus for any change in state, we can expand Equation 8.8.1 to

$$\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys} \tag{8.8.2}$$

How does this simple equation relate to the entropy change of the universe ΔS_{univ} that we know is the sole criterion for spontaneous change from the second law of thermodynamics? Starting with the definition

$$\Delta S_{univ} = \Delta S_{surr} + \Delta S_{sys} \tag{8.8.3}$$

we would first like to get rid of ΔS_{surr}. How can a chemical reaction (a change in the *system*) affect the entropy of the *surroundings*? Because most reactions are either exothermic or endothermic, they are accompanied by heat q_p across the system boundary (we are considering constant pressure processes). The enthalpy change of the reaction ΔH_{sys} is the "flow" of heat into the system from the surroundings under constant pressure, so the heat "withdrawn" from the surroundings will be $-q_p$.

From the thermodynamic definition of entropy, the change of the entropy of the surroundings will be

$$\Delta S_{surr} = -\frac{q_p}{T} = -\frac{\Delta H_{sys}}{T}. \tag{8.8.4}$$

We can therefore rewrite Equation 8.8.3 as

$$\Delta S_{univ} = \frac{-\Delta H_{sys}}{T} + \Delta S_{sys} \tag{8.8.5}$$

Multiplying through by $-T$, we obtain

$$-T\,\Delta S_{univ} = \Delta H_{sys} - T\,\Delta S_{sys} \tag{8.8.6}$$

which expresses the entropy change of the universe in terms of thermodynamic properties of the *system* exclusively.

If $-T\Delta S_{univ}$ is denoted by ΔG, then we have Equation 8.8.2 which defines the *Gibbs energy* change for the process.

$$\Delta G = \Delta H - T\Delta S$$

$T\,\Delta S_{total}$ $T\,\Delta S_{surr}$ $T\,\Delta S_{system}$

The criterion for predicting spontaneity is based on (ΔG), the change in G, at constant temperature and pressure. Although very few chemical reactions actually occur under conditions of constant temperature and pressure, most systems can be brought back to the initial temperature and pressure without significantly affecting the value of thermodynamic state functions such as G. At constant temperature and pressure,

$$\Delta G = \Delta H - T\Delta S \tag{8.8.7}$$

where all thermodynamic quantities are those of the system. Recall that at constant pressure, $\Delta H = q$, whether a process is reversible or irreversible, and

$$T\Delta S = q_{rev}. \tag{8.8.8}$$

Using these expressions, we can reduce Equation 8.8.7 to

$$\Delta G = q - q_{rev}. \tag{8.8.9}$$

Thus ΔG is the difference between the heat released during a process (via a reversible or an irreversible path) and the heat released for the same process occurring in a reversible manner. Under the special condition in which a process occurs reversibly, $q = q_{rev}$ and $\Delta G = 0$. As we shall soon see, if ΔG is zero, the system is at equilibrium, and there will be no net change.

What about processes for which $\Delta G \neq 0$? To understand how the sign of ΔG for a system determines the direction in which change is spontaneous, we can rewrite the relationship between ΔS and q_{rev}, discussed earlier.

$$\Delta S = \frac{q_{rev}}{T}$$

with the definition of ΔH in terms of q_{rev}

$$q_{rev} = \Delta H$$

to obtain

$$\Delta S_{\text{surr}} = -\frac{\Delta H_{\text{sys}}}{T} \tag{8.8.10}$$

Thus the entropy change of the surroundings is related to the enthalpy change of the system. We have stated that for a spontaneous reaction, $\Delta S_{univ} > 0$, so substituting we obtain

$$\begin{aligned} \Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0 \\ &= \Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} > 0 \end{aligned}$$

Multiplying both sides of the inequality by $-T$ reverses the sign of the inequality; rearranging,

$$\Delta H_{sys} - T\Delta S_{sys} < 0 \tag{8.8.11}$$

which is equal to ΔG (Equation 8.8.7). We can therefore see that for a spontaneous process, $\Delta G_{sys} < 0$.

The relationship between the entropy change of the surroundings and the heat gained or lost by the system provides the key connection between the thermodynamic properties of the system and the change in entropy of the universe. The relationship shown in Equation 8.8.7 allows us to predict spontaneity by focusing exclusively on the thermodynamic properties and temperature of the system. We predict that highly exothermic processes ($\Delta H \ll 0$) that increase the entropy of a system ($\Delta S_{sys} \gg 0$) would therefore occur spontaneously. An example of such a process is the decomposition of ammonium nitrate fertilizer. Ammonium nitrate was also used to destroy the Murrah Federal Building in Oklahoma City, Oklahoma, in 1995. For a system at constant temperature and pressure, we can summarize the following results:

- If $\Delta G < 0$, the process occurs spontaneously.
- If $\Delta G = 0$, the system is at equilibrium.
- If $\Delta G > 0$, the process is not spontaneous as written but occurs spontaneously in the reverse direction.

To further understand how the various components of ΔG dictate whether a process occurs spontaneously, we now look at a simple and familiar physical change: the conversion of liquid water to water vapor.

Example 8.8.1: Vaporizing Water

At Room Temperature (100 °C)

If the conversion of liquid water to water vapor is carried out at 1 atm and the normal boiling point of 100.00 °C (373.15 K), we can calculate ΔG from the experimentally measured value of ΔH_{vap} (40.657 kJ/mol). For vaporizing 1 mol of water, $\Delta H = 40,657; J$, so the process is highly endothermic. From the definition of ΔS (Equation 8.8.10), we know that for 1 mol of water,

$$\begin{aligned}\Delta S_{\text{vap}} &= \frac{\Delta H_{\text{vap}}}{T_{\text{b}}} \\ &= \frac{40{,}657\ \text{J}}{373.15\ \text{K}} \\ &= 108.96\ \text{J/K}\end{aligned}$$

Hence there is an increase in the disorder of the system. At the normal boiling point of water,

$$\begin{aligned}\Delta G_{100^\circ\text{C}} &= \Delta H_{100^\circ\text{C}} - T\Delta S_{100^\circ\text{C}} \\ &= 40{,}657\ \text{J} - [(373.15\ \text{K})(108.96\ \text{J/K})] \\ &= 0\ \text{J}\end{aligned}$$

The energy required for vaporization offsets the increase in entropy of the system. Thus $\Delta G = 0$, and the liquid and vapor are in equilibrium, as is true of any liquid at its boiling point under standard conditions.

Above Room Temperature (110 °C)

Now suppose we were to superheat 1 mol of liquid water to 110°C. The value of ΔG for the vaporization of 1 mol of water at 110°C, assuming that ΔH and ΔS do not change significantly with temperature, becomes

$$\begin{aligned}\Delta G_{110^\circ\text{C}} &= \Delta H - T\Delta S \\ &= 40{,}657\ \text{J} - [(383.15\ \text{K})(108.96\ \text{J/K})] \\ &= -1{,}091\ \text{J}\end{aligned}$$

Since $\Delta G < 0$, the vaporization of water is predicted to occur spontaneously and irreversibly at 110 °C.

Below Room Temperature (90 °C)

We can also calculate ΔG for the vaporization of 1 mol of water at a temperature below its normal boiling point—for example, 90°C—making the same assumptions:

$$\begin{aligned}\Delta G_{90^\circ\text{C}} &= \Delta H - T\Delta S \\ &= 40{,}657\ \text{J} - [(363.15\ \text{K})(108.96\ \text{J/K})] \\ &= 1{,}088\ \text{J}\end{aligned}$$

Since $\Delta G > 0$, water does not spontaneously convert to water vapor at 90 °C. When using all the digits in the calculator display in carrying out our calculations, $\Delta G_{110^\circ\text{C}} = 1090\ \text{J} = -\Delta G_{90^\circ\text{C}}$, as we would predict.

Equilibrium Temperature

We can also calculate the temperature at which liquid water is in equilibrium with water vapor. Inserting the values of ΔH and ΔS into the definition of ΔG (Equation 8.8.7), setting $\Delta G = 0$, and solving for T,

$$\begin{aligned}0 &= 40,657\,J - T(108.96\,J/K) \\ T &= 373.15\,K\end{aligned}$$

Thus $\Delta G = 0$ at $T = 373.15\,K$ and $1\ atm$, which indicates that liquid water and water vapor are in equilibrium; this temperature is called the normal boiling point of water.

At temperatures greater than 373.15 K, ΔG is negative, and water evaporates spontaneously and irreversibly. Below 373.15 K, ΔG is positive, and water does not evaporate spontaneously. Instead, water vapor at a temperature less than 373.15 K and 1 atm

will spontaneously and irreversibly condense to liquid water. Figure 8.8.1 shows how the ΔH and $T\Delta S$ terms vary with temperature for the vaporization of water. When the two lines cross, $\Delta G = 0$, and $\Delta H = T\Delta S$.

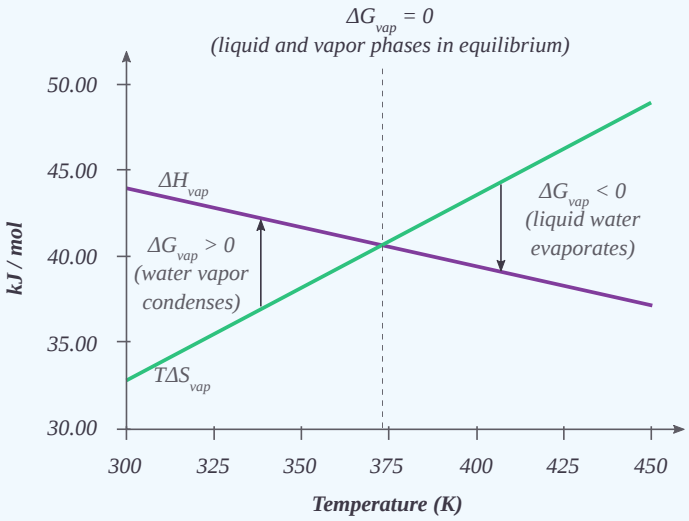


Figure 8.8.1: Temperature Dependence of ΔH and TΔS for the Vaporization of Water. Both ΔH and TΔS are temperature dependent, but the lines have opposite slopes and cross at 373.15 K at 1 atm, where ΔH = TΔS. Because ΔG = ΔH − TΔS, at this temperature ΔG = 0, indicating that the liquid and vapor phases are in equilibrium. The normal boiling point of water is therefore 373.15 K. Above the normal boiling point, the $T\Delta S$ term is greater than ΔH, making ΔG < 0; hence, liquid water evaporates spontaneously. Below the normal boiling point, the ΔH term is greater than $T\Delta S$, making ΔG > 0. Thus liquid water does not evaporate spontaneously, but water vapor spontaneously condenses to liquid. (CC BY-NC; Ümit Kaya)

A similar situation arises in the conversion of liquid egg white to a solid when an egg is boiled. The major component of egg white is a protein called albumin, which is held in a compact, ordered structure by a large number of hydrogen bonds. Breaking them requires an input of energy ($\Delta H > 0$), which converts the albumin to a highly disordered structure in which the molecules aggregate as a disorganized solid ($\Delta S > 0$). At temperatures greater than 373 K, the $T\Delta S$ term dominates, and $\Delta G < 0$, so the conversion of a raw egg to a hard-boiled egg is an irreversible and spontaneous process above 373 K.

Figure 8.8.1

ΔH	ΔS	$-T\Delta S$	ΔG
- (exothermic)	+ (products more disordered)	- (favors spontaneity)	- (spontaneous at all T)
- (exothermic)	- (products less disordered)	+ (opposes spontaneity)	- (spontaneous) at low T + (non-spontaneous) at high T **"Enthalpically-driven process"**
+ (endothermic)	+ (products more disordered)	- (favors spontaneity)	+ (non-spontaneous) at low T - (spontaneous) at high T **"Entropically-driven process"**
+ (endothermic)	- (products less disordered)	+ (opposes spontaneity)	+ (non-spontaneous at all T)

Enthalpically vs. Entropically Driving Reactions

Some textbooks and teachers say that the free energy, and thus the spontaneity of a reaction, depends on both the enthalpy and entropy changes of a reaction, and they sometimes even refer to reactions as "energy driven" or "entropy driven" depending on whether ΔH or the $T\Delta S$ term dominates. This is technically correct, but misleading because it disguises the important fact that ΔS_{total}, which this equation expresses in an indirect way, is the *only* criterion of spontaneous change.

Consider the following possible states for two different types of molecules with some attractive force:

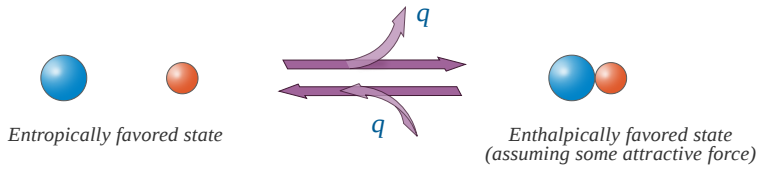


Figure 8.8.2: An enthalpic favored reaction. (CC BY-NC; Ümit Kaya)

There would appear to be greater entropy on the left (state 1) than on the right (state 2). Thus the entropic change for the reaction as written (i.e. going to the right) would be (-) in magnitude, and the energetic contribution to the free energy change would be (+) (i.e. unfavorable) for the reaction as written.

In going to the right, there is an attractive force and the molecules adjacent to each other is a lower energy state (heat energy, q, is liberated). To go to the left, we have to overcome this attractive force (input heat energy) and the left direction is unfavorable with regard to heat energy q. The change in enthalpy is (-) in going to the right (q released), and this enthalpy change is negative (-) in going to the right (and (+) in going to the left). This reaction as written, is therefore, *enthalpically favorable* and *entropically unfavorable*. Hence, It is *enthalpically driven*.

From Table 8.8.1, it would appear that we might be able to get the reaction to go to the right at low temperatures (lower temperature would minimize the energetic contribution of the entropic change). Looking at the same process from an opposite direction:

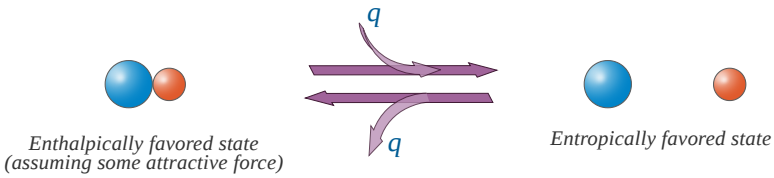


Figure 8.8.3: An entropically favored reaction. (CC BY-NC; Ümit Kaya)

This reaction as written, is *entropically favorable*, and *enthalpically unfavorable;* it is *entropically driven*. From Table 8.8.1, it would appear that we might be able to get the reaction to go to the right at high temperatures (high temperature would increase the energetic contribution of the entropic change).

The Relationship between ΔG and Work

In the previous subsection, we learned that the value of ΔG allows us to predict the spontaneity of a physical or a chemical change. In addition, the magnitude of ΔG for a process provides other important information. The change in Gibbs energy is equal to the maximum amount of work that a system can perform on the surroundings while undergoing a spontaneous change (at constant temperature and pressure):

$$\Delta G = w_{max}. \tag{8.8.12}$$

To see why this is true, let's look again at the relationships among free energy, enthalpy, and entropy expressed in Equation 8.8.7. We can rearrange this equation as follows:

$$\Delta H = \Delta G + T\Delta S \tag{8.8.13}$$

This equation tells us that when energy is released during an exothermic process ($\Delta H < 0$), such as during the combustion of a fuel, some of that energy can be used to do work ($\Delta G < 0$), while some is used to increase the entropy of the universe ($T\Delta S > 0$). Only if the process occurs infinitely slowly in a perfectly reversible manner will the entropy of the universe be unchanged. Because no real system is perfectly reversible, the entropy of the universe increases during all processes that produce energy. As a result, no process that uses stored energy can ever be 100% efficient; that is, ΔH will never equal ΔG because ΔS has a positive value.

One of the major challenges facing engineers is to maximize the efficiency of converting stored energy to useful work or converting one form of energy to another. As indicated in Table **8.8.2**, the efficiencies of various energy-converting devices vary widely. For example, an internal combustion engine typically uses only 25%–30% of the energy stored in the hydrocarbon fuel to perform work; the rest of the stored energy is released in an unusable form as heat. In contrast, gas–electric hybrid engines, now used in several models of automobiles, deliver approximately 50% greater fuel efficiency. A large electrical generator is highly efficient (approximately 99%) in converting mechanical to electrical energy, but a typical incandescent light bulb is one of the least efficient devices known (only approximately 5% of the electrical energy is converted to light). In contrast, a mammalian liver cell is a relatively efficient machine and can use fuels such as glucose with an efficiency of 30%–50%.

Table **8.8.2**: Approximate Thermodynamic Efficiencies of Various Devices

Device	Energy Conversion	Approximate Efficiency (%)
large electrical generator	mechanical → electrical	99
chemical battery	chemical → electrical	90
home furnace	chemical → heat	65
small electric tool	electrical → mechanical	60
space shuttle engine	chemical → mechanical	50
mammalian liver cell	chemical → chemical	30–50
spinach cell	light → chemical	30
internal combustion engine	chemical → mechanical	25–30
fluorescent light	electrical → light	20
solar cell	light → electricity	10
incandescent light bulb	electricity → light	5
yeast cell	chemical → chemical	2–4

Standard Free-Energy Change

We have seen that there is no way to measure absolute enthalpies, although we can measure changes in enthalpy (ΔH) during a chemical reaction. Because enthalpy is one of the components of Gibbs free energy, we are consequently unable to measure absolute free energies; we can measure only changes in free energy. The standard free-energy change (ΔG°) is the change in free energy when one substance or a set of substances in their standard states is converted to one or more other substances, also in their standard states. The standard free-energy change can be calculated from the definition of free energy, if the standard enthalpy and entropy changes are known, using Equation 8.8.14:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{8.8.14}$$

If ΔS° and ΔH° for a reaction have the same sign, then the sign of ΔG^o depends on the relative magnitudes of the ΔH° and TΔS° terms. It is important to recognize that a positive value of ΔG^o for a reaction does not mean that no products will form if the reactants in their standard states are mixed; it means only that at equilibrium the concentrations of the products will be less than the concentrations of the reactants.

> A positive ΔG^o means that the equilibrium constant is less than 1.

Example 8.8.1

Calculate the standard free-energy change (ΔG°) at 25°C for the reaction

$$\mathrm{H_2\,(g) + O_2\,(g) \rightleftharpoons H_2O_2\,(l)}$$

At 25°C, the standard enthalpy change (ΔH°) is −187.78 kJ/mol, and the absolute entropies of the products and reactants are:

- $S°(H_2O_2)$ = 109.6 J/(mol•K),
- $S°(O_2)$ = 205.2 J/(mol•K), and
- $S°(H_2)$ = 130.7 J/(mol•K).

Is the reaction spontaneous as written?

Given: balanced chemical equation, ΔH° and S° for reactants and products

Asked for: spontaneity of reaction as written

Strategy:

A. Calculate ΔS° from the absolute molar entropy values given.
B. Use Equation 8.8.14, the calculated value of ΔS°, and other data given to calculate ΔG^o for the reaction.
C. Use the value of ΔG^o to determine whether the reaction is spontaneous as written.

Solution

A To calculate ΔG^o for the reaction, we need to know ΔH°, ΔS°, and T. We are given ΔH°, and we know that T = 298.15 K. We can calculate ΔS° from the absolute molar entropy values provided using the "products minus reactants" rule:

$$\begin{aligned}\Delta S^\circ &= S^\circ(\mathrm{H_2O_2}) - [S^\circ(\mathrm{O_2}) + S^\circ(\mathrm{H_2})] \\ &= [1\ \mathrm{mol\ H_2O_2} \times 109.6\ \mathrm{J/(mol \cdot K)}] \\ &\quad - \{[1\ \mathrm{mol\ H_2} \times 130.7\ \mathrm{J/(mol \cdot K)}] + [1\ \mathrm{mol\ O_2} \times 205.2\ \mathrm{J/(mol \cdot K)}]\} \\ &= -226.3\ \mathrm{J/K\ (per\ mole\ of\ H_2O_2)}\end{aligned}$$

As we might expect for a reaction in which 2 mol of gas is converted to 1 mol of a much more ordered liquid, ΔS° is very negative for this reaction.

B Substituting the appropriate quantities into Equation 8.8.14,

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -187.78\ \mathrm{kJ/mol} - (298.15\ \mathrm{K})[-226.3\ \mathrm{J/(mol \cdot K)} \times 1\ \mathrm{kJ/1000\ J}] \\ &= -187.78\ \mathrm{kJ/mol} + 67.47\ \mathrm{kJ/mol} \\ &= -120.31\ \mathrm{kJ/mol}\end{aligned}$$

The negative value of ΔG^o indicates that the reaction is spontaneous as written. Because ΔS° and ΔH° for this reaction have the same sign, the sign of ΔG^o depends on the relative magnitudes of the ΔH° and TΔS° terms. In this particular case, the enthalpy term dominates, indicating that the strength of the bonds formed in the product more than compensates for the unfavorable ΔS° term and for the energy needed to break bonds in the reactants.

Exercise 8.8.1

Calculate the standard free-energy change (ΔG°) at 25°C for the reaction

$$\mathrm{2\,H_2\,(g) + N_2\,(g) \rightleftharpoons N_2H_4\,(l).}$$

At 25°C, the standard enthalpy change (ΔH°) is 50.6 kJ/mol, and the absolute entropies of the products and reactants are $S°(N_2H_4)$ = 121.2 J/(mol•K), $S°(N_2)$ = 191.6 J/(mol•K), and $S°(H_2)$ = 130.7 J/(mol•K). Is the reaction spontaneous as written?

Answer

149.5 kJ/mol; no

Tabulated values of standard free energies of formation allow chemists to calculate the values of ΔG^o for a wide variety of chemical reactions rather than having to measure them in the laboratory. The standard free energy of formation (ΔG°_f)of a compound is the change in free energy that occurs when 1 mol of a substance in its standard state is formed from the component elements in their standard states. By definition, the standard free energy of formation of an element in its standard state is zero at 298.15 K. One mole of Cl_2 gas at 298.15 K, for example, has $\Delta G^\circ_f = 0$. The standard free energy of formation of a compound can be calculated from the standard enthalpy of formation (ΔH°_f) and the standard entropy of formation (ΔS°_f) using the definition of free energy:

$$\Delta G^o_f = \Delta H^o_f - T\Delta S^o_f \tag{8.8.15}$$

Using standard free energies of formation to calculate the standard free energy of a reaction is analogous to calculating standard enthalpy changes from standard enthalpies of formation using the familiar "products minus reactants" rule:

$$\Delta G^o_{rxn} = \sum m\Delta G^o_f(products) - \sum n\Delta G^o_f(reactants) \tag{8.8.16}$$

where m and n are the stoichiometric coefficients of each product and reactant in the balanced chemical equation. A very large negative ΔG^o indicates a strong tendency for products to form spontaneously from reactants; it does not, however, necessarily indicate that the reaction will occur rapidly. To make this determination, we need to evaluate the kinetics of the reaction.

"Products minus Reactants" Rule

The ΔG^o of a reaction can be calculated from tabulated ΔG^o_f values (Table T1) using the "products minus reactants" rule.

Example 8.8.2

Calculate ΔG^o for the reaction of isooctane with oxygen gas to give carbon dioxide and water. Use the following data:

- ΔG°_f(isooctane) = −353.2 kJ/mol,
- $\Delta G^\circ_f(CO_2)$ = −394.4 kJ/mol, and
- $\Delta G^\circ_f(H_2O)$ = −237.1 kJ/mol.

Is the reaction spontaneous as written?

Given: balanced chemical equation and values of ΔG°_f for isooctane, CO_2, and H_2O

Asked for: spontaneity of reaction as written

Strategy:

Use the "products minus reactants" rule to obtain ΔG°_{rxn}, remembering that ΔG°_f for an element in its standard state is zero. From the calculated value, determine whether the reaction is spontaneous as written.

Solution

The balanced chemical equation for the reaction is as follows:

$$C_8H_{18}\,(l) + \tfrac{25}{2}\,O_2\,(g) \longrightarrow 8\,CO_2\,(g) + 9\,H_2O\,(l)$$

We are given ΔG°_f values for all the products and reactants except O_2(g). Because oxygen gas is an element in its standard state, $\Delta G^\circ_f\,(O_2)$ is zero. Using the "products minus reactants" rule,

$$\begin{aligned}\Delta G^\circ &= [8\Delta G^\circ_f(CO_2) + 9\Delta G^\circ_f(H_2O)] - \left[1\Delta G^\circ_f(C_8H_{18}) + \frac{25}{2}\Delta G^\circ_f(O_2)\right]\\ &= [(8\text{ mol})(-394.4\text{ kJ/mol}) + (9\text{ mol})(-237.1\text{ kJ/mol})]\\ &\quad - \left[(1\text{ mol})(-353.2\text{ kJ/mol}) + \left(\frac{25}{2}\text{ mol}\right)(0\text{ kJ/mol})\right]\\ &= -4935.9\text{ kJ (per mol of } C_8H_{18})\end{aligned}$$

Because ΔG^o is a large negative number, there is a strong tendency for the spontaneous formation of products from reactants (though not necessarily at a rapid rate). Also notice that the magnitude of ΔG^o is largely determined by the ΔG°_f of the stable products: water and carbon dioxide.

Exercise 8.8.2

Calculate ΔG^o for the reaction of benzene with hydrogen gas to give cyclohexane using the following data

- ΔG°_f(benzene) = 124.5 kJ/mol
- ΔG°_f (cyclohexane) = 217.3 kJ/mol.

Is the reaction spontaneous as written?

Answer

92.8 kJ; no

Calculated values of ΔG^o are extremely useful in predicting whether a reaction will occur spontaneously if the reactants and products are mixed under standard conditions. We should note, however, that very few reactions are actually carried out under standard conditions, and calculated values of ΔG^o may not tell us whether a given reaction will occur spontaneously under nonstandard conditions. What determines whether a reaction will occur spontaneously is the free-energy change (ΔG) under the actual experimental conditions, which are usually different from ΔG°. If the ΔH and TΔS terms for a reaction have the same sign, for example, then it may be possible to reverse the sign of ΔG by changing the temperature, thereby converting a reaction that is not thermodynamically spontaneous, having $K_{eq} < 1$, to one that is, having a $K_{eq} > 1$, or vice versa. Because ΔH and ΔS usually do not vary greatly with temperature in the absence of a phase change, we can use tabulated values of ΔH° and ΔS° to calculate ΔG^o at various temperatures, as long as no phase change occurs over the temperature range being considered.

In the absence of a phase change, neither ΔH nor ΔS vary greatly with temperature.

Example 8.8.3

Calculate (a) ΔG^o and (b) $\Delta G_{300°C}$ for the reaction $N_2(g)+3H_2(g)\rightleftharpoons 2NH_3(g)$, assuming that ΔH and ΔS do not change between 25°C and 300°C. Use these data:

- $S°(N_2)$ = 191.6 J/(mol•K),
- $S°(H_2)$ = 130.7 J/(mol•K),
- $S°(NH_3)$ = 192.8 J/(mol•K), and
- ΔH°_f (NH_3) = −45.9 kJ/mol.

Given: balanced chemical equation, temperatures, S° values, and ΔH°_f for NH_3

Asked for: ΔG^o and ΔG at 300°C

Strategy:

A. Convert each temperature to kelvins. Then calculate ΔS° for the reaction. Calculate ΔH° for the reaction, recalling that ΔH°_f for any element in its standard state is zero.
B. Substitute the appropriate values into Equation 8.8.14 to obtain ΔG^o for the reaction.
C. Assuming that ΔH and ΔS are independent of temperature, substitute values into Equation 8.8.7 to obtain ΔG for the reaction at 300°C.

Solution

A To calculate ΔG^o for the reaction using Equation 8.8.14, we must know the temperature as well as the values of ΔS° and ΔH°. At standard conditions, the temperature is 25°C, or 298 K. We can calculate ΔS° for the reaction from the absolute molar entropy values given for the reactants and the products using the “products minus reactants” rule:

$$\begin{aligned}\Delta S^\circ_{rxn} &= 2S^\circ(NH_3) - [S^\circ(N_2) + 3S^\circ(H_2)] \\ &= [2\text{ mol } NH_3 \times 192.8\text{ J/(mol}\cdot\text{K)}] \\ &\quad - \{[1\text{ mol } N_2 \times 191.6\text{ J/(mol}\cdot\text{K)}] + [3\text{ mol } H_2 \times 130.7\text{ J/(mol}\cdot\text{K)}]\} \\ &= -198.1\text{ J/K (per mole of } N_2)\end{aligned}$$

We can also calculate ΔH° for the reaction using the "products minus reactants" rule. The value of ΔH°_f (NH_3) is given, and ΔH°_f is zero for both N_2 and H_2:

$$\begin{aligned}\Delta H^\circ_{rxn} &= 2\Delta H^\circ_f(NH_3) - [\Delta H^\circ_f(N_2) + 3\Delta H^\circ_f(H_2)] \\ &= [2 \times (-45.9\text{ kJ/mol})] - [(1 \times 0\text{ kJ/mol}) + (3 \times 0\text{ kJ/mol})] \\ &= -91.8\text{ kJ(per mole of } N_2)\end{aligned}$$

B Inserting the appropriate values into Equation 8.8.14

$$\begin{aligned}\Delta G^\circ_{rxn} &= \Delta H^\circ - T\Delta S^\circ \\ &= (-91.8\text{ kJ}) - (298\text{ K})(-198.1\text{ J/K})(1\text{ kJ}/1000\text{ J}) \\ &= -32.7\text{ kJ (per mole of } N_2)\end{aligned}$$

C To calculate ΔG for this reaction at 300°C, we assume that ΔH and ΔS are independent of temperature (i.e., $\Delta H_{300°C}$ = H° and $\Delta S_{300°C}$ = ΔS°) and insert the appropriate temperature (573 K) into Equation 8.8.7:

$$\begin{aligned}\Delta G_{300°C} &= \Delta H_{300°C} - (573\text{ K})(\Delta S_{300°C}) \\ &= \Delta H^\circ - (573\text{ K})\Delta S^\circ \\ &= (-91.8\text{ kJ}) - (573\text{ K})(-198.1\text{ J/K})(1\text{ kJ}/1000\text{ J}) \\ &= 21.7\text{ kJ (per mole of } N_2)\end{aligned}$$

In this example, changing the temperature has a major effect on the thermodynamic spontaneity of the reaction. Under standard conditions, the reaction of nitrogen and hydrogen gas to produce ammonia is thermodynamically spontaneous, but in practice, it is too slow to be useful industrially. Increasing the temperature in an attempt to make this reaction occur more rapidly also changes the thermodynamics by causing the −TΔS° term to dominate, and the reaction is no longer spontaneous at high temperatures; that is, its K_{eq} is less than one. This is a classic example of the conflict encountered in real systems between thermodynamics and kinetics, which is often unavoidable.

? Exercise 8.8.3

Calculate

a. ΔG° and
b. $\Delta G_{750°C}$

for the following reaction

$$2\,NO\,(g) + O_2\,(g) \rightleftharpoons 2\,NO_2\,(g)$$

which is important in the formation of urban smog. Assume that ΔH and ΔS do not change between 25.0°C and 750°C and use these data:

- S°(NO) = 210.8 J/(mol•K),
- S°(O_2) = 205.2 J/(mol•K),
- S°(NO_2) = 240.1 J/(mol•K),
- ΔH°_f(NO_2) = 33.2 kJ/mol, and
- ΔH°_f (NO) = 91.3 kJ/mol.

Answer a

−72.5 kJ/mol of O_2

Answer b

33.8 kJ/mol of O_2

The effect of temperature on the spontaneity of a reaction, which is an important factor in the design of an experiment or an industrial process, depends on the sign and magnitude of both ΔH° and ΔS°. The temperature at which a given reaction is at equilibrium can be calculated by setting $\Delta G^o = 0$ in Equation 8.8.14, as illustrated in Example 8.8.4.

Example 8.8.4

As you saw in Example 8.8.3, the reaction of nitrogen and hydrogen gas to produce ammonia is one in which ΔH° and ΔS° are both negative. Such reactions are predicted to be thermodynamically spontaneous at low temperatures but nonspontaneous at high temperatures. Use the data in Example 8.8.3 to calculate the temperature at which this reaction changes from spontaneous to nonspontaneous, assuming that ΔH° and ΔS° are independent of temperature.

Given: ΔH° and ΔS°

Asked for: temperature at which reaction changes from spontaneous to nonspontaneous

Strategy:

Set ΔG^o equal to zero in Equation 8.8.14 and solve for T, the temperature at which the reaction becomes nonspontaneous.

Solution

In Example 8.8.3, we calculated that ΔH° is −91.8 kJ/mol of N_2 and ΔS° is −198.1 J/K per mole of N_2, corresponding to ΔG^o = −32.7 kJ/mol of N_2 at 25°C. Thus the reaction is indeed spontaneous at low temperatures, as expected based on the signs of ΔH° and ΔS°. The temperature at which the reaction becomes nonspontaneous is found by setting ΔG^o equal to zero and rearranging Equation 8.8.14 to solve for T:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 0$$

$$\Delta H^\circ = T\Delta S^\circ$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{(-91.8\ \text{kJ})(1000\ \text{J/kJ})}{-198.1\ \text{J/K}} = 463\ \text{K}$$

This is a case in which a chemical engineer is severely limited by thermodynamics. Any attempt to increase the rate of reaction of nitrogen with hydrogen by increasing the temperature will cause reactants to be favored over products above 463 K.

Exercise 8.8.4

As you found in the exercise in Example 8.8.3, ΔH° and ΔS° are both negative for the reaction of nitric oxide and oxygen to form nitrogen dioxide. Use those data to calculate the temperature at which this reaction changes from spontaneous to nonspontaneous.

Answer

792.6 K

Summary

- The change in Gibbs free energy, which is based solely on changes in state functions, is the criterion for predicting the spontaneity of a reaction.
- Free-energy change

$$\Delta G = \Delta H - T\Delta S$$

- Standard free-energy change

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

We can predict whether a reaction will occur spontaneously by combining the entropy, enthalpy, and temperature of a system in a new state function called Gibbs free energy (G). The change in free energy (ΔG) is the difference between the heat released during

a process and the heat released for the same process occurring in a reversible manner. If a system is at equilibrium, $\Delta G = 0$. If the process is spontaneous, $\Delta G < 0$. If the process is not spontaneous as written but is spontaneous in the reverse direction, $\Delta G > 0$. At constant temperature and pressure, ΔG is equal to the maximum amount of work a system can perform on its surroundings while undergoing a spontaneous change. The standard free-energy change ($\Delta G°$) is the change in free energy when one substance or a set of substances in their standard states is converted to one or more other substances, also in their standard states. The standard free energy of formation (ΔG°_f), is the change in free energy that occurs when 1 mol of a substance in its standard state is formed from the component elements in their standard states. Tabulated values of standard free energies of formation are used to calculate ΔG^o for a reaction.

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8.E: PRINCIPLES OF THERMODYNAMICS (EXERCISES)

These are homework exercises to accompany the Textmap created for "Principles of Modern Chemistry" by Oxtoby et al. Complementary General Chemistry question banks can be found for other Textmaps and can be accessed here.

8.E.1 Q3

Write detailed calculation down for each question involved in gambling,

a. How many “microstates” are there for the cards that come up from five random cards each from a separate deck?
b. What is the probability of getting 5 queens of hearts?
c. What is the probability of getting any specific hand of five cards?

8.E.2 Q5

Is the above reaction spontaneous under 1 atm and room temperature? If so, what are the driving factors?

$$3\,NO\,(g) \rightleftharpoons N_2O\,(g) + NO_2\,(g)$$

8.E.3 Q9

For each of the following scenarios predict the system's entropy change whether it is $\Delta S < 0$, $\Delta S = 0$, or $\Delta S > 0$.

a. Increasing the amount of quarters being flipped from 2 to 4.
b. Moving a child from a 30 ft. × 30 ft. room to a 5 ft. × 5 ft. room to play in .
c. Increasing the temperature of a non-ideal polyatomic gas.

8.E.4 Q10

Determine whether the change in entropy for the processes listed down below are positive or negative:

a. condensing of iodine gas into a solid
b. diffusion of an ideal gas

8.E.5 Q11

Osmium melts at 3,027 °C and has an enthalpy change of fusion of 31.0 kJ/mol. Calculate the entropy of fusion of osmium.

8.E.6 Q13

Trouton's Rule is used to estimate the molar enthalpy of vaporization. What is iodine's enthalpy of vaporization if its normal boiling point is 184.4ºC?

8.E.7 Q15

If 0.250 mol Argon is expanded reversibly and isothermally at 400 K in its compressible oven from an initial volume of 12.0 L to a final volume of 30.0 L, what will the ΔU, q, w, ΔH, and ΔS for the gas?

8.E.8 Q17

Consider this. Exactly 2 moles of ice undergoes three different processes.

I. heated reversibly at atmospheric pressure from temperature X to 0 °C, then
II. melted reversibly at 0 °C. Finally
III. it was heated reversibly at atmospheric pressure up to an unknown temperature Y.

Find temperature X & Y and identify ΔS_{surr}.

Given:

- ΔH_{fus} = 6007 J.mol^{-1}
- C_p (ice) = 38 J.K^{-1}.mol^{-1}
- C_p (water) = 75 J.K^{-1}.mol^{-1}
- ΔS_{I} = 12.034 J.K^{-1}
- ΔS_{III} = 136 J.K^{-1}

8.E.9 Q18

Suppose 2 moles of water at standard temperature (25°C) and pressure is spontaneously evaporated by allowing it to fall onto a nickel plate maintained at 125°C. Calculate ΔS for the water, ΔS for the nickel plate, and ΔS_{total} if $C_{p(H_2O)(l)}$= 75.4 J/(K.mol) and $C_{p(H_2O)(g)}$ = 36.0 J/(K.mol). Take ΔH_{vap} = 40.68 KJ/mol for water and its boiling point of 100°C.

8.E.10 Q19

A 181.49 g sample of lead at 97.0ºC initially is added to a coffee cup calorimeter that contains 150.0 g water which is at 24.7ºC. The equilibrium temperature is 29.4ºC, assuming that there is no heat lost to the calorimeter or the environment. The molar heat capacity of lead (C_p(Pb)) is 26.4 J K^{-1} mol^{-1} and that of water ($C_p(H_2O)$) is 75.2 J K^{-1} mol^{-1}. What is ΔS for the lead sample, ΔS for the water sample, and ΔS_{total} for this process?

8.E.11 Q20

Copper has a heat capacity of 38.5 J K^{-1} mol^{-1}, approximately independent of temperature between 0°C to 100°C. Calculate the enthalpy and entropy change of 5.00 moles of copper as it is cooled at atmospheric pressure from 100°C to 0°C.

8.E.12 Q23

The alkaline earth metals react with oxygen to give the following compounds:

$$2\,Be\,(g) + O_2\,(g) \longrightarrow 2\,BeO\,(s)$$

$$2\,Mg\,(g) + O_2\,(g) \longrightarrow 2\,MgO\,(s)$$

$$2\,Ca\,(g) + O_2\,(g) \longrightarrow 2\,CaO\,(s)$$

Compute ΔS for each reaction, and identify a periodic trend about the entropy.

8.E.13 Q27

Is the entropy change in the reaction positive, negative or zero and why?

$$CH_4\,(g) + 2\,O_2\,(g) \longrightarrow CO_2\,(g) + 2\,H_2O\,(l)$$

Hint: You don't need to actually calculate the change in entropy to determine whether the change in entropy is positive or negative. Think about it conceptually.

8.E.14 Q33

At **25.0°C** the reaction below is not spontaneous.

$$2\,H_2O\,(g) \longrightarrow 2\,H_2\,(g) + O_2\,(g)$$

with $\Delta G = +228.59\ \frac{kJ}{mol}$

If the above reaction were coupled with the following nonspontaneous reaction, could it be made to proceed? Why or Why not?

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

with $\Delta G = -16.48\ \frac{kJ}{mol}$

8.E.15 Q35A

A reaction at constant temperature and pressure is spontaneous if $\Delta G < 0$ and nonspontaneous if $\Delta G > 0$. Over what range of temperatures is each of the following processes spontaneous? Assume that all gases are at a pressure of 1 atm. (Hint: Use Tables T1 to calculate ΔH and ΔS (assumed independent of temperature and equal to $\Delta H°$ and $\Delta S°$, respectively, and then use the definition of ΔG).

a. Photosynthesis, a reaction of how plants produce food for themselves and animals, and convert carbon dioxide into water:

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

b. The combustion reaction of propane, found in gas grills and some fireplaces:

$$C_3H_8\,(g) + 5\,O_2\,(g) \longrightarrow 3\,CO_2\,(g) + 4\,H_2O\,(l)$$

c. Methane burning in O_2 gas.

$$CH_4\,(g) + 2\,O_2\,(g) \longrightarrow CO_2\,(g) + 2\,H_2O\,(l)$$

8.E.16 Q35B

Over what temperatures are these reactions spontaneous (under constant pressure and temperature)? You may need to use Table 1.

a. $\mathrm{S(s, rhombic) + Zn(s) \rightarrow ZnS(s, sphalerite)}$
b. $\mathrm{2\,Cu(s) + Cl_2 \rightarrow 2\,CuCl(s)}$
c. $\mathrm{4\,Al(s) + 3\,O_2(g) \rightarrow 2\,Al_2O_3(s)}$

8.E.17 Q37

Determine if the following reaction is spontaneous at 25°C by evaluating $\Delta H°_{rxn}$, $\Delta S°_{rxn}$ and $\Delta G°_{rxn}$.

$$\mathrm{N_2H_4(l) + O_2(g) \longrightarrow N_2(g) + 2\,H_2O(l)}$$

8.E.18 Q39

A thermodynamic engine operates cyclically and reversibly between two temperatures reservoirs, absorbing heat from the high-temperature bath at 600 K and discarding heat to low-temperature bath at 300 K.

a. What is the thermodynamic efficiency of the engine?
b. How much heat is absorbed from the high-temperature bath if -1800 J of heat is discarded to the low-temperature bath during each cycle?
c. How much work does the engine perform in one cycle of operation?

8.E.19 Q41

Acetone ($\mathrm{C_3H_6O}$) is an volatile liquid with a normal boiling point of 56°C and a molar enthalpy of vaporization of 29.1 kJ mol^{-1}. What is the molar entropy of vaporization of acetone under 1 atm of pressure?

8.E.20 Q53

Under standard conditions and 25°C, you have this reversible process

$$\mathrm{Sn(s, white) \longrightarrow Sn(s, gray)}$$

a. Is the change in entropy (ΔS) for this reaction positive or negative? Calculate the change in entropy using Table T1.
b. Calculate (ΔS) for the reaction if ΔH for this reaction is -2.1 kJ/mol.

8.E.21 Q59

Compute the ΔG_f° for the following reaction the reaction. The ΔG_f° of H_2SO_3 (aq) is -537.81 kJ mol^{-1}, the ΔG_f° of SO_2 (g) is -300.19 kJ mol^{-1}, and the ΔG_f° of H_2O (g) is -120.42 kJ mol^{-1}.

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

8.E.22 Q61

Professor Nesral wants to create some water through the combustion of hydrogen. This reaction is depicted as follows:

$$\mathrm{2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(g)}$$

Is this reaction spontaneous? Prove it by calculating $\Delta G°$ at 298.15K. Suppose that Nesral asks his friend in El Azizia, Libya, where the temperature is around $57°C$ (330K), to perform the same reaction. Calculate the Gibbs energy for this value and compare it to $\Delta G°$.

Relevant Information:

Entropy Values ($S°$; $\frac{J}{mol\,K}$)

- Hydrogen: **130.6**
- Water: **188.7**
- Oxygen: **205.6**

Enthalpy Values($H°$; $\frac{kJ}{mol}$)

- ΔH_f° Water: **−241.826**

8.E.23 Q63A

The concentration of sodium in the plasma is approximately 0.14 M. While in the fluid outside of the plasma, sodium concentration is about 0.5 M.

a. In what direction will the sodium ions spontaneously move past the cell wall?
b. The spontaneous process of movement in part a is called "passive transport". Movement in the opposite direction is called "active transport" and requires work to happen. Calculate the amount of free energy required to move 5 moles of Na^+ by active transport (non-spontaneous direction) at 273 K.

8.E.24 Q63B

For a hypothetical nerve cell, the sodium ion concentration is 0.015 M outside the cell and 0.00045 M inside the cell. Active transport involves using proteins and chemical energy stored in ATP to move the ions in a thermodynamically unfavorable direction. Assuming that conditions in the cell allow the hydrolysis of a single ATP molecule to give 2.05×10^{-18} J of usable enegy. How many molecules of ATP would be needed to move 0.005 moles of sodium ions using active transport at standard conditions? You can assume that the sodium ion concentrations remain constant.

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CHAPTER OVERVIEW

9: CHEMICAL EQUILIBRIUM

Chemical equilibrium is the state in which both reactants and products are present in concentrations which have no further tendency to change with time. This results when the forward reaction proceeds at the same rate as the reverse reaction. Thus, no net changes in the concentrations of the reactant(s) and product(s) are observed. This is known as dynamic equilibrium

9.1: The Nature of Chemical Equilibrium
9.2: The Empirical Law of Mass Action
9.3: Thermodynamic Description of the Equilibrium State
9.4: The Law of Mass Action for Related and Simultaneous Equilibria
9.5: Gas-Phase and Heterogeneous Reaction Equilibria
9.6: The Direction of Change in Chemical Reactions- Empirical Description
9.7: The Direction of Change in Chemical Reactions - Thermodynamic Explanation
9.8: Distribution between Immiscible Phases - Extraction and Separation Processes
9.E: Chemical Equilibrium (Exercises)

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9.1: THE NATURE OF CHEMICAL EQUILIBRIUM

LEARNING OBJECTIVES

- To understand what is meant by chemical equilibrium.

In the last chapter, we discussed the principles of chemical kinetics, which deal with the *rate of change*, or how quickly a given chemical reaction occurs. We now turn our attention to the *extent* to which a reaction occurs and how reaction conditions affect the final concentrations of reactants and products. For most of the reactions that we have discussed so far, you may have assumed that once reactants are converted to products, they are likely to remain that way. In fact, however, virtually all chemical reactions are *reversible* to some extent. That is, an opposing reaction occurs in which the products react, to a greater or lesser degree, to re-form the reactants. Eventually, the forward and reverse reaction rates become the same, and the system reaches **chemical equilibrium,** the point at which the composition of the system no longer changes with time.



Figure **9.1.1**: Dinitrogen tetroxide is a powerful oxidizer that reacts spontaneously upon contact with various forms of hydrazine, which makes the pair a popular propellant combination for rockets. Nitrogen dioxide at −196 °C, 0 °C, 23 °C, 35 °C, and 50 °C. (NO_2) converts to the colorless dinitrogen tetroxide (N_2O_4) at low temperatures, and reverts to NO_2 at higher temperatures. (CC BY-SA 3.0; Eframgoldberg).

Chemical equilibrium is a dynamic process that consists of a forward reaction, in which reactants are converted to products, and a reverse reaction, in which products are converted to reactants. At equilibrium, the forward and reverse reactions proceed at equal rates. Consider, for example, a simple system that contains only one reactant and one product, the reversible dissociation of dinitrogen tetroxide ($\mathbf{N_2O_4}$) to nitrogen dioxide ($\mathbf{NO_2}$). You may recall that $\mathbf{NO_2}$ is responsible for the brown color we associate with smog. When a sealed tube containing solid $\mathbf{N_2O_4}$ (mp = −9.3°C; bp = 21.2°C) is heated from −78.4°C to 25°C, the red-brown color of $\mathbf{NO_2}$ appears (Figure **9.1.1**). The reaction can be followed visually because the product ($\mathbf{NO_2}$) is colored, whereas the reactant ($\mathbf{N_2O_4}$) is colorless:

$$\underset{\textit{colorless}}{\mathbf{N_2O_4\,(g)}} \underset{\mathbf{k_r}}{\overset{\mathbf{k_f}}{\rightleftharpoons}} \underset{\textit{red–brown}}{\mathbf{2\,NO_2\,(g)}} \tag{9.1.1}$$

The double arrow indicates that both the forward reaction

$$\mathbf{N_2O_4\,(g)} \xrightarrow{\mathbf{k_f}} \mathbf{2\,NO_2\,(g)} \tag{9.1.2}$$

and reverse reaction

$$\mathbf{2\,NO_2\,(g)} \xrightarrow{\mathbf{k_r}} \mathbf{N_2O_4\,(g)} \tag{9.1.3}$$

occurring simultaneously (i.e, the reaction is reversible). However, this does not necessarily mean the system is equilibrium as the following chapter demonstrates.

Figure **9.1.2** shows how the composition of this system would vary as a function of time at a constant temperature. If the initial concentration of $\mathbf{NO_2}$ were zero, then it increases as the concentration of $\mathbf{N_2O_4}$ decreases. Eventually the composition of the system stops changing with time, and chemical equilibrium is achieved. Conversely, if we start with a sample that contains no $\mathbf{N_2O_4}$ but an initial $\mathbf{NO_2}$ concentration twice the initial concentration of $\mathbf{N_2O_4}$ (Figure **9.1.2***a*), in accordance with the stoichiometry of the reaction, we reach exactly the same equilibrium composition (Figure **9.1.2***b*). Thus equilibrium can be approached from either direction in a chemical reaction.

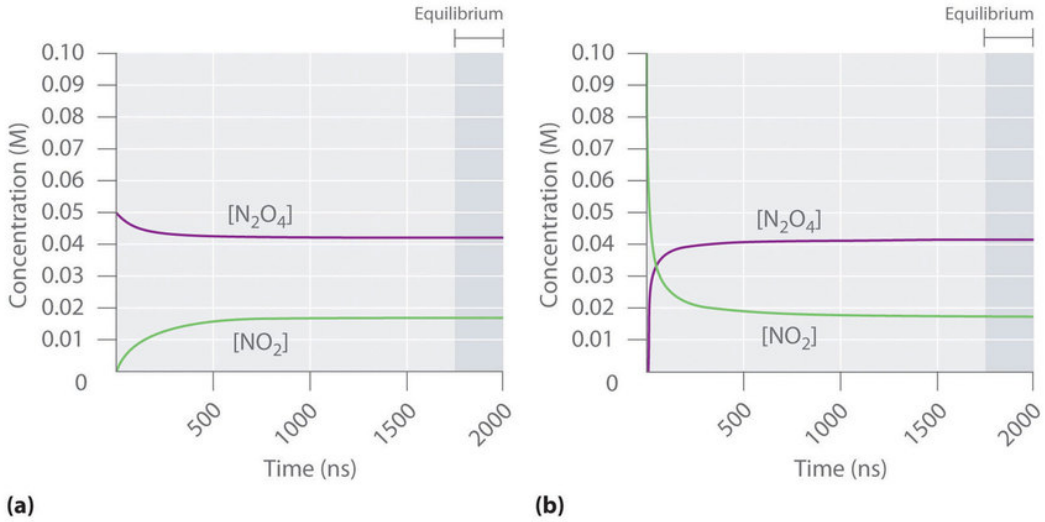


Figure **9.1.2**: The Composition of $\mathbf{N_2O_4/NO_2}$ Mixtures as a Function of Time at Room Temperature. (a) Initially, this idealized system contains 0.0500 M gaseous $\mathbf{N_2O_4}$ and no gaseous $\mathbf{NO_2}$. The concentration of $\mathbf{N_2O_4}$ decreases with time as the concentration of $\mathbf{NO_2}$ increases. (b) Initially, this system contains 0.1000 M $\mathbf{NO_2}$ and no $\mathbf{N_2O_4}$. The concentration of $\mathbf{NO_2}$ decreases with time as the concentration of $\mathbf{N_2O_4}$ increases. In both cases, the final concentrations of the substances are the same: $[\mathbf{N_2O_4}]$ = 0.0422 M and $[\mathbf{NO_2}]$ = 0.0156 M at equilibrium. (CC BY-SA-NC; Anonymous by request)

Figure **9.1.3** shows the forward and reverse reaction rates for a sample that initially contains pure $\mathbf{NO_2}$. Because the initial concentration of $\mathbf{N_2O_4}$ is zero, the forward reaction rate (dissociation of $\mathbf{N_2O_4}$) is initially zero as well. In contrast, the reverse reaction rate (dimerization of $\mathbf{NO_2}$) is initially very high ($\mathbf{2.0 \times 10^6}\ M/s$), but it decreases rapidly as the concentration of $\mathbf{NO_2}$ decreases. As the concentration of $\mathbf{N_2O_4}$ increases, the rate of dissociation of $\mathbf{N_2O_4}$ increases—but more slowly than the dimerization of $\mathbf{NO_2}$—because the reaction is only first order in $\mathbf{N_2O_4}$ (rate = $k_f[N_2O_4]$, where k_f is the rate constant for the forward reaction in Equations 9.1.1 and 9.1.2). Eventually, the forward and reverse reaction rates become identical, $k_f = k_r$, and the system has reached chemical equilibrium. If the forward and reverse reactions occur at different rates, then the system is not at equilibrium.

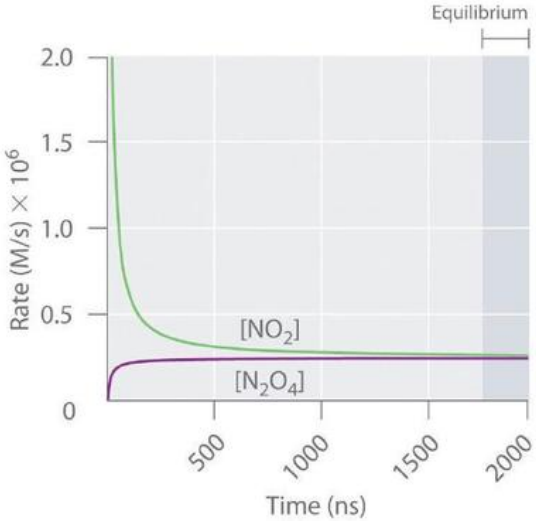


Figure **9.1.3**: The Forward and Reverse Reaction Rates as a Function of Time for the $N_{2}O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ System Shown in Part (b) in Figure **9.1.2**. (CC BY-SA-NC; Anonymous by request)

The rate of dimerization of $\mathbf{NO_2}$ (reverse reaction) decreases rapidly with time, as expected for a second-order reaction. Because the initial concentration of $\mathbf{N_2O_4}$ is zero, the rate of the dissociation reaction (forward reaction) at $t = 0$ is also zero. As the dimerization reaction proceeds, the $\mathbf{N_2O_4}$ concentration increases, and its rate of dissociation also increases. Eventually the rates of the two reactions are equal: chemical equilibrium has been reached, and the concentrations of $\mathbf{N_2O_4}$ and $\mathbf{NO_2}$ no longer change.

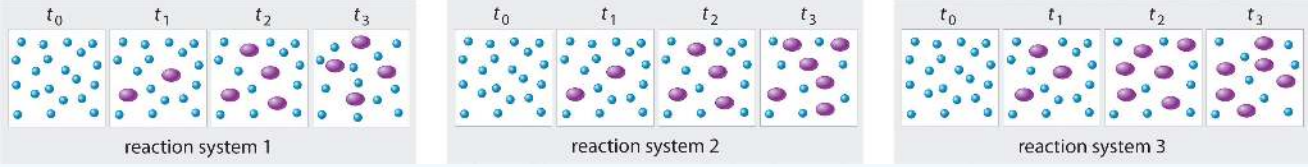
> *At equilibrium, the forward reaction rate is equal to the reverse reaction rate.*

EXAMPLE 9.1.1

The three reaction systems (1, 2, and 3) depicted in the accompanying illustration can all be described by the equation:

$$2A \rightleftharpoons B$$

where the blue circles are A and the purple ovals are B. Each set of panels shows the changing composition of one of the three reaction mixtures as a function of time. Which system took the longest to reach chemical equilibrium?



In reaction system 1 theree are four purple ovals at t3. In reaction system 2 there are size purple ovals at t3. In reaction system systems there are six ovals at t2 and t3.

Given: three reaction systems

Asked for: relative time to reach chemical equilibrium

Strategy:

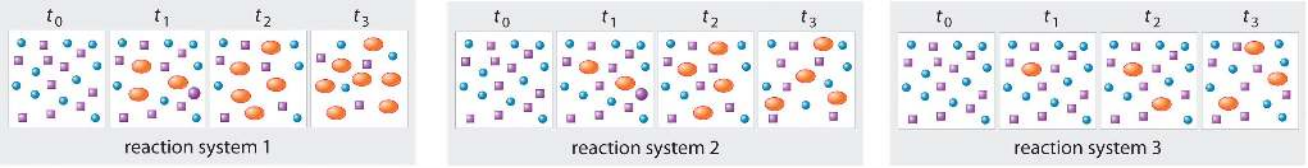
Compare the concentrations of A and B at different times. The system whose composition takes the longest to stabilize took the longest to reach chemical equilibrium.

Solution:

In systems 1 and 3, the concentration of A decreases from t_0 through t_2 but is the same at both t_2 and t_3. Thus systems 1 and 3 are at equilibrium by t_3. In system 2, the concentrations of A and B are still changing between t_2 and t_3, so system 2 may not yet have reached equilibrium by t_3. Thus system 2 took the longest to reach chemical equilibrium.

EXERCISE 9.1.1

In the following illustration, A is represented by blue circles, B by purple squares, and C by orange ovals; the equation for the reaction is A + B ⇌ C. The sets of panels represent the compositions of three reaction mixtures as a function of time. Which, if any, of the systems shown has reached equilibrium?



In reaction system 1 there are seven orange ovals at t3. In reaction system two there are four orange ovals at t3. In reaction system three there are three orange ovals at t3.

Answer

system 2



A Video Introduction to Dynamic Equilibrium: Introduction to Dynamic Equilibrium(opens in new window) [youtu.be]

9.1.1 SUMMARY

At equilibrium, the forward and reverse reactions of a system proceed at equal rates. Chemical equilibrium is a dynamic process consisting of forward and reverse reactions that proceed at equal rates. At equilibrium, the composition of the system no longer changes with time. The composition of an equilibrium mixture is independent of the direction from which equilibrium is approached.

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- **15.1: The Concept of Equilibrium** is licensed CC BY-NC-SA 3.0.

9.2: THE EMPIRICAL LAW OF MASS ACTION

LEARNING OBJECTIVES

- To know the relationship between the equilibrium constant and the rate constants for the forward and reverse reactions.
- To write an equilibrium constant expression for any reaction.
- To understand how different phases affect equilibria.

Because an equilibrium state is achieved when the forward reaction rate equals the reverse reaction rate, under a given set of conditions there must be a relationship between the composition of the system at equilibrium and the kinetics of a reaction (represented by rate constants). We can show this relationship using the decomposition reaction of $\mathrm{N_2O_4}$ to $\mathrm{NO_2}$. Both the forward and reverse reactions for this system consist of a single elementary reaction, so the reaction rates are as follows:

$$\text{forward rate} = k_f[\mathrm{N_2O_4}] \tag{9.2.2}$$

and

$$\text{reverse rate} = k_r[\mathrm{NO_2}]^2 \tag{9.2.3}$$

At equilibrium, the forward rate equals the reverse rate (definition of equilibrium):

$$k_f[\mathrm{N_2O_4}] = k_r[\mathrm{NO_2}]^2 \tag{9.2.4}$$

so

$$\frac{k_f}{k_r} = \frac{[\mathrm{NO_2}]^2}{[\mathrm{N_2O_4}]} \tag{9.2.5}$$

The ratio of the rate constants gives us a new constant, the **equilibrium constant** (K), which is defined as follows:

$$K = \frac{k_f}{k_r} \tag{9.2.6}$$

Hence there is a fundamental relationship between chemical kinetics and chemical equilibrium: under a given set of conditions, the composition of the equilibrium mixture is determined by the magnitudes of the rate constants for the forward and the reverse reactions.

> The equilibrium constant is equal to the rate constant for the forward reaction divided by the rate constant for the reverse reaction.

Table 9.2.1 lists the initial and equilibrium concentrations from five different experiments using the reaction system described by Equation 9.2.2. At equilibrium the magnitude of the quantity $[\mathrm{NO_2}]^2/[\mathrm{N_2O_4}]$ is essentially the same for all five experiments. In fact, no matter what the initial concentrations of $\mathrm{NO_2}$ and $\mathrm{N_2O_4}$ are, at equilibrium the quantity $[\mathrm{NO_2}]^2/[\mathrm{N_2O_4}]$ will always be $6.53 \pm 0.03 \times 10^{-3}$ at 25°C, which corresponds to the ratio of the rate constants for the forward and reverse reactions (Equation 9.2.6). That is, at a given temperature, the equilibrium constant for a reaction always has the same value, even though the specific concentrations of the reactants and products vary depending on their initial concentrations.

Table 9.2.1: Initial and Equilibrium Concentrations for $NO_2 : N_2O_4$ Mixtures at 25°C

	Initial Concentrations		Concentrations at Equilibrium		
Experiment	$[N_2O_4]$ (M)	$[NO_2]$ (M)	$[N_2O_4]$ (M)	$[NO_2]$ (M)	$K = [NO_2]^2/[N_2O_4]$
1	0.0500	0.0000	0.0417	0.0165	6.54×10^{-3}
2	0.0000	0.1000	0.0417	0.0165	6.54×10^{-3}
3	0.0750	0.0000	0.0647	0.0206	6.56×10^{-3}
4	0.0000	0.0750	0.0304	0.0141	6.54×10^{-3}
5	0.0250	0.0750	0.0532	0.0186	6.50×10^{-3}

9.2.1 DEVELOPING AN EQUILIBRIUM CONSTANT EXPRESSION

In 1864, the Norwegian chemists Cato Guldberg (1836–1902) and Peter Waage (1833–1900) carefully measured the compositions of many reaction systems at equilibrium. They discovered that for any reversible reaction of the general form

$$aA + bB \rightleftharpoons cC + dD \tag{9.2.7}$$

where A and B are reactants, C and D are products, and a, b, c, and d are the stoichiometric coefficients in the balanced chemical equation for the reaction, the ratio of the product of the equilibrium concentrations of the products (raised to their coefficients in the balanced chemical equation) to the product of the equilibrium concentrations of the reactants (raised to their coefficients in the balanced chemical equation) is always a constant under a given set of conditions. This relationship is known as the law of mass action and can be stated as follows:

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{9.2.8}$$

where K is the equilibrium constant for the reaction. Equation 9.2.7 is called the equilibrium equation, and the right side of Equation 9.2.8 is called the equilibrium constant expression. The relationship shown in Equation 9.2.8 is true for any pair of opposing reactions regardless of the mechanism of the reaction or the number of steps in the mechanism.

The equilibrium constant can vary over a wide range of values. The values of K shown in Table 9.2.2, for example, vary by 60 orders of magnitude. Because products are in the numerator of the equilibrium constant expression and reactants are in the denominator, values of K greater than 10^3 indicate a strong tendency for reactants to form products. In this case, chemists say that equilibrium lies to the right as written, favoring the formation of products. An example is the reaction between H_2 and Cl_2 to produce HCl, which has an equilibrium constant of 1.6×10^{33} at 300 K. Because H_2 is a good reductant and Cl_2 is a good oxidant, the reaction proceeds essentially to completion. In contrast, values of K less than 10^{-3} indicate that the ratio of products to reactants at equilibrium is very small. That is, reactants do not tend to form products readily, and the equilibrium lies to the left as written, favoring the formation of reactants.

Table 9.2.2: Equilibrium Constants for Selected Reactions*

Reaction	Temperature (K)	Equilibrium Constant (K)
$S(s) + O_2(g) \rightleftharpoons SO_2(g)$	300	4.4×10^{53}
$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$	500	2.4×10^{47}
$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$	300	1.6×10^{33}
$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$	300	4.1×10^{18}
$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$	300	4.2×10^{13}
$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$	300	2.7×10^{8}
$H_2(g) + D_2(g) \rightleftharpoons 2HD(g)$	100	1.92
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	300	2.9×10^{-1}
$I_2(g) \rightleftharpoons 2I(g)$	800	4.6×10^{-7}
$Br_2(g) \rightleftharpoons 2Br(g)$	1000	4.0×10^{-7}
$Cl_2(g) \rightleftharpoons 2Cl(g)$	1000	1.8×10^{-9}
$F_2(g) \rightleftharpoons 2F(g)$	500	7.4×10^{-13}

*Equilibrium constants vary with temperature. The K values shown are for systems at the indicated temperatures.

You will also notice in Table 9.2.2 that equilibrium constants have no units, even though Equation 9.2.8 suggests that the units of concentration might not always cancel because the exponents may vary. **In fact, equilibrium constants are calculated using "effective concentrations," or activities, of reactants and products, which are the ratios of the measured concentrations to a standard state of 1 M.** As shown in Equation 9.2.9, the units of concentration cancel, which makes K unitless as well:

$$\frac{[A]_{measured}}{[A]_{standard\ state}} = \frac{\cancel{M}}{\cancel{M}} = \frac{\frac{\cancel{mol}}{\cancel{L}}}{\frac{\cancel{mol}}{\cancel{L}}} \tag{9.2.9}$$

Many reactions have equilibrium constants between 1000 and 0.001 ($10^3 \geq K \geq 10^{-3}$), neither very large nor very small. At equilibrium, these systems tend to contain significant amounts of both products and reactants, indicating that there is not a strong tendency to form either products from reactants or reactants from products. An example of this type of system is the reaction of gaseous hydrogen and deuterium, a component of high-stability fiber-optic light sources used in ocean studies, to form HD:

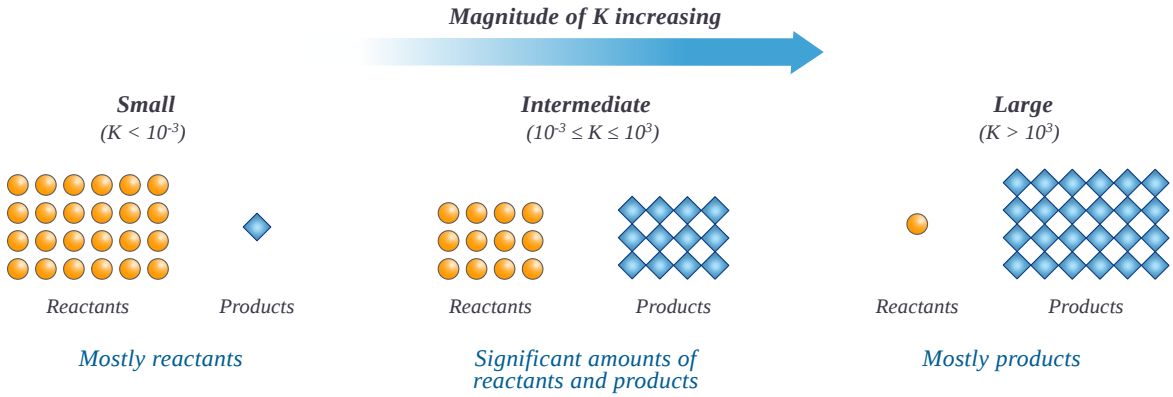
$$H_2(g) + D_2(g) \rightleftharpoons 2HD(g) \tag{9.2.10}$$

The equilibrium constant expression for this reaction is

$$K = \frac{[HD]^2}{[H_2][D_2]} \tag{9.2.11}$$

with K varying between 1.9 and 4 over a wide temperature range (100–1000 K). Thus an equilibrium mixture of H_2, D_2, and HD contains significant concentrations of both product and reactants.

Figure 9.2.1 summarizes the relationship between the magnitude of K and the relative concentrations of reactants and products at equilibrium for a general reaction, written as reactants \rightleftharpoons products. Because there is a direct relationship between the kinetics of a reaction and the equilibrium concentrations of products and reactants (Equations 9.2.9 and 9.2.8), when $k_f \gg k_r$, K is a **large** number, and the concentration of products at equilibrium predominate. This corresponds to an essentially irreversible reaction. Conversely, when $k_f \ll k_r$, K is a very **small** number, and the reaction produces almost no products as written. Systems for which $k_f \approx k_r$ have significant concentrations of both reactants and products at equilibrium.



Composition of equilibrium mixture

Figure 9.2.1: The Relationship between the Composition of the Mixture at Equilibrium and the Magnitude of the Equilibrium Constant. The larger the K, the farther the reaction proceeds to the right before equilibrium is reached, and the greater the ratio of products to reactants at equilibrium. (CC BY-NC; Ümit Kaya)

A large value of the equilibrium constant K means that products predominate at equilibrium; a small value means that reactants predominate at equilibrium.

EXAMPLE 9.2.1

Write the equilibrium constant expression for each reaction.

- $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
- $CO(g) + \frac{1}{2}O_2(g) \rightleftharpoons CO_2(g)$
- $2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$

Given: balanced chemical equations

Asked for: equilibrium constant expressions

Strategy:

Refer to Equation 9.2.8. Place the arithmetic product of the concentrations of the products (raised to their stoichiometric coefficients) in the numerator and the product of the concentrations of the reactants (raised to their stoichiometric coefficients) in the denominator.

Solution:

The only product is ammonia, which has a coefficient of 2. For the reactants, N_2 has a coefficient of 1 and H_2 has a coefficient of 3. The equilibrium constant expression is as follows:

$$\frac{[NH_3]^2}{[N_2][H_2]^3}$$

The only product is carbon dioxide, which has a coefficient of 1. The reactants are CO, with a coefficient of 1, and O_2, with a coefficient of $\frac{1}{2}$. Thus the equilibrium constant expression is as follows:

$$\frac{[CO_2]}{[CO][O_2]^{1/2}}$$

This reaction is the reverse of the reaction in part b, with all coefficients multiplied by 2 to remove the fractional coefficient for $\mathbf{O_2}$. The equilibrium constant expression is therefore the inverse of the expression in part b, with all exponents multiplied by 2:

$$\frac{[CO]^2[O_2]}{[CO_2]^2}$$

? EXERCISE 9.2.1

Write the equilibrium constant expression for each reaction.

a. $\mathrm{N_2O\,(g)} \rightleftharpoons \mathrm{N_2\,(g)} + \frac{1}{2}\,\mathrm{O_2\,(g)}$
b. $\mathrm{2\,C_8H_{18}\,(g)} + \mathrm{25\,O_2\,(g)} \rightleftharpoons \mathrm{16\,CO_2\,(g)} + \mathrm{18\,H_2O\,(g)}$
c. $\mathrm{H_2\,(g)} + \mathrm{I_2\,(g)} \rightleftharpoons \mathrm{2\,HI\,(g)}$

Answer a

$$K = \frac{[N_2][O_2]^{1/2}}{[N_2O]}$$

Answer b

$$K = \frac{[CO_2]^{16}[H_2O]^{18}}{[C_8H_{18}]^2[O_2]^{25}}$$

Answer c

$$K = \frac{[HI]^2}{[H_2][I_2]}$$

✓ EXAMPLE 9.2.2

Predict which systems at equilibrium will (a) contain essentially only products, (b) contain essentially only reactants, and (c) contain appreciable amounts of both products and reactants.

1. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)} \qquad K_{(700K)} = 54$
2. $2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)} \qquad K_{(1200K)} = 3.1 \times 10^{-18}$
3. $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)} \qquad K_{(613K)} = 97$
4. $2O_{3(g)} \rightleftharpoons 3O_{2(g)} \qquad K_{(298K)} = 5.9 \times 10^{55}$

Given: systems and values of K

Asked for: composition of systems at equilibrium

Strategy:

Use the value of the equilibrium constant to determine whether the equilibrium mixture will contain essentially only products, essentially only reactants, or significant amounts of both.

Solution:

a. Only system 4 has $K >> 10^3$, so at equilibrium it will consist of essentially only products.
b. System 2 has $K << 10^{-3}$, so the reactants have little tendency to form products under the conditions specified; thus, at equilibrium the system will contain essentially only reactants.
c. Both systems 1 and 3 have equilibrium constants in the range $10^3 \geq K \geq 10^{-3}$, indicating that the equilibrium mixtures will contain appreciable amounts of both products and reactants.

? EXERCISE 9.2.2

Hydrogen and nitrogen react to form ammonia according to the following balanced chemical equation:

$$3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

Values of the equilibrium constant at various temperatures were reported as

- $K_{25°C} = 3.3 \times 10^8$,
- $K_{177°C} = 2.6 \times 10^3$, and
- $K_{327°C} = 4.1$.

a. At which temperature would you expect to find the highest proportion of H_2 and N_2 in the equilibrium mixture?
b. Assuming that the reaction rates are fast enough so that equilibrium is reached quickly, at what temperature would you design a commercial reactor to operate to maximize the yield of ammonia?

Answer a

327°C, where K is smallest

Answer b

25°C

9.2.2 VARIATIONS IN THE FORM OF THE EQUILIBRIUM CONSTANT EXPRESSION

Because equilibrium can be approached from either direction in a chemical reaction, the equilibrium constant expression and thus the magnitude of the equilibrium constant depend on the form in which the chemical reaction is written. For example, if we write the reaction described in Equation 9.2.7 in reverse, we obtain the following:

$$cC + dD \rightleftharpoons aA + bB \tag{9.2.12}$$

The corresponding equilibrium constant K' is as follows:

$$K' = \frac{[A]^a[B]^b}{[C]^c[D]^d} \tag{9.2.13}$$

This expression is the inverse of the expression for the original equilibrium constant, so $K' = 1/K$. That is, when we write a reaction in the reverse direction, the equilibrium constant expression is inverted. For instance, the equilibrium constant for the reaction $N_2O_4 \rightleftharpoons 2NO_2$ is as follows:

$$K = \frac{[NO_2]^2}{[N_2O_4]} \tag{9.2.14}$$

but for the opposite reaction, $2NO_2 \rightleftharpoons N_2O_4$, the equilibrium constant K′ is given by the inverse expression:

$$K' = \frac{[N_2O_4]}{[NO_2]^2} \tag{9.2.15}$$

Consider another example, the formation of water: $2H_{2(g)} + O_{2(g)} \rightleftharpoons 2H_2O_{(g)}$. Because H_2 is a good reductant and O_2 is a good oxidant, this reaction has a very large equilibrium constant ($K = 2.4 \times 10^{47}$ at 500 K). Consequently, the equilibrium constant for the reverse reaction, the decomposition of water to form O_2 and H_2, is very small: $K' = 1/K = 1/(2.4 \times 10^{47}) = 4.2 \times 10^{-48}$. As suggested by the very small equilibrium constant, and fortunately for life as we know it, a substantial amount of energy is indeed needed to dissociate water into H_2 and O_2.

> The equilibrium constant for a reaction written in reverse is the *inverse* of the equilibrium constant for the reaction as written originally.

Writing an equation in different but chemically equivalent forms also causes both the equilibrium constant expression and the magnitude of the equilibrium constant to be different. For example, we could write the equation for the reaction

$$2NO_2 \rightleftharpoons N_2O_4 \tag{9.2.16}$$

as

$$NO_2 \rightleftharpoons \frac{1}{2}N_2O_4 \tag{9.2.17}$$

with the equilibrium constant K″ is as follows:

$$K'' = \frac{[N_2O_4]^{1/2}}{[NO_2]} \tag{9.2.18}$$

The values for K′ (Equation 9.2.15) and K″ are related as follows:

$$K'' = (K')^{1/2} = \sqrt{K'} \tag{9.2.19}$$

In general, if all the coefficients in a balanced chemical equation were subsequently multiplied by n, then the new equilibrium constant is the original equilibrium constant raised to the nth power.

EXAMPLE 9.2.3: THE HABER PROCESS

At 745 K, K is 0.118 for the following reaction:

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

What is the equilibrium constant for each related reaction at 745 K?

a. $\mathrm{2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g)}$
b. $\mathrm{\frac{1}{2}\,N_2(g) + \frac{3}{2}\,H_2(g) \rightleftharpoons NH_3(g)}$

Given: balanced equilibrium equation, K at a given temperature, and equations of related reactions

Asked for: values of K for related reactions

Strategy:

Write the equilibrium constant expression for the given reaction and for each related reaction. From these expressions, calculate K for each reaction.

Solution:

The equilibrium constant expression for the given reaction of $\mathrm{N_2(g)}$ with $\mathrm{H_2(g)}$ to produce $\mathrm{NH_3(g)}$ at 745 K is as follows:

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = 0.118$$

This reaction is the reverse of the one given, so its equilibrium constant expression is as follows:

$$K' = \frac{1}{K} = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{1}{0.118} = 8.47$$

In this reaction, the stoichiometric coefficients of the given reaction are divided by 2, so the equilibrium constant is calculated as follows:

$$K'' = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}} = K^{1/2} = \sqrt{K} = \sqrt{0.118} = 0.344$$

EXERCISE

At 527°C, the equilibrium constant for the reaction

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

is 7.9×10^4. Calculate the equilibrium constant for the following reaction at the same temperature:

$$\mathrm{SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}\,O_2(g)}$$

Answer

3.6×10^{-3}

9.2.3 LAW OF MASS ACTION FOR GAS-PHASE REACTIONS

For reactions that involve species in solution, the concentrations used in equilibrium calculations are usually expressed in moles/liter. For gases, however, the concentrations are usually expressed in terms of partial pressures rather than molarity, where the standard state is 1 atm of pressure. The symbol K_p is used to denote equilibrium constants calculated from partial pressures. For the general reaction

$$a\,\mathrm{A} + b\,\mathrm{B} \rightleftharpoons c\,\mathrm{C} + d\,\mathrm{D}$$

in which all the components are gases, the equilibrium constant expression can be written as the ratio of the partial pressures of the products and reactants (each raised to its coefficient in the chemical equation):

$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b} \tag{9.2.20}$$

Thus K_p for the decomposition of N_2O_4 (Equation 9.2.2) is as follows:

$$K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}} \tag{9.2.21}$$

Like K, K_p is a unitless quantity because the quantity that is actually used to calculate it is an "effective pressure," the ratio of the measured pressure to a standard state of 1 bar (approximately 1 atm), which produces a unitless quantity. The "effective pressure" is called the **fugacity**, just as activity is the effective concentration.

Because partial pressures are usually expressed in atmospheres or mmHg, the molar concentration of a gas and its partial pressure do not have the same numerical value. Consequently, the numerical values of K and K_p are usually different. They are, however, related by the ideal gas constant (R) and the absolute temperature (T):

$$K_p = K(RT)^{\Delta n} \tag{9.2.22}$$

where K is the equilibrium constant expressed in units of concentration and Δn is the difference between the numbers of moles of gaseous products and gaseous reactants ($n_p - n_r$). The temperature is expressed as the absolute temperature in Kelvin. According to Equation 9.2.22, $K_p = K$ only if the moles of gaseous products and gaseous reactants are the same (i.e., $\Delta n = 0$). For the decomposition of N_2O_4, there are 2 mol of gaseous product and 1 mol of gaseous reactant, so $\Delta n = 1$. Thus, for this reaction,

$$K_p = K(RT)^1 = KRT \tag{9.2.23}$$

✔ EXAMPLE 9.2.4: THE HABER PROCESS (AGAIN)

The equilibrium constant for the reaction of nitrogen and hydrogen to give ammonia is 0.118 at 745 K. The balanced equilibrium equation is as follows:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

What is K_p for this reaction at the same temperature?

Given: equilibrium equation, equilibrium constant, and temperature

Asked for: K_p

Strategy:

Use the coefficients in the balanced chemical equation to calculate Δn. Then use Equation 9.2.22 to calculate K from K_p.

Solution:

This reaction has 2 mol of gaseous product and 4 mol of gaseous reactants, so $\Delta n = (2 - 4) = -2$. We know K, and $T = 745\ K$. Thus, from Equation 9.2.19, we have the following:

$$K_p = K(RT)^{-2} = \frac{K}{(RT)^2} = \frac{0.118}{\{[0.08206(L \cdot atm)/(mol \cdot K)][745\ K]\}^2} = 3.16 \times 10^{-5}$$

Because K_p is a unitless quantity, the answer is $K_p = 3.16 \times 10^{-5}$.

? EXERCISE 9.2.4:

Calculate K_p for the reaction

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

at 527°C, if $K = 7.9 \times 10^4$ at this temperature.

Answer

$K_p = 1.2 \times 10^3$

9.2.4 LAW OF MASS ACTION FOR REACTIONS INVOLVING PURE SUBSTANCES AND MULTIPLE PHASES

When the products and reactants of a reaction at equilibrium in a single phase (e.g., liquid, gas or solids of different lattices), the system is a **homogeneous equilibrium**. In such situations, the concentrations of the reactants and products can vary over a wide range. In contrast, a system where the reactants and products are in two or more phase is called a **heterogeneous equilibrium** (e.g, the reaction of a gas with a solid or liquid or two different solid lattices in co-existing).

Because the molar concentrations of pure liquids and solids normally do not vary greatly with temperature, their concentrations are treated as constants, which allows us to simplify equilibrium constant expressions that involve pure solids or liquids.The reference states for pure solids and liquids are those forms stable at 1 bar (approximately 1 atm), which are assigned an activity of 1. (Recall that the density of water, and thus its volume, changes by only a few percentage points between 0 °C and 100 °C.)

Consider the following reaction, which is used in the final firing of some types of pottery to produce brilliant metallic glazes:

$$\mathrm{CO_2\,(g) + C\,(s) \rightleftharpoons 2\,CO\,(g)} \tag{9.2.24}$$

The glaze is created when metal oxides are reduced to metals by the product, carbon monoxide. The equilibrium constant expression for this reaction is as follows:

$$K = \frac{[CO]^2}{[CO_2][C]} \tag{9.2.25}$$

Because graphite is a solid, however, its molar concentration, determined from its density and molar mass, is essentially constant and has the following value:

$$[C] = \frac{2.26\ \cancel{g}/\cancel{cm^3}}{12.01\ \cancel{g}/mol} \times 1000\ \cancel{cm^3}/L = 188\ mol/L = 188\ M \tag{9.2.26}$$

We can rearrange Equation 9.2.26 so that the constant terms are on one side:

$$K[C] = K(188) = \frac{[CO]^2}{[CO_2]} \tag{9.2.27}$$

Incorporating the constant value of $[C]$ into the equilibrium equation for the reaction in Equation 9.2.27,

$$K' = \frac{[CO]^2}{[CO_2]} \tag{9.2.28}$$

The equilibrium constant for this reaction can also be written in terms of the partial pressures of the gases:

$$K_p = \frac{(P_{CO})^2}{P_{CO_2}} \tag{9.2.29}$$

Incorporating all the constant values into K' or K_p allows us to focus on the substances whose concentrations change during the reaction.

Although the concentrations of pure liquids or solids are not written explicitly in the equilibrium constant expression, these substances must be present in the reaction mixture for chemical equilibrium to occur. Whatever the concentrations of CO and CO_2, the system described in Equation 9.2.24 will reach chemical equilibrium only if a stoichiometric amount of solid carbon or excess solid carbon has been added so that some is still present once the system has reached equilibrium. As shown in Figure 9.2.2, it does not matter whether 1 g or 100 g of solid carbon is present; in either case, the composition of the gaseous components of the system will be the same at equilibrium.

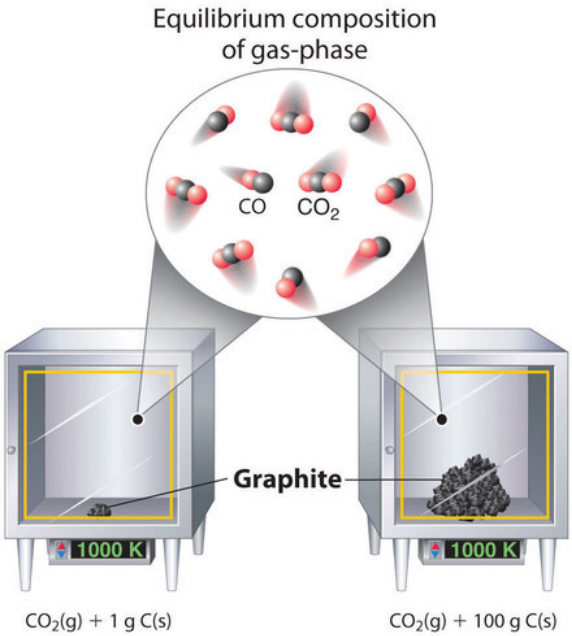


Figure **9.2.2**: Effect of the Amount of Solid Present on Equilibrium in a Heterogeneous Solid–Gas System. In the system, the equilibrium composition of the gas phase at a given temperature, 1000 K in this case, is the same whether a small amount of solid carbon (left) or a large amount (right) is present.

EXAMPLE 9.2.1

Write each expression for K, incorporating all constants, and K_p for the following equilibrium reactions.

a. $PCl_{3(l)} + Cl_{2(g)} \rightleftharpoons PCl_{5(s)}$
b. $Fe_3O_{4(s)} + 4H_{2(g)} \rightleftharpoons 3Fe_{(s)} + 4H_2O_{(g)}$

Given: balanced equilibrium equations

Asked for: expressions for K and K_p

Strategy:

Find K by writing each equilibrium constant expression as the ratio of the concentrations of the products and reactants, each raised to its coefficient in the chemical equation. Then express K_p as the ratio of the partial pressures of the products and reactants, each also raised to its coefficient in the chemical equation.

Solution

This reaction contains a pure solid (PCl_5) and a pure liquid (PCl_3). Their concentrations do not appear in the equilibrium constant expression because they do not change significantly. So

$$K = \frac{1}{[Cl_2]}$$

and

$$K_p = \frac{1}{P_{Cl_2}}$$

This reaction contains two pure solids (Fe_3O_4 and Fe), which do not appear in the equilibrium constant expressions. The two gases do, however, appear in the expressions:

$$K = \frac{[H_2O]^4}{[H_2]^4}$$

and

$$K_p = \frac{(P_{H_2O})^4}{(P_{H_2})^4}$$

? EXERCISE 9.2.1

Write the expressions for K and K_p for the following reactions.

a. $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$

b. $\underset{glucose}{C_6H_{12}O_{6(s)}} + 6O_{2(g)} \rightleftharpoons 6CO_{2(g)} + 6H_2O_{(g)}$

Answer a

$K = [CO_2]$ and $K_p = P_{CO_2}$

Answer b

$K = \frac{[CO_2]^6[H_2O]^6}{[O_2]^6}$ and $K_p = \frac{(P_{CO_2})^6(P_{H_2O})^6}{(P_{O_2})^6}$

For reactions carried out in solution, the concentration of the solvent is omitted from the equilibrium constant expression even when the solvent appears in the balanced chemical equation for the reaction. The concentration of the solvent is also typically much greater than the concentration of the reactants or products (recall that pure water is about 55.5 M, and pure ethanol is about 17 M). Consequently, the solvent concentration is essentially constant during chemical reactions, and the solvent is therefore treated as a pure liquid. The equilibrium constant expression for a reaction contains only those species whose concentrations could change significantly during the reaction.

> The concentrations of pure solids, pure liquids, and solvents are omitted from equilibrium constant expressions because they do not change significantly during reactions when enough is present to reach equilibrium.

9.2.5 SUMMARY

- The law of mass action describes a system at equilibrium in terms of the concentrations of the products and the reactants.
- For a system involving one or more gases, either the molar concentrations of the gases or their partial pressures can be used.
- Definition of equilibrium constant in terms of forward and reverse rate constants:

$$K = \frac{k_f}{k_r}$$

- Equilibrium constant expression (law of mass action):

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

- Equilibrium constant expression for reactions involving gases using partial pressures:

$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$$

- Relationship between K_p and K:

$$K_p = K(RT)^{\Delta n}$$

The ratio of the rate constants for the forward and reverse reactions at equilibrium is the equilibrium constant (K), a unitless quantity. The composition of the equilibrium mixture is therefore determined by the magnitudes of the forward and reverse rate constants at equilibrium. Under a given set of conditions, a reaction will always have the same K. For a system at equilibrium, the law of mass action relates K to the ratio of the equilibrium concentrations of the products to the concentrations of the reactants raised to their respective powers to match the coefficients in the equilibrium equation. The ratio is called the equilibrium constant expression. When a reaction is written in the reverse direction, K and the equilibrium constant expression are inverted. For gases, the equilibrium constant expression can be written as the ratio of the partial pressures of the products to the partial pressures of the reactants, each raised to a power matching its coefficient in the chemical equation. An equilibrium constant calculated from partial pressures (K_p) is related to K by the ideal gas constant (R), the temperature (T), and the change in the number of moles of gas during the reaction. An equilibrated system that contains products and reactants in a single phase is a homogeneous equilibrium; a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium.

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9.3: THERMODYNAMIC DESCRIPTION OF THE EQUILIBRIUM STATE

LEARNING OBJECTIVES

- Gibbs Energy is a state function defined as $G = H–TS$.
- The practical utility of the Gibbs function is that ΔG for any process is negative if it leads to an increase in the entropy of the world. Thus spontaneous change at a given temperature and pressure can only occur when it would lead to a decrease in G.
- The sign of the standard free energy change ΔG^o of a chemical reaction determines whether the reaction will tend to proceed in the forward or reverse direction.
- Similarly, the relative signs of ΔH^o and ΔH^o determine whether the spontaneity of a chemical reaction will be affected by the temperature, and if so, in what way.
- The existence of sharp melting and boiling points reflects the differing temperature dependancies of the free energies of the solid, liquid, and vapor phases of a pure substance, which are in turn reflect their differing entropies.

Previously, we saw that it is the **sum** of the entropy changes of the system and surroundings that determines whether a process will occur spontaneously. In chemical thermodynamics we prefer to focus our attention on the system rather than the surroundings, and would like to avoid having to calculate the entropy change of the surroundings explicitly.

In this unit we introduce a new thermodynamic function, the *free energy*, which turns out to be the single most useful criterion for predicting the direction of a chemical reaction and the composition of the system at equilibrium. However, the term "free energy", although still widely used, is rather misleading, so we will often refer to it as "Gibbs energy." The free energy enables us to do this for changes that occur at a constant temperature and pressure (the *Gibbs energy*) or constant temperature and volume (the *Helmholtz energy*.)

9.3.1 FREE ENERGY: THE GIBBS FUNCTION

The Gibbs energy (also known as the *Gibbs function* or *Gibbs Potential*) is defined as

$$G = H–TS \tag{9.3.1}$$

in which S refers to the entropy of the *system*. Since H, T and S are all state functions, so is G. Thus for any change in state (under constant temperature), we can write the extremely important relation

$$\Delta G = \Delta H–T\Delta S \tag{9.3.2}$$

How does this simple equation encompass the entropy change of the world ΔS_{total}, which we already know is the sole criterion for spontaneous change from the second law of thermodynamics? Starting with the definition

$$\Delta S_{total} = \Delta S_{surr} + \Delta S_{sys} \tag{9.3.3}$$

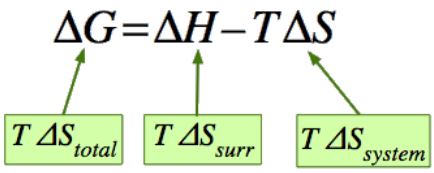
we would first like to get rid of ΔS_{surr}. How can a chemical reaction (a change in the *system*) affect the entropy of the *surroundings*? Because most reactions are either exothermic or endothermic, they are accompanied by a flow of heat q_p across the system boundary. The enthalpy change of the reaction ΔH is defined as the flow of heat into the system from the surroundings when the reaction is carried out at constant pressure, so the heat withdrawn from the surroundings will be $–q_p$ which will cause the entropy of the surroundings to change by $–q_p/T = –\Delta H/T$. We can therefore rewrite Equation 9.3.3 as

$$\Delta S_{total} = \frac{-\Delta H}{T} + \Delta S_{sys} \tag{9.3.4}$$

Multiplying each side by $–T$, we obtain

$$-T\Delta S_{total} = \Delta H - T\Delta S_{sys} \tag{9.3.5}$$

which expresses the entropy change of the world in terms of thermodynamic properties of the *system* exclusively. If $–T\Delta S_{total}$ is denoted by ΔG, then we have Equation 9.3.2 which defines the *Gibbs energy* change for the process.



From the foregoing, you should convince yourself that G will decrease in any process occurring at constant temperature and pressure which is accompanied by an overall increase in the entropy. The constant temperature is a consequence of the temperature and the enthalpy appearing in the preceding Equation 9.3.5. Since most chemical and phase changes of interest to chemists take place under such conditions, the Gibbs energy is the most useful of all the thermodynamic properties of a substance, and (as we shall see in the lesson that follows this one) it is closely linked to the equilibrium constant.

Some textbooks and teachers say that the free energy, and thus the spontaneity of a reaction, depends on both the enthalpy and entropy changes of a reaction, and they sometimes even refer to reactions as "energy driven" or "entropy driven" depending on whether ΔH or the $T\Delta S$ term dominates. This is technically correct, but misleading because it disguises the important fact that ΔS_{total}, which this equation expresses in an indirect way, is the *only* criterion of spontaneous change.

HELMHOLTZ ENERGY IS ALSO A "FREE ENERGY"

We will deal only with the Gibbs energy in this course. The Helmholtz free energy is of interest mainly to chemical engineers (whose industrial-scale processes are often confined to tanks and reactors of fixed volume) and some geochemists whose interest is centered on the chemistry that occurs deep within the earth's surface.

9.3.2 GIBBS ENERGY AND CHEMICAL CHANGE

Remember that ΔG is meaningful only for changes in which the *temperature and pressure remain constant*. These are the conditions under which most reactions are carried out in the laboratory; the system is usually open to the atmosphere (constant pressure) and we begin and end the process at room temperature (after any heat we have added or which is liberated by the reaction has dissipated.) The importance of the Gibbs function can hardly be over-stated: it serves as the single master variable that determines whether a given chemical change is thermodynamically possible. Thus if the free energy of the reactants is greater than that of the products, the entropy of the world will increase when the reaction takes place as written, and so the reaction will tend to take place spontaneously. Conversely, if the free energy of the products exceeds that of the reactants, then the reaction will not take place in the direction written, but it will tend to proceed in the reverse direction.

> *ΔG serves as the single master variable that determines whether a given chemical change is thermodynamically possible. Moreover, it determines the direction and extent of chemical change.*

In a spontaneous change, Gibbs energy always decreases and never increases. This of course reflects the fact that the entropy of the world behaves in the exact opposite way (owing to the negative sign in the $T\Delta S$ term).

$$\mathrm{H_2O\,(l)} \rightarrow \mathrm{H_2O\,(s)} \tag{9.3.6}$$

water below its freezing point undergoes a decrease in its entropy, but the heat released into the surroundings more than compensates for this, so the entropy of the world increases, the free energy of the H_2O diminishes, and the process proceeds spontaneously.

> *In a spontaneous change, Gibbs energy **always** decreases and never increases.*

An important consequence of the one-way downward path of the free energy is that once it reaches its minimum possible value, all net change comes to a halt. This, of course, represents the state of chemical equilibrium. These relations are nicely summarized as follows:

- $\Delta G < 0$: reaction can spontaneously proceed to the right:

$$A \rightarrow B$$

- $\Delta G > 0$: reaction can spontaneously proceed to the left:

$$A \leftarrow B$$

- $\Delta G = 0$: the reaction is at **equilibrium** and both $[A]$ and $[B]$ will not change:

$$A \rightleftharpoons B.$$

9.3.3 NO NEED TO FIND THE VALUE OF ΔG FOR A SPECIFIC REACTION!

This might seem strange, given the key importance ΔG in determining whether or not a reaction will take place in a given direction. It turns out, however, that it is almost never necessary to explicitly evaluate ΔG. As we will show in the lesson that follows this one, it is far more convenient to work with the equilibrium constant of a reaction, within which ΔG is "hidden". This is just as well, because for most reactions

(those that take place in solutions or gas mixtures) the value of ΔG depends on the **proportions** of the various reaction components in the mixture; it is not a simple sum of the "products minus reactants" type, as is the case with ΔH.

Recalling the condition for spontaneous change

$$\Delta G = \Delta H - T\Delta S < 0 \tag{9.3.7}$$

it is apparent that the temperature dependence of ΔG depends almost entirely on the entropy change associated with the process. (We say "almost" because the values of ΔH and ΔS are themselves slightly temperature dependent; both gradually increase with temperature). In particular, notice that in the above equation **the sign of the entropy change determines whether the reaction becomes more or less spontaneous as the temperature is raised.** For any given reaction, the sign of ΔH can also be positive or negative. This means that there are four possibilities for the influence that temperature can have on the spontaneity of a process:

9.3.3.1 CASE 1: $\Delta H < 0$ AND $\Delta S > 0$

Both enthalpic ΔH and entropic $-T\Delta S$ terms will be negative, so ΔG will be negative regardless of the temperature. An exothermic reaction whose entropy increases will be spontaneous at all temperatures.

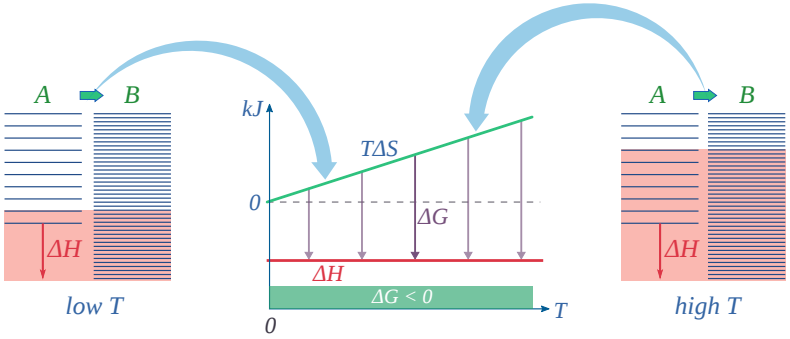


Figure **9.3.1**: A hypothetical $\mathbf{A} \longrightarrow \mathbf{B}$ reaction that is favored enthalpically and entropically (spontaneous at all temperatures). (CC BY 4.0; Ümit Kaya via LibreTexts)

9.3.3.2 CASE 2: $\Delta H < 0$ AND $\Delta S < 0$

If the reaction is sufficiently exothermic it can force ΔG negative only at temperatures below which $|T\Delta S| < |\Delta H|$. This means that there is a temperature $T = \Delta H/\Delta S$ at which the reaction is at equilibrium; the reaction will only proceed spontaneously below this temperature. The freezing of a liquid or the condensation of a gas are the most common examples of this condition.

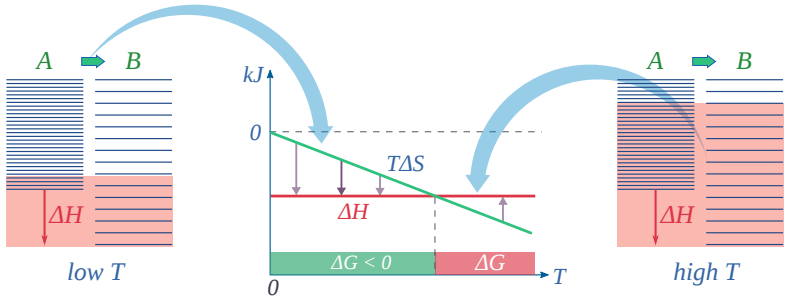


Figure **9.3.2**: A hypothetical $\mathbf{A} \longrightarrow \mathbf{B}$ reaction that is favored enthalpically and is not favored entropically (spontaneous at low temperatures). (CC BY 4.0; Ümit Kaya via LibreTexts)

9.3.3.3 CASE 3: $\Delta H > 0$ AND $\Delta S > 0$

This is the reverse of the previous case; the entropy increase must overcome the handicap of an endothermic process so that $T\Delta S > \Delta H$. Since the effect of the temperature is to "magnify" the influence of a positive ΔS, the process will be spontaneous at temperatures above $T = \Delta H/\Delta S$. (Think of melting and boiling.)

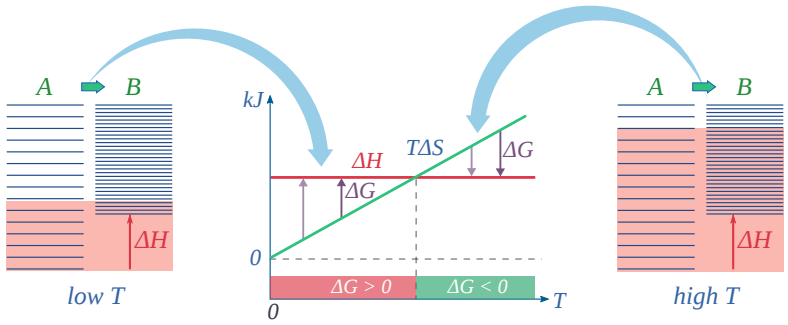


Figure **9.3.3**: A hypothetical **A ⟶ B** reaction that is not favored enthalpically and is favored entropically (spontaneous at high temperatures). (CC BY 4.0; Ümit Kaya via LibreTexts)

9.3.3.4 CASE 4: $\Delta H > 0$ AND $\Delta S < 0$

With both ΔH and ΔS working against it, this kind of process will not proceed spontaneously at any temperature. Substance A always has a greater number of accessible energy states, and is therefore always the preferred form.

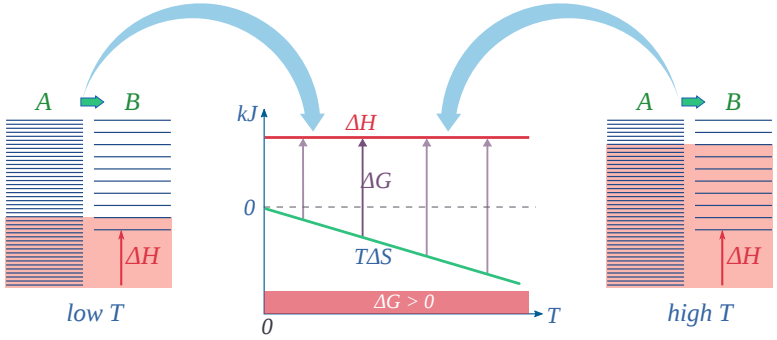


Figure **9.3.4**: A hypothetical **A ⟶ B** reaction that is not favored enthalpically and is not is favored entropically (not spontaneous at temperatures). (CC BY 4.0; Ümit Kaya via LibreTexts)

The plots above are the important ones; do not try to memorize them, but make sure you understand and can explain or reproduce them for a given set of ΔH and ΔS.

- Their most important differentiating features are the position of the ΔH line (above or below the is $T\Delta S$ line), and the slope of the latter, which of course depends on the sign of ΔS.
- The reaction A → B will occur spontaneously only when ΔG is negative (blue arrows pointing down.)
- $T\Delta S$ plots are not quite straight lines as shown here. Similarly, the lines representing ΔH are even more curved.

The other two plots on each diagram are only for the chemistry-committed.

- Each pair of energy-level diagrams depicts the relative spacing of the microscopic energy levels in the reactants and products as reflected by the value of $\Delta S°$. (The greater the entropy, the more closely-spaced are the quantized microstates.)
- The red shading indicates the range of energy levels that are accessible to the system at each temperature. The spontaneous direction of the reaction will always be in the direction in which the red shading overlaps the greater number of energy levels, resulting in the maximum dispersal of thermal energy.
- Note that the vertical offsets correspond to $\Delta H°$ for the reaction.
- Never forget that it is the ability of thermal energy to spread into as many of these states as possible that determines the tendency of the process to take place. None of this is to scale, of course!

9.3.4 THE STANDARD GIBBS ENERGY

You have already been introduced to the terms such as $\Delta U°$ and $\Delta H°$ in which the $°$ sign indicates that all components (reactants and products) are in their *standard states*. This concept of standard states is especially important in the case of the free energy, so let's take a few moments to review it. More exact definitions of the conventional standard states can be found in most physical chemistry textbooks. In specialized fields such as biochemistry and oceanography, alternative definitions may apply. For example, the "standard pH" of zero

(corresponding to $[H^+] = 1\,M$) is impractical in biochemistry, so pH = 7 is commonly employed. For most practical purposes, the following definitions are good enough:

- **gases:** 1 atmosphere partial pressure
- **pure liquids:** the liquid under a total (hydrostatic) pressure of 1 atm.
- **solutes:** an effective concentration of 1 mol L^{-1} (1 mol dm^{-3}). ("Effective" concentrations approach real concentrations as the latter approach zero; for practical purposes, these can be considered identical at real concentrations smaller than about 10^{-4} molar.)
- **solids:** the pure solid under 1 atm pressure

REMINDER ON STANDARD STATES

- There is actually no "standard temperature", but because most thermodynamics tables list values for 298.15 K (25° C), this temperature is usually implied.
- These same definitions apply to standard enthalpies and internal energies.
- Do not confuse these thermodynamic standard states with the "standard temperature and pressure" (STP) widely employed in gas law calculations.

To make use of Gibbs energies to predict chemical changes, we need to know the free energies of the individual components of the reaction. For this purpose we can combine the standard enthalpy of formation and the standard entropy of a substance to get its **standard free energy of formation**

$$\Delta G_f^o = \Delta H_f^o - T\Delta S_f^o \tag{9.3.8}$$

Recall that the symbol ° refers to the *standard state* of a substance measured under the conditions of 1 atm pressure or an effective concentration of 1 mol L^{-1} and a temperature of 298 K. Then determine the standard Gibbs energy of the reaction according to

$$\Delta G^o = \sum \Delta G_f^o\,(\text{products}) - \sum \Delta G_f^o\,(\text{reactants}) \tag{9.3.9}$$

As with standard heats of formation, the standard free energy of a substance represents the free energy change associated with the formation of the substance from the elements in their most stable forms as they exist under the standard conditions of 1 atm pressure and 298 K. Standard Gibbs free energies of formation are normally found directly from tables. Once the values for all the reactants and products are known, the standard Gibbs energy change for the reaction is found by Equation 9.3.8. Most tables of thermodynamic values list ΔG_f^o values for common substances (e.g., Table T2), which can, of course, always be found from values of $\Delta H_f°$ and $\Delta S_f°$.

EXAMPLE 9.3.1

Find the standard Gibbs energy change for the reaction

$$\mathrm{CaCO_3\,(s)} \rightarrow \mathrm{CaO\,(s) + CO_2\,(g)}$$

The ΔG_f^{oo} values for the three components of this reaction system are $\mathrm{CaCO_3\,(s)}$: –1128 kJ mol^{-1}, CaO*(s)*: –603.5 kJ mol^{-1}, CO_2*(g)*: –137.2 kJ mol^{-1}.

Solution

Substituting into Equation 9.3.8, we have

$$\Delta G^o = (-603.5 - 137.2) - (-1128)\,kJ\,mol^{-1} = +130.9\,kJ\,mol^{-1}$$

This indicates that the process is not spontaneous under standard conditions (i.e., solid calcium carbone will not form solid calcium oxide and CO_2 at 1 atm partial pressure at 25° C).

Comment: This reaction is carried out on a huge scale to manufacture cement, so it is obvious that the process can be spontaneous under different conditions.

The practical importance of the Gibbs energy is that it allows us to make predictions based on the properties ($\Delta G°$ values) of the reactants and products themselves, eliminating the need to experiment. But bear in mind that while thermodynamics always correctly predicts whether a given process *can* take place (is spontaneous in the thermodynamic sense), it is unable to tell us if it *will* take place at an observable rate.

> *When thermodynamics says "no", it means exactly that. When it says "yes", it means "maybe".*

EXAMPLE 9.3.2

The reaction

$$\tfrac{1}{2}\,O_2\,(g) + H_2\,(g) \longrightarrow H_2O\,(l)$$

is used in fuel cells to produce an electrical current. The reaction can also be carried out by direct combustion.

Thermodynamic data: molar entropies in J mol^{-1} K^{-1}: O_2(g) 205.0; H_2(g)130.6; H_2O(l) 70.0; H_2O(l) $\Delta H°_f$ = –285.9 kJ mol^{-1}.

Use this information to find

a. The amount of heat released when the reaction takes place by direct combustion;
b. The amount of electrical work the same reaction can perform when carried out in a fuel cell at 298 K under reversible conditions;
c. The amount of heat released under the same conditions.

Solution

First, we need to find $\Delta H°$ and $\Delta S°$ for the process. Recalling that the standard enthalpy of formation of the elements is zero,

$$\begin{aligned}\Delta H° &= \Delta H°_f(\text{products}) - \Delta H°_f(\text{reactants}) \\ &= -285.9\ kJ\ mol^{-1} - 0 \\ &= -285.9\ kJ\ mol^{-1}\end{aligned}$$

Similarly,

$$\begin{aligned}\Delta S° &= S°_f(\text{products}) - S°_f(\text{reactants}) \\ &= (70.0) - (½ \times 205.0 + 130.6) \\ &= -163\ J\ K^{-1} mol^{-1}\end{aligned}$$

a. When the hydrogen and oxygen are combined directly, the heat released will be $\Delta H° = -285.9\ kJ\ mol^{-1}$.
b. The maximum electrical work the fuel cell can perform is given by

$$\begin{aligned}\Delta G° &= \Delta H° - T\Delta S° \\ &= -285.9\ kJ\ mol^{-1} - (298\ K)(-163\ JK^{-1} mol^{-1}). \\ &= -237.2\ kJ\ mol^{-1}.\end{aligned}$$

c. The heat released in the fuel cell reaction is the difference between the enthalpy change (the total energy available) and the reversible work that was expended:

$$\begin{aligned}\Delta H° - \Delta G° &= T\Delta S° \\ &= (298\ K)(-163\ JK^{-1} mol^{-1}) \\ &= -48,800\ J\ mol^{-1} \\ &= -48.8\ kJ\ mol^{-1}.\end{aligned}$$

The foregoing example illustrates an important advantage of fuel cells. Although direct combustion of a mole of hydrogen gas yields more energy than is produced by the same net reaction within the fuel cell, the latter, in the form of electrical energy, can be utilized at nearly 100-percent energy efficiency by a motor or some other electrical device. If the thermal energy released by direct combustion were supplied to a heat engine, second-law considerations would require that at least half of this energy be "wasted" to the surroundings.

ΔG VS. ΔG°: WHAT'S THE DIFFERENCE?

Δ*G*° refer to *single, specific chemical changes* in which all components (reactants and products) are in their *standard states*.

The $\Delta G°_f$ of a substance, like $\Delta H°_f$, refers to the reaction in which that substance is formed from the elements as they exist in their most stable forms at 1 atm pressure and (usually) 298 K. Both of these terms are by definition zero for the elements in their standard states. There are only a few common cases in which this might create some ambiguity:

Table **9.3.1**: Standard Gibbs Energies of Select Substances

Stable Form	ΔG_f° (kJ mol^{-1})	Unstable Form	ΔG_f° (kJ mol^{-1})
O_2 (g)	0	O_3 (g)	163.2
C(graphite)	0	C(diamond)	2.9
S(rhombic)	0	S(monoclinic)	0.1
P(white)	0	P_4 (g)	24.4

Ions in aqueous solution are a special case; their standard free energies are relative to the hydrated hydrogen ion H^+ (aq) which is assigned $\Delta G_f^\circ = 0$.

ΔG is very different from ΔG°. The distinction is nicely illustrated in Figure **9.3.5** in which ΔG is plotted on a vertical axis for two hypothetical reactions having opposite signs of ΔG°. The horizontal axis schematically expresses the relative concentrations of reactants and products at any point of the process. Note that the origin corresponds to the composition at which half of the reactants have been converted into products.

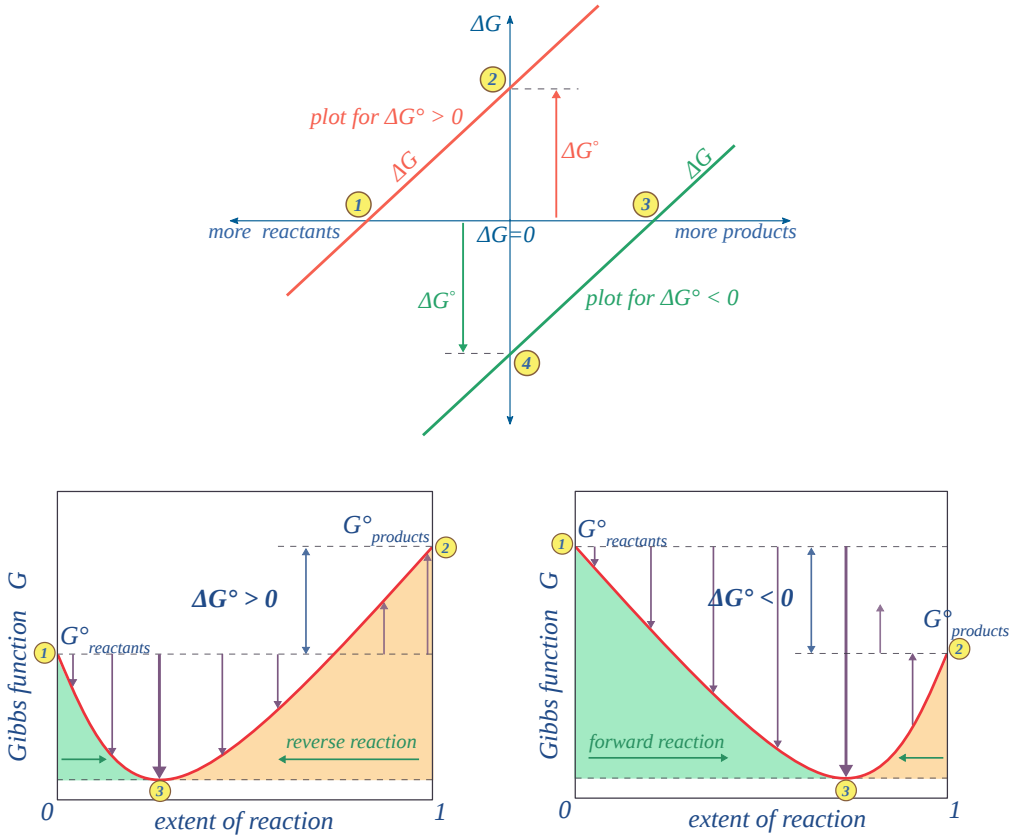


Figure **9.3.5**: (CC BY 4.0; Ümit Kaya via LibreTexts)

Take careful note of the following:

- for the $\Delta G^\circ > 0$ reaction. Notice that there are an infinite number of these values, depending on the progress of the reaction. In contrast there is only a single value (2) of ΔG°, corresponding to the composition at which $\Delta G = 0$ (1).
- At this point, some products have been formed, but the composition is still dominated by reactants.
- If we begin at a composition to the left of (1), ΔG will be negative and the composition will move to the right. Similarly if we begin with a composition to the right of (1), ΔG will be positive and the composition will move to the left.
- The plot on the right is for the $\Delta G^\circ < 0$ reaction, for which ΔG° is shown at (4). At its equilibrium point (3), there are more products than reactants. If we start at a composition to the right of (3), the composition will tend to move to the left. If the initial composition is to the left of (3), the reaction will tend to proceed to the right.
- What would happen if ΔG° were 0? The equilibrium point of such a reaction would be at the origin, corresponding to half the reactants being converted to products.

The important principle you should understand from this is that a negative $\Delta G°$ does not mean that the reactants will be completely transformed into products. By the same token, a positive $\Delta G°$ does not mean that no products are formed at all.

It should now be clear from the discussion above that a given reaction carried out under standard conditions is characterized by a *single value* of $\Delta G°$.

The reason for the Gibbs energy minimum at equilibrium relates to the increase in entropy when products and reactants coexist in the same phase. As seen in the plot, even a minute amount of "contamination" of products by reactants reduces the free energy below that of the pure products. In contrast, composition of a chemical reaction system undergoes continual change until the equilibrium state is reached. So the a single reaction can have an infinite number of ΔG values, reflecting the infinite possible compositions between the extremes of pure reactants (zero extent of reaction) and pure products (unity extent of reaction).

In the example of a reaction A → B, depicted in the above diagram, the standard free energy of the products (2) is smaller than that of the reactants (1), so the reaction will take place spontaneously. This does not mean that each mole of pure A will be converted into one mole of pure B. For reactions in which products and reactants occupy a single phase (gas or solution), the meaning of "spontaneous" is that the equilibrium composition (3) will correspond to an extent of reaction greater than 0.5 but smaller than unity.Note, however, that for $\Delta G°$ values in excess of about ±50 kJ mol^{-1}, the equilibrium composition will be negligibly different from zero or unity extent-of-reaction. The physical meaning of ΔG is that it tells us how far the free energy of the system has changed from $G°$ of the pure reactants (1). As the reaction proceeds to the right, the composition changes, and ΔG begins to fall. When the composition reaches (3), ΔG reaches its minimum value and further reaction would cause it to rise. But because free energy can only decrease but never increase, this does not happen. The composition of the system remains permanently at its equilibrium value.

A *G vs.* extent-of-reaction diagram for a non-spontaneous reaction can be interpreted in a similar way; the equilibrium composition (3) will correspond to an extent of reaction greater than zero but less than 0.5. In this case, the minimum at (3) reflects the increase in entropy when the reactants are "contaminated" by a small quantity of products.

If all this detail about ΔG seems a bit overwhelming, do not worry: it all gets hidden in the equilibrium constant and reaction quotient that we discuss in the next lesson!

9.3.5 INTERPRETATION OF STANDARD GIBBS ENERGY CHANGES

Although it is ΔG rather than ΔG^o that serves as a criterion for spontaneous change at constant temperature and pressure, ΔG^o values are so readily available that they are often used to get a rough idea of whether a given chemical change is possible. This is practical to do in some cases, but not in others:

EXAMPLE

It generally works for reactions such as

$$4\,NH_3\,(g) + 5\,O_2\,(g) \longrightarrow 4\,NO\,(g) + 6\,H_2O\,(g)$$

with $\Delta G^o = -1,010\,kJ$.

(industrially important for the manufacture of nitric acid) because ΔG^o is so negative that the reaction will be spontaneous and virtually complete under just about any reasonable set of conditions.

EXAMPLE

The following reaction expresses the fact that the water molecule is thermodynamically stable:

$$2\,H_2\,(g) + \tfrac{1}{2}\,O_2(g) \longrightarrow H_2O\,(l)$$

with $\Delta G^o = -237.2\,kJ$.

Note that this refers to *liquid* water (the standard state of H_2O at 25°). If you think about it, a negative standard Gibbs energy of formation (of which this is an example) can in fact be considered a definition of molecular stability.

EXAMPLE

Similarly, dissociation of dihydrogen into its atoms is highly unlikely under standard conditions:

$$H_2O\,(g) \longrightarrow 2\,H\,(g) + O\,(g)$$

with $\Delta G^o = +406.6\,kJ$.

Again, an analogous situation would apply to any stable molecule.

EXAMPLE

Now consider the dissociation of dinitrogen tetroxide

$$N_2O_4\,(g) \longrightarrow 2\,NO_2\,(g)$$

with $\Delta G^o = +2.8kJ$.

in which the positive value of $\Delta G°$ tells us that N_2O_4 at 1 atm pressure will not change into two moles of NO_2 at the same pressure, but owing to the small absolute value of $\Delta G°$, we can expect the spontaneity of the process to be quite sensitive to both the temperature (as shown in the table below) and to the pressure in exactly the way the Le Chatelier principle predicts.

EXAMPLE

For reactions involving dissolved ions, one has to be quite careful. Thus for the dissociation of the weak hydrofluoric acid

$$HF\,(aq) \longrightarrow H^+\,(aq) + F^-\,(aq)$$

with $\Delta G^o = -317\,kJ$.

it is clear that a 1 mol/L solution of HF will not dissociate into 1M ions, but this fact is not very useful because if the HF is added to water, the initial concentration of the fluoride ion will be zero (and that of H^+ very close to zero), and the Le Chatelier principle again predicts that *some* dissociation will be spontaneous.

EXAMPLE

It is common knowledge that dissociation of water into hydrogen- and hydroxyl ions occurs only very sparingly:

$$H_2O\,(l) \longrightarrow H^+\,(aq) + OH^-\,(aq)$$

with $\Delta G^o = 79.9\,kJ$.

which correctly predicts that the water will not form 1M (effective concentration) of the ions, but this is hardly news if you already know that the product of these ion concentrations can never exceed 10^{-14} at 298K.

EXAMPLE

Finally, consider this most familiar of all phase change processes, the vaporization of liquid water:

$$H_2O\,(l) \longrightarrow H_2O\,(g)$$

with $\Delta G^o = 8.58\,kJ$.

Conversion of liquid water to its vapor at 1 atm partial pressure does not take place at 25° C, at which temperature the equilibrium partial pressure of the vapor (the "vapor pressure") is only 0.031 atm (23.8 torr.) Gaseous H_2O at a pressure of 1 atm can only exist at 100° C. Of course, water left in an open container at room temperature will spontaneously evaporate if the partial pressure of water vapor in the air is less than 0.031 atm, corresponding to a relative humidity of under 100%

9.3.6 FINDING THE EQUILIBRIUM TEMPERATURE

A reaction is in its equilibrium state when

$$\Delta G = \Delta H – T\Delta S = 0 \tag{9.3.10}$$

The temperature at which this occurs is given by

$$T = \frac{\Delta H}{\Delta S} \tag{9.3.11}$$

If we approximate ΔH by ΔH^o and ΔS by ΔS^o, so Equation 9.3.10 would be

$$\Delta G \approx \Delta H^o – T\Delta S^o = 0 \tag{9.3.12}$$

We can then estimate the normal boiling point of a liquid. From the following thermodynamic data for water:

$$\begin{array}{ccc} H_2O(l) & \rightarrow & H_2O(g) \\ -285.9 & & -241.8 \quad \Delta H^\circ = +44.1\ kJ \\ 69.9 & & 188.7 \quad \Delta S^\circ = +118.7\ J\ K^{-1} \end{array}$$

CAUTION!

Because ΔH° values are normally expressed in kilojoules while ΔS° is given in joules, a very common student error is to overlook the need to express both in the same units.

We find that liquid water is in equilibrium with water vapor at a partial pressure of 1 atm when the temperature is

$$T = \frac{44,100\ J}{118.7\ J\ K^{-1}} = 371.5\ K \tag{9.3.13}$$

But "*the normal boiling point of water is 373 K*", you say? Very true. The reason we are off here is that both ΔH° and ΔS° have their own temperature dependencies; we are using the "standard" 25° values without correcting them to 100° C. Nevertheless, if you think about it, the fact that we can estimate the boiling point of a liquid from a table of thermodynamic data should be rather impressive! Of course, the farther one gets from 298 K, the more unreliable will be the result. Thus for the dissociation of dihydrogen into its atoms,

$$\begin{array}{ccc} H_2(g) & \rightarrow & 2\ H(g) \\ 0 & & 2 \times (218.0) \quad \Delta H^\circ = +436.0\ kJ \\ 130.6 & & 2 \times (114.6) \quad \Delta S^\circ = +98.6\ J\ K^{-1} \end{array}$$

$$T = \frac{436,000\ J}{98.6\ JK^{-1}} = 4,420\ K \tag{9.3.14}$$

All one can say here is that H_2 will break down at something over 3000 K or so. (You may already know that *all* molecules will dissociate into their atoms at high temperatures.) We tend to think of high temperatures as somehow "forcing" molecules to dissociate into their atoms, but this is wrong. In order to get the H–H bond to vibrate so violently through purely thermal excitation that the atoms would fly apart, a temperature more like 30,000 K would be required. The proper interpretation is at the temperature corresponding to $\Delta H/T\Delta S$, the molecule *spontaneously* absorbs energy from the surroundings sufficient to overcome the H-H bond strength.

9.3.7 PREDICTING THE EFFECTS OF TEMPERATURE

The $T\Delta S$ term interacts with the ΔH term in ΔG to determine whether the reaction can take place at a given temperature. This can be more clearly understood by examining plots of $T\Delta S^o$ and ΔH^o as functions of the temperature for some actual reactions. Of course these parameters refer to standard states that generally do not correspond to the temperatures, pressures, or concentrations that might be of interest in an actual case. Nevertheless, these quantities are easily found and they can usefully predict the way that temperature affects these systems.

9.3.7.1 CASE 1: EXOTHERMIC REACTION, ΔS° > 0

$$\mathrm{C(graphite) + O_2\,(g) \longrightarrow CO_2\,(g)}$$

- $\Delta H^o = -393\ kJ$
- $\Delta G^o = -394\ kJ$ at $298\ K$

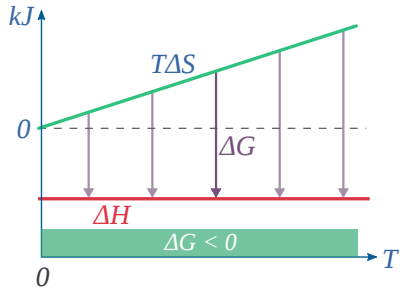


Figure **9.3.6**: (CC BY 4.0; Ümit Kaya via LibreTexts)

This *combustion reaction*, like most such reactions, is **spontaneous at all temperatures**. The positive entropy change is due mainly to the greater mass of CO_2 molecules compared to those of O_2.

9.3.7.2 CASE 2: EXOTHERMIC REACTION, ΔS° < 0

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

- $\Delta H^o = -46.2\,kJ$
- $\Delta G^o = -16.4\,kJ$ at $298\,K$

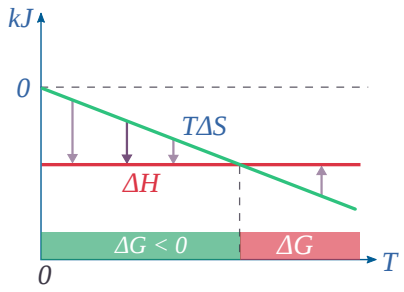


Figure **9.3.7**: (CC BY 4.0; Ümit Kaya via LibreTexts)

The decrease in moles of gas in the **Haber ammonia synthesis** drives the entropy change negative, making the reaction **spontaneous only at low temperatures**. Thus higher T, which speeds up the reaction, also reduces its extent.

9.3.7.3 CASE 3: ENDOTHERMIC REACTION, ΔS° > 0

$$N_2O_4\,(g) \longrightarrow 2\,NO_2\,(g)$$

- $\Delta H^o = 55.3\,kJ$
- $\Delta G^o = +2.8\,kJ$ at $298\,K$

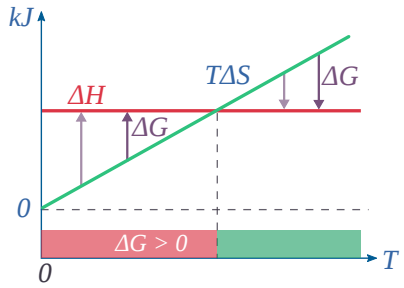


Figure **9.3.8**: (CC BY 4.0; Ümit Kaya via LibreTexts)

Dissociation reactions are typically endothermic with positive entropy change, and are therefore **spontaneous at high temperatures**. Ultimately, all molecules decompose to their atoms at sufficiently high temperatures.

9.3.7.4 CASE 4: ENDOTHERMIC REACTION, ΔS° < 0

$$\tfrac{1}{2}\,N_2\,(g) + O_2\ (g) \longrightarrow NO_2\,(g)$$

- $\Delta H^\circ = 33.2\,kJ$
- $\Delta S^o = -249\,J\,K^{-1}$
- $\Delta G^o = +51.3\,kJ$ at $298\,K$

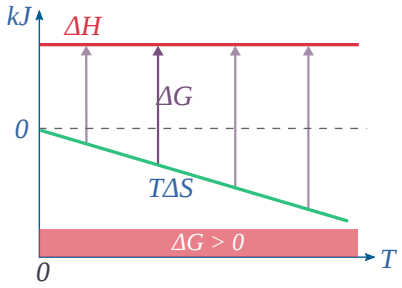


Figure **9.3.9**: (CC BY 4.0; Ümit Kaya via LibreTexts)

This reaction is **not spontaneous at any temperature**, meaning that *its reverse is always spontaneous*. But because the reverse reaction is kinetically inhibited, NO_2 can exist indefinitely at ordinary temperatures even though it is thermodynamically unstable.

9.3.8 CONCLUDING REMARKS ON GIBBS ENERGY

The appellation “free energy” for G has led to so much confusion that many scientists now refer to it simply as the *Gibbs energy*. The “free” part of the older name reflects the steam-engine origins of thermodynamics with its interest in converting heat into work: ΔG is the maximum amount of energy, which can be “freed” from the system to perform useful work. By "useful", we mean work other than that which is associated with the expansion of the system. This is most commonly in the form of electrical work (moving electric charge through a potential difference), but other forms of work (osmotic work, increase in surface area) are also possible.

A much more serious difficulty with the Gibbs function, particularly in the context of chemistry, is that although G has the *units* of energy (joules, or in its intensive form, J mol^{-1}), it lacks one of the most important attributes of energy in that it is not *conserved*. Thus, although the free energy always falls when a gas expands or a chemical reaction takes place spontaneously, there need be no compensating *increase* in energy anywhere else. Referring to G as an energy also reinforces the false but widespread notion that a fall in energy must accompany any change. But if we accept that energy is conserved, it is apparent that the only necessary condition for change (whether the dropping of a weight, expansion of a gas, or a chemical reaction) is the *redistribution* of energy. The quantity $\(-\Delta G\)$ associated with a process represents the quantity of energy that is “shared and spread”, which as we have already explained is the meaning of the increase in the entropy. The quotient $-\Delta G/T$ is in fact identical with ΔS_{total}, the entropy change of the world, whose increase is the primary criterion for any kind of change.

G differs from the thermodynamic quantities H and S in another significant way: it has no physical reality as a property of matter, whereas H and S can be related to the quantity and distribution of energy in a collection of molecules. The free energy is simply a useful construct that serves as a criterion for change and makes calculations easier.

WHAT GIBBS ENERGY IS NOT...

- Gibbs Energy is not free energy
- Gibbs Energy is not energy
- Gibbs Energy is not even "real"

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9.4: THE LAW OF MASS ACTION FOR RELATED AND SIMULTANEOUS EQUILIBRIA

LEARNING OBJECTIVES

- To know the relationship between the equilibrium constant and the rate constants for the forward and reverse reactions.
- To write an equilibrium constant expression for any reaction.

9.4.1 RELATIONSHIP AMONG EQUILIBRIUM EXPRESSIONS

Chemists frequently need to know the equilibrium constant for a reaction that has not been previously studied. In such cases, the desired reaction can often be written as the sum of other reactions for which the equilibrium constants are known. The equilibrium constant for the unknown reaction can then be calculated from the tabulated values for the other reactions.

To illustrate this procedure, let's consider the reaction of N_2 with O_2 to give NO_2. This reaction is an important source of the NO_2 that gives urban smog its typical brown color. The reaction normally occurs in two distinct steps. In the first reaction (1), N_2 reacts with O_2 at the high temperatures inside an internal combustion engine to give NO. The released NO then reacts with additional O_2 to give NO_2 (2). The equilibrium constant for each reaction at 100°C is also given.

1. $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)} \qquad K_1 = 2.0 \times 10^{-25}$
2. $2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)} \qquad K_2 = 6.4 \times 10^{9}$

Summing reactions (1) and (2) gives the overall reaction of N_2 with O_2:

3. $N_{2(g)} + 2O_{2(g)} \rightleftharpoons 2NO_{2(g)} \qquad K_3 = ?$

The equilibrium constant expressions for the reactions are as follows:

$$K_1 = \frac{[NO]^2}{[N_2][O_2]} \qquad K_2 = \frac{[NO_2]^2}{[NO]^2[O_2]} \qquad K_3 = \frac{[NO_2]^2}{[N_2][O_2]^2} \tag{9.4.1}$$

What is the relationship between K_1, K_2, and K_3, all at 100°C? The expression for K_1 has $[NO]^2$ in the numerator, the expression for K_2 has $[NO]^2$ in the denominator, and $[NO]^2$ does not appear in the expression for K_3. Multiplying K_1 by K_2 and canceling the $[NO]^2$ terms,

$$K_1K_2 = \frac{\cancel{[NO]^2}}{[N_2][O_2]} \times \frac{[NO_2]^2}{\cancel{[NO]^2}\,[O_2]} = \frac{[NO_2]^2}{[N_2][O_2]^2} = K_3 \tag{9.4.2}$$

Thus the product of the equilibrium constant expressions for K_1 and K_2 is the same as the equilibrium constant expression for K_3:

$$K_3 = K_1K_2 = (2.0 \times 10^{-25})(6.4 \times 10^{9}) = 1.3 \times 10^{-15} \tag{9.4.3}$$

The equilibrium constant for a reaction that is the sum of two or more reactions is equal to the product of the equilibrium constants for the individual reactions. In contrast, recall that according to Hess's Law, ΔH for the sum of two or more reactions is the sum of the ΔH values for the individual reactions.

NOTE

To determine K for a reaction that is the sum of two or more reactions, add the reactions but multiply the equilibrium constants.

EXAMPLE 9.4.6

The following reactions occur at 1200°C:

1. $CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)} \qquad K_1 = 9.17 \times 10^{-2}$
2. $CH_{4(g)} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + 4H_{2(g)} \qquad K_2 = 3.3 \times 10^{4}$

Calculate the equilibrium constant for the following reaction at the same temperature.

3. $CO_{(g)} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + H_2O_{(g)} + H_{2(g)} \qquad K_3 = ?$

Given: two balanced equilibrium equations, values of K, and an equilibrium equation for the overall reaction

Asked for: equilibrium constant for the overall reaction

Strategy:

Arrange the equations so that their sum produces the overall equation. If an equation had to be reversed, invert the value of K for that equation. Calculate K for the overall equation by multiplying the equilibrium constants for the individual equations.

Solution:

The key to solving this problem is to recognize that reaction 3 is the sum of reactions 1 and 2:

$$CO_{(g)} + \cancel{3H_{2(g)}} \rightleftharpoons \cancel{CH_{4(g)}} + H_2O_{(g)} \tag{9.4.4}$$

$$\cancel{CH_{4(g)}} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + \cancel{3H_{2(g)}} + H_{2(g)} \tag{9.4.5}$$

$$CO_{(g)} + 3H_{2(g)} \rightleftharpoons CS_{2(g)} + H_2O_{(g)} + H_{2(g)} \tag{9.4.6}$$

The values for K_1 and K_2 are given, so it is straightforward to calculate K_3:

$$K_3 = K_1K_2 = (9.17 \times 10^{-2})(3.3 \times 10^4) = 3.03 \times 10^3 \tag{9.4.7}$$

? EXERCISE 9.4.6

In the first of two steps in the industrial synthesis of sulfuric acid, elemental sulfur reacts with oxygen to produce sulfur dioxide. In the second step, sulfur dioxide reacts with additional oxygen to form sulfur trioxide. The reaction for each step is shown, as is the value of the corresponding equilibrium constant at 25°C. Calculate the equilibrium constant for the overall reaction at this same temperature.

1. $\frac{1}{8}S_{8(s)} + O_{2(g)} \rightleftharpoons SO_{2(g)}$ $K_1 = 4.4 \times 10^{53}$
2. $SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)}$ $K_2 = 2.6 \times 10^{12}$
3. $\frac{1}{8}S_{8(s)} + \frac{3}{2}O_{2(g)} \rightleftharpoons SO_{3(g)}$ $K_3 = ?$

Answer

$K_3 = 1.1 \times 10^{66}$

9.4.2 SUMMARY

An equilibrium system that contains products and reactants in a single phase is a homogeneous equilibrium; a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium. When a reaction can be expressed as the sum of two or more reactions, its equilibrium constant is equal to the product of the equilibrium constants for the individual reactions.

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9.5: GAS-PHASE AND HETEROGENEOUS REACTION EQUILIBRIA

LEARNING OBJECTIVES

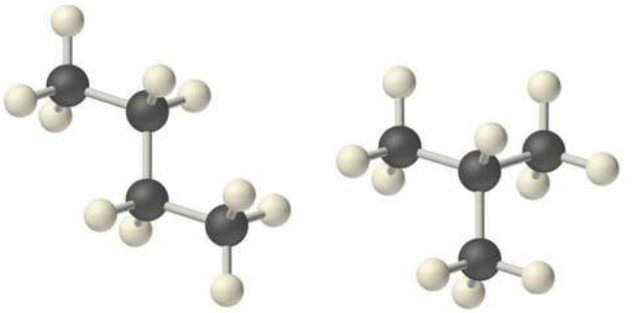
- To solve quantitative problems involving chemical equilibriums.

There are two fundamental kinds of equilibrium problems:

1. those in which we are given the concentrations of the reactants and the products at equilibrium (or, more often, information that allows us to calculate these concentrations), and we are asked to calculate the equilibrium constant for the reaction; and
2. those in which we are given the equilibrium constant and the initial concentrations of reactants, and we are asked to calculate the concentration of one or more substances at equilibrium. In this section, we describe methods for solving both kinds of problems.

9.5.1 CALCULATING AN EQUILIBRIUM CONSTANT FROM EQUILIBRIUM CONCENTRATIONS

The equilibrium constant for the decomposition of $CaCO_{3(s)}$ to $CaO_{(s)}$ and $CO_{2(g)}$ is $K = [CO_2]$. At 800°C, the concentration of CO_2 in equilibrium with solid $CaCO_3$ and CaO is $2.5 \times 10^{-3}\ M$. Thus K at 800°C is 2.5×10^{-3} (remember that equilibrium constants are unitless). A more complex example of this type of problem is the conversion of n-butane, an additive used to increase the volatility of gasoline, into isobutane (2-methylpropane).



This reaction can be written as follows:

$$n\text{-butane}_{(g)} \rightleftharpoons \text{isobutane}_{(g)} \tag{9.5.1}$$

and the equilibrium constant $K = [\text{isobutane}]/[\text{n-butane}]$. At equilibrium, a mixture of n-butane and isobutane at room temperature was found to contain 0.041 M isobutane and 0.016 M n-butane. Substituting these concentrations into the equilibrium constant expression,

$$\begin{aligned} K &= \frac{[\text{isobutane}]}{[\text{n-butane}]} \\ &= \frac{0.041\ M}{0.016\ M} \\ &= 2.6 \end{aligned}$$

Thus the equilibrium constant for the reaction as written is 2.6.

EXAMPLE 9.5.1

The reaction between gaseous sulfur dioxide and oxygen is a key step in the industrial synthesis of sulfuric acid:

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

A mixture of SO_2 and O_2 was maintained at 800 K until the system reached equilibrium. The equilibrium mixture contained

- $5.0 \times 10^{-2}\ M\ SO_3$,
- $3.5 \times 10^{-3}\ M\ O_2$, and
- $3.0 \times 10^{-3}\ M\ SO_2$.

Calculate K and K_p at this temperature.

Given: balanced equilibrium equation and composition of equilibrium mixture

Asked for: equilibrium constant

Strategy

Write the equilibrium constant expression for the reaction. Then substitute the appropriate equilibrium concentrations into this equation to obtain K.

Solution

Substituting the appropriate equilibrium concentrations into the equilibrium constant expression,

$$K = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(5.0 \times 10^{-2})^2}{(3.0 \times 10^{-3})^2(3.5 \times 10^{-3})} = 7.9 \times 10^4$$

To solve for K_p, we need to identify Δn where $\Delta n = 2 - 3 = -1$ and then

$$K_p = K(RT)^{\Delta n}$$
$$K_p = 7.9 \times 10^4[(0.08206\ L \cdot atm/mol \cdot K)(800K)]^{-1}$$
$$K_p = 1.2 \times 10^3$$

EXERCISE 9.5.1

Hydrogen gas and iodine react to form hydrogen iodide via the reaction

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

A mixture of H_2 and I_2 was maintained at 740 K until the system reached equilibrium. The equilibrium mixture contained

- 1.37×10^{-2} M HI,
- 6.47×10^{-3} M H_2, and
- 5.94×10^{-4} M I_2.

Calculate K and K_p for this reaction.

Answer (K)

$K = 48.8$

Answer (K_p)

$K_p = 48.8$

Chemists are not often given the concentrations of all the substances, and they are not likely to measure the equilibrium concentrations of all the relevant substances for a particular system. In such cases, we can obtain the equilibrium concentrations from the initial concentrations of the reactants and the balanced chemical equation for the reaction, as long as the equilibrium concentration of one of the substances is known. Example **9.5.2** shows one way to do this.

EXAMPLE 9.5.2

A 1.00 mol sample of $NOCl$ was placed in a 2.00 L reactor and heated to 227°C until the system reached equilibrium. The contents of the reactor were then analyzed and found to contain 0.056 mol of Cl_2. Calculate K at this temperature. The equation for the decomposition of $NOCl$ to NO and Cl_2 is as follows:

$$\mathrm{2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)}$$

Given: balanced equilibrium equation, amount of reactant, volume, and amount of one product at equilibrium

Asked for: K

Strategy:

A. Write the equilibrium constant expression for the reaction. Construct a table showing the initial concentrations, the changes in concentrations, and the final concentrations (as initial concentrations plus changes in concentrations).

B. Calculate all possible initial concentrations from the data given and insert them in the table.

C. Use the coefficients in the balanced chemical equation to obtain the changes in concentration of all other substances in the reaction. Insert those concentration changes in the table.

D. Obtain the final concentrations by summing the columns. Calculate the equilibrium constant for the reaction.

Solution

A The first step in any such problem is to balance the chemical equation for the reaction (if it is not already balanced) and use it to derive the equilibrium constant expression. In this case, the equation is already balanced, and the equilibrium constant expression is as follows:

$$K = \frac{[NO]^2[Cl_2]}{[NOCl]^2}$$

To obtain the concentrations of $NOCl$, NO, and Cl_2 at equilibrium, we construct a table showing what is known and what needs to be calculated. We begin by writing the balanced chemical equation at the top of the table, followed by three lines corresponding to the initial concentrations, the changes in concentrations required to get from the initial to the final state, and the final concentrations.

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	[NOCl]	[NO]	[Cl_2]
Initial			
Change			
Final			

B Initially, the system contains 1.00 mol of $NOCl$ in a 2.00 L container. Thus $[NOCl]_i = 1.00\ mol/2.00\ L = 0.500\ M$. The initial concentrations of NO and Cl_2 are $0\ M$ because initially no products are present. Moreover, we are told that at equilibrium the system contains 0.056 mol of Cl_2 in a 2.00 L container, so $[Cl_2]_f = 0.056\ mol/2.00\ L = 0.028\ M$. We insert these values into the following table:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	[NOCl]	[NO]	[Cl_2]
Initial	0.500	0	0
Change			
Final			0.028

C We use the stoichiometric relationships given in the balanced chemical equation to find the change in the concentration of Cl_2, the substance for which initial and final concentrations are known:

$$\Delta[Cl_2] = 0.028\ M_{(final)} - 0.00\ M_{(initial)}] = +0.028\ M$$

According to the coefficients in the balanced chemical equation, 2 mol of NO are produced for every 1 mol of Cl_2, so the change in the NO concentration is as follows:

$$\Delta[NO] = \left(\frac{0.028\ \cancel{mol\ Cl_2}}{L}\right)\left(\frac{2\ mol\ NO}{1\ \cancel{mol\ Cl_2}}\right) = 0.056\ M$$

Similarly, 2 mol of $NOCl$ are consumed for every 1 mol of Cl_2 produced, so the change in the $NOCl$ concentration is as follows:

$$\Delta[NOCl] = \left(\frac{0.028\ \cancel{mol\ Cl_2}}{L}\right)\left(\frac{-2\ mol\ NOCl}{1\ \cancel{mol\ Cl_2}}\right) = -0.056\ M$$

We insert these values into our table:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	[NOCl]	[NO]	[Cl_2]
Initial	0.500	0	0
Change	−0.056	+0.056	+0.028
Final			0.028

D We sum the numbers in the $[NOCl]$ and $[NO]$ columns to obtain the final concentrations of NO and $NOCl$:

$$[NO]_f = 0.000\ M + 0.056\ M = 0.056\ M$$

$$[NOCl]_f = 0.500\ M + (-0.056\ M) = 0.444 M$$

We can now complete the table:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	[$NOCl$]	[NO]	[Cl_2]
initial	0.500	0	0
change	−0.056	+0.056	+0.028
final	0.444	0.056	0.028

We can now calculate the equilibrium constant for the reaction:

$$K = \frac{[NO]^2[Cl_2]}{[NOCl]^2} = \frac{(0.056)^2(0.028)}{(0.444)^2} = 4.5 \times 10^{-4}$$

? EXERCISE 9.5.2

The German chemist Fritz Haber (1868–1934; Nobel Prize in Chemistry 1918) was able to synthesize ammonia (NH_3) by reacting $0.1248\ M\ H_2$ and $0.0416\ M\ N_2$ at about 500°C. At equilibrium, the mixture contained 0.00272 M NH_3. What is K for the reaction

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

at this temperature? What is K_p?

Answer (K)

$K = 0.105$

Answer (K_p)

$K_p = 2.61 \times 10^{-5}$

9.5.2 CALCULATING EQUILIBRIUM CONCENTRATIONS FROM THE EQUILIBRIUM CONSTANT

To describe how to calculate equilibrium concentrations from an equilibrium constant, we first consider a system that contains only a single product and a single reactant, the conversion of n-butane to isobutane (Equation 9.5.1), for which K = 2.6 at 25°C. If we begin with a 1.00 M sample of n-butane, we can determine the concentration of n-butane and isobutane at equilibrium by constructing a table showing what is known and what needs to be calculated, just as we did in Example 9.5.2.

$$\text{n-butane}(g) \rightleftharpoons \text{isobutane}(g) \tag{9.5.2}$$

ICE	[n-butane$_{(g)}$]	[isobutane$_{(g)}$]
Initial		
Change		
Final		

The initial concentrations of the reactant and product are both known: [n-butane]i = 1.00 M and [isobutane]i = 0 M. We need to calculate the equilibrium concentrations of both n-butane and isobutane. Because it is generally difficult to calculate final concentrations directly, we focus on the change in the concentrations of the substances between the initial and the final (equilibrium) conditions. If, for example, we define the change in the concentration of isobutane (Δ[isobutane]) as +x, then the change in the concentration of n-butane is Δ[n-butane] = −x. This is because the balanced chemical equation for the reaction tells us that 1 mol of n-butane is consumed for every 1 mol of isobutane produced. We can then express the final concentrations in terms of the initial concentrations and the changes they have undergone.

$$\text{n-butane}_{(g)} \rightleftharpoons \text{isobutane}_{(g)} \tag{9.5.3}$$

ICE	[n-butane$_{(g)}$]	[isobutane$_{(g)}$]
Initial	1.00	0
Change	−x	+x
Final	(1.00 − x)	(0 + x) = x

Substituting the expressions for the final concentrations of n-butane and isobutane from the table into the equilibrium equation,

$$K = \frac{[\text{isobutane}]}{[\text{n-butane}]} = \frac{x}{1.00 - x} = 2.6 \tag{9.5.4}$$

Rearranging and solving for x,

$$\begin{aligned} x &= 2.6(1.00 - x) = 2.6 - 2.6x \\ x + 2.6x &= 2.6 \\ x &= 0.72 \end{aligned}$$

We obtain the final concentrations by substituting this x value into the expressions for the final concentrations of n-butane and isobutane listed in the table:

$$[\text{n-butane}]_f = (1.00 - x)M = (1.00 - 0.72)M = 0.28\ M \tag{9.5.5}$$

$$[\text{isobutane}]_f = (0.00 + x)M = (0.00 + 0.72)M = 0.72\ M \tag{9.5.6}$$

We can check the results by substituting them back into the equilibrium constant expression to see whether they give the same K that we used in the calculation:

$$K = \frac{[\text{isobutane}]}{[\text{n-butane}]} = \left(\frac{0.72\ \cancel{M}}{0.28\ \cancel{M}}\right) = 2.6 \tag{9.5.7}$$

This is the same K we were given, so we can be confident of our results.

Example **9.5.3** illustrates a common type of equilibrium problem that you are likely to encounter.

EXAMPLE 9.5.3

The water–gas shift reaction is important in several chemical processes, such as the production of H_2 for fuel cells. Thisreaction can be written as follows:

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$

$K = 0.106$ at 700 K. If a mixture of gases that initially contains 0.0150 M H_2 and 0.0150 M CO_2 is allowed to equilibrate at 700 K, what are the final concentrations of all substances present?

Given: balanced equilibrium equation, K, and initial concentrations

Asked for: final concentrations

Strategy:

A. Construct a table showing what is known and what needs to be calculated. Define x as the change in the concentration of one substance. Then use the reaction stoichiometry to express the changes in the concentrations of the other substances in terms of x. From the values in the table, calculate the final concentrations.

B. Write the equilibrium equation for the reaction. Substitute appropriate values from the ICE table to obtain x.

C. Calculate the final concentrations of all species present. Check your answers by substituting these values into the equilibrium constant expression to obtain K.

Solution

A The initial concentrations of the reactants are $[H_2]_i = [CO_2]_i = 0.0150\ M$. Just as before, we will focus on the change in the concentrations of the various substances between the initial and final states. If we define the change in the concentration of H_2O as x, then $\Delta[H_2O] = +x$. We can use the stoichiometry of the reaction to express the changes in the concentrations of the other substances in terms of x. For example, 1 mol of CO is produced for every 1 mol of H_2O, so the change in the CO concentration can be expressed as $\Delta[CO] = +x$. Similarly, for every 1 mol of H_2O produced, 1 mol each of H_2 and CO_2 are consumed, so the change in the concentration of the reactants is $\Delta[H_2] = \Delta[CO_2] = -x$. We enter the values in the following table and calculate the final concentrations.

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$

ICE	$[H_2]$	$[CO_2]$	$[H_2O]$	$[CO]$
Initial	0.0150	0.0150	0	0
Change	−x	−x	+x	+x
Final	(0.0150 − x)	(0.0150 − x)	x	x

B We can now use the equilibrium equation and the given K to solve for x:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(x)(x)}{(0.0150-x)(0.0150-x)} = \frac{x^2}{(0.0150-x)^2} = 0.106$$

We could solve this equation with the quadratic formula, but it is far easier to solve for x by recognizing that the left side of the equation is a perfect square; that is,

$$\frac{x^2}{(0.0150-x)^2} = \left(\frac{x}{0.0150-x}\right)^2 = 0.106$$

Taking the square root of the middle and right terms,

$$\frac{x^2}{(0.0150-x)^2} = (0.106)^{1/2} = 0.326$$

$$x = (0.326)(0.0150) - 0.326x$$

$$1.326x = 0.00489$$

$$x = 0.00369 = 3.69 \times 10^{-3}$$

C The final concentrations of all species in the reaction mixture are as follows:

- $[H_2]_f = [H_2]_i + \Delta[H_2] = (0.0150 - 0.00369)\ M = 0.0113\ M$
- $[CO_2]_f = [CO_2]_i + \Delta[CO_2] = (0.0150 - 0.00369)\ M = 0.0113\ M$
- $[H_2O]_f = [H_2O]_i + \Delta[H_2O] = (0 + 0.00369)\ M = 0.00369\ M$
- $[CO]_f = [CO]_i + \Delta[CO] = (0 + 0.00369)\ M = 0.00369\ M$

We can check our work by inserting the calculated values back into the equilibrium constant expression:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(0.00369)^2}{(0.0113)^2} = 0.107$$

To two significant figures, this K is the same as the value given in the problem, so our answer is confirmed.

? EXERCISE 9.5.3

Hydrogen gas reacts with iodine vapor to give hydrogen iodide according to the following chemical equation:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

$K = 54$ at 425°C. If 0.172 M H_2 and I_2 are injected into a reactor and maintained at 425°C until the system equilibrates, what is the final concentration of each substance in the reaction mixture?

Answer

$[HI]_f = 0.270\ M\ [H_2]_f = [I_2]_f = 0.037\ M$

In Example **9.5.3**, the initial concentrations of the reactants were the same, which gave us an equation that was a perfect square and simplified our calculations. Often, however, the initial concentrations of the reactants are not the same, and/or one or more of the products may be present when the reaction starts. Under these conditions, there is usually no way to simplify the problem, and we must determine the equilibrium concentrations with other means. Such a case is described in Example **9.5.4**.

✔ EXAMPLE 9.5.4

In the water–gas shift reaction shown in Example **9.5.3**, a sample containing 0.632 M CO_2 and 0.570 M H_2 is allowed to equilibrate at 700 K. At this temperature, $K = 0.106$. What is the composition of the reaction mixture at equilibrium?

Given: balanced equilibrium equation, concentrations of reactants, and K

Asked for: composition of reaction mixture at equilibrium

Strategy:

A. Write the equilibrium equation. Construct a table showing the initial concentrations of all substances in the mixture. Complete the table showing the changes in the concentrations (x) and the final concentrations.

B. Write the equilibrium constant expression for the reaction. Substitute the known K value and the final concentrations to solve for x.

C. Calculate the final concentration of each substance in the reaction mixture. Check your answers by substituting these values into the equilibrium constant expression to obtain K.

Solution

A $[CO_2]_i = 0.632\ M$ and $[H_2]_i = 0.570\ M$. Again, x is defined as the change in the concentration of H_2O: $\Delta[H_2O] = +x$. Because 1 mol of CO is produced for every 1 mol of H_2O, the change in the concentration of CO is the same as the change in the concentration of H2O, so Δ[CO] = +x. Similarly, because 1 mol each of H_2 and CO_2 are consumed for every 1 mol of H_2O produced, $\Delta[H_2] = \Delta[CO_2] = -x$. The final concentrations are the sums of the initial concentrations and the changes in concentrations at equilibrium.

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$

ICE	$H_{2(g)}$	$CO_{2(g)}$	$H_2O_{(g)}$	$CO_{(g)}$
Initial	0.570	0.632	0	0
Change	−x	−x	+x	+x
Final	(0.570 − x)	(0.632 − x)	x	x

B We can now use the equilibrium equation and the known K value to solve for x:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{x^2}{(0.570 - x)(0.632 - x)} = 0.106$$

In contrast to Example **9.5.3**, however, there is no obvious way to simplify this expression. Thus we must expand the expression and multiply both sides by the denominator:

$$x^2 = 0.106(0.360 - 1.20x + x^2)$$

Collecting terms on one side of the equation,

$$0.894x^2 + 0.127x - 0.0382 = 0$$

This equation can be solved using the quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.127 \pm \sqrt{(0.127)^2 - 4(0.894)(-0.0382)}}{2(0.894)}$$

$$x = 0.148 \text{ and } -0.290$$

Only the answer with the positive value has any physical significance, so $\Delta[H_2O] = \Delta[CO] = +0.148M$, and $\Delta[H_2] = \Delta[CO_2] = -0.148\ M$.

C The final concentrations of all species in the reaction mixture are as follows:

- $[H_2]_f [= [H_2]_i + \Delta[H_2] = 0.570\ M - 0.148\ M = 0.422M$
- $[CO_2]_f = [CO_2]_i + \Delta[CO_2] = 0.632\ M - 0.148\ M = 0.484M$
- $[H_2O]_f = [H_2O]_i + \Delta[H_2O] = 0\ M + 0.148\ M = 0.148\ M$
- $[CO]_f = [CO]_i + \Delta[CO] = 0M + 0.148\ M = 0.148M$

We can check our work by substituting these values into the equilibrium constant expression:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(0.148)^2}{(0.422)(0.484)} = 0.107$$

Because K is essentially the same as the value given in the problem, our calculations are confirmed.

? EXERCISE 9.5.4

The exercise in Example **9.5.1** showed the reaction of hydrogen and iodine vapor to form hydrogen iodide, for which $K = 54$ at 425°C. If a sample containing 0.200 M H_2 and 0.0450 M I_2 is allowed to equilibrate at 425°C, what is the final concentration of each substance in the reaction mixture?

Answer

$[H_I]_f = 0.0882\ M$

$[H_2]_f = 0.156\ M$

$[I_2]_f = 9.2 \times 10^{-4} M$

In many situations it is not necessary to solve a quadratic (or higher-order) equation. Most of these cases involve reactions for which the equilibrium constant is **either very small ($K \leq 10^{-3}$) or very large ($K \geq 10^{3}$)**, which means that the change in the concentration (defined as x) is essentially negligible compared with the initial concentration of a substance. Knowing this simplifies the calculations dramatically, as illustrated in Example **9.5.5**.

✔ EXAMPLE 9.5.5

Atmospheric nitrogen and oxygen react to form nitric oxide:

$$\mathrm{N_2(g) + O_2(g) \rightleftharpoons 2NO(g)} \tag{9.5.8}$$

with $K_p = 2.0 \times 10^{-31}$ at 25°C.

What is the partial pressure of **NO** in equilibrium with N_2 and O_2 in the atmosphere (at 1 atm) $P_{N_2} = 0.78\ atm$ and $P_{O_2} = 0.21\ atm$?

Given: balanced equilibrium equation and values of K_p, P_{O_2}, and P_{N_2}

Asked for: partial pressure of NO

Strategy:

A. Construct a table and enter the initial partial pressures, the changes in the partial pressures that occur during the course of the reaction, and the final partial pressures of all substances.

B. Write the equilibrium equation for the reaction. Then substitute values from the table to solve for the change in concentration (x).

C. Calculate the partial pressure of NO. Check your answer by substituting values into the equilibrium equation and solving for K.

Solution

A Because we are given Kp and partial pressures are reported in atmospheres, we will use partial pressures. The initial partial pressure of O_2 is 0.21 atm and that of N_2 is 0.78 atm. If we define the change in the partial pressure of NO as 2x, then the change in the partial pressure of O_2 and of N_2 is −x because 1 mol each of N_2 and of O_2 is consumed for every 2 mol of NO produced. Each substance has a final partial pressure equal to the sum of the initial pressure and the change in that pressure at equilibrium.

$$\mathrm{N_2(g) + O_2(g) \rightleftharpoons 2NO(g)} \tag{9.5.9}$$

ICE	P_{N_2}	P_{O_2}	P_{NO}
Initial	0.78	0.21	0
Change	−x	−x	+2x
Final	(0.78 − x)	(0.21 − x)	2x

B Substituting these values into the equation for the equilibrium constant,

$$K_p = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})} = \frac{(2x)^2}{(0.78 - x)(0.21 - x)} = 2.0 \times 10^{-31}$$

In principle, we could multiply out the terms in the denominator, rearrange, and solve the resulting quadratic equation. In practice, it is far easier to recognize that an equilibrium constant of this magnitude means that the extent of the reaction will be very small; therefore, the x value will be negligible compared with the initial concentrations. If this assumption is correct, then to two significant figures, (0.78 − x) = 0.78 and (0.21 − x) = 0.21. Substituting these expressions into our original equation,

$$\frac{(2x)^2}{(0.78)(0.21)} = 2.0 \times 10^{-31}$$

$$\frac{4x^2}{0.16} = 2.0 \times 10^{-31}$$

$$x^2 = \frac{0.33 \times 10^{-31}}{4}$$

$$x = 9.1 \times 10^{-17}$$

C Substituting this value of x into our expressions for the final partial pressures of the substances,

- $P_{NO} = 2x\ atm = 1.8 \times 10^{-16}\ atm$
- $P_{N_2} = (0.78 - x)\ atm = 0.78\ atm$
- $P_{O_2} = (0.21 - x)\ atm = 0.21\ atm$

From these calculations, we see that our initial assumption regarding x was correct: given two significant figures, 2.0×10^{-16} is certainly negligible compared with 0.78 and 0.21. When can we make such an assumption? As a general rule, if x is less than about 5% of the total, or $10^{-3} > K > 10^{3}$, then the assumption is justified. Otherwise, we must use the quadratic formula or some other approach. The results we have obtained agree with the general observation that toxic NO, an ingredient of smog, does not form from atmospheric concentrations of N_2 and O_2 to a substantial degree at 25°C. We can verify our results by substituting them into the original equilibrium equation:

$$K_p = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})} = \frac{(1.8 \times 10^{-16})^2}{(0.78)(0.21)} = 2.0 \times 10^{-31}$$

The final K_p agrees with the value given at the beginning of this example.

? EXERCISE 9.5.5

Under certain conditions, oxygen will react to form ozone, as shown in the following equation:

$$3O_{2(g)} \rightleftharpoons 2O_{3(g)}$$

with $K_p = 2.5 \times 10^{-59}$ at 25°C. What ozone partial pressure is in equilibrium with oxygen in the atmosphere ($P_{O_2} = 0.21\ atm$)?

Answer

$4.8 \times 10^{-31}\ atm$

Another type of problem that can be simplified by assuming that changes in concentration are negligible is one in which the equilibrium constant is very large (K ≥ 10^3). A large equilibrium constant implies that the reactants are converted almost entirely to products, so we can assume that the reaction proceeds 100% to completion. When we solve this type of problem, we view the system as equilibrating from the products side of the reaction rather than the reactants side. This approach is illustrated in Example **9.5.6**.

✓ EXAMPLE 9.5.6

The chemical equation for the reaction of hydrogen with ethylene (C_2H_4) to give ethane (C_2H_6) is as follows:

$$H_{2(g)} + C_2H_{4(g)} \overset{Ni}{\rightleftharpoons} C_2H_{6(g)}$$

with $K = 9.6 \times 10^{18}$ at 25°C. If a mixture of 0.200 M H_2 and 0.155 M C_2H_4 is maintained at 25°C in the presence of a powdered nickel catalyst, what is the equilibrium concentration of each substance in the mixture?

Given: balanced chemical equation, K, and initial concentrations of reactants

Asked for: equilibrium concentrations

Strategy:

A. Construct a table showing initial concentrations, concentrations that would be present if the reaction were to go to completion, changes in concentrations, and final concentrations.

B. Write the equilibrium constant expression for the reaction. Then substitute values from the table into the expression to solve for x (the change in concentration).

C. Calculate the equilibrium concentrations. Check your answers by substituting these values into the equilibrium equation.

Solution:

A From the magnitude of the equilibrium constant, we see that the reaction goes essentially to completion. Because the initial concentration of ethylene (0.155 M) is less than the concentration of hydrogen (0.200 M), ethylene is the limiting reactant; that is, no more than 0.155 M ethane can be formed from 0.155 M ethylene. If the reaction were to go to completion, the concentration of ethane would be 0.155 M and the concentration of ethylene would be 0 M. Because the concentration of hydrogen is greater than what is needed for complete reaction, the concentration of unreacted hydrogen in the reaction mixture would be 0.200 M − 0.155 M = 0.045 M. The equilibrium constant for the forward reaction is very large, so the equilibrium constant for the reverse reaction must be very small. The problem then is identical to that in Example **9.5.5**. If we define −x as the change in the ethane concentration for the reverse reaction, then the change in the ethylene and hydrogen concentrations is +x. The final equilibrium concentrations are the sums of the concentrations for the forward and reverse reactions.

$$H_{2(g)} + C_2H_{4(g)} \overset{Ni}{\rightleftharpoons} C_2H_{6(g)}$$

IACE	$[H_{2(g)}]$	$[C_2H_{4(g)}]$	$[C_2H_{6(g)}]$
Initial	0.200	0.155	0
Assuming 100% reaction	0.045	0	0.155
Change	+x	+x	−x
Final	(0.045 + x)	(0 + x)	(0.155 − x)

B Substituting values into the equilibrium constant expression,

$$K = \frac{[C_2H_6]}{[H_2][C_2H_4]} = \frac{0.155 - x}{(0.045 + x)x} = 9.6 \times 10^{18}$$

Once again, the magnitude of the equilibrium constant tells us that the equilibrium will lie far to the right as written, so the reverse reaction is negligible. Thus x is likely to be very small compared with either 0.155 M or 0.045 M, and the equation can be simplified [(0.045 + x) = 0.045 and (0.155 − x) = 0.155] as follows:

$$K = \frac{0.155}{0.045x} = 9.6 \times 10^{18}$$

$$x = 3.6 \times 10^{-19}$$

C The small x value indicates that our assumption concerning the reverse reaction is correct, and we can therefore calculate the final concentrations by evaluating the expressions from the last line of the table:

- $[C_2H_6]_f = (0.155 - x)\ M = 0.155\ M$
- $[C_2H_4]_f = x\ M = 3.6 \times 10^{-19} M$
- $[H_2]_f = (0.045 + x)\ M = 0.045\ M$

We can verify our calculations by substituting the final concentrations into the equilibrium constant expression:

$$K = \frac{[C_2H_6]}{[H_2][C_2H_4]} = \frac{0.155}{(0.045)(3.6 \times 10^{-19})} = 9.6 \times 10^{18}$$

This K value agrees with our initial value at the beginning of the example.

? EXERCISE 9.5.6

Hydrogen reacts with chlorine gas to form hydrogen chloride:

$$H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)}$$

with $K_p = 4.0 \times 10^{31}$ at 47°C. If a mixture of 0.257 M H_2 and 0.392 M Cl_2 is allowed to equilibrate at 47°C, what is the equilibrium composition of the mixture?

Answer

$[H_2]_f = 4.8 \times 10^{-32}\ M$

$[Cl_2]_f = 0.135\ M$

$[HCl]_f = 0.514\ M$

9.5.3 SUMMARY

Various methods can be used to solve the two fundamental types of equilibrium problems:

1. those in which we calculate the concentrations of reactants and products at equilibrium and
2. those in which we use the equilibrium constant and the initial concentrations of reactants to determine the composition of the equilibrium mixture.

When an equilibrium constant is calculated from equilibrium concentrations, molar concentrations or partial pressures are substituted into the equilibrium constant expression for the reaction. Equilibrium constants can be used to calculate the equilibrium concentrations of reactants and products by using the quantities or concentrations of the reactants, the stoichiometry of the balanced chemical equation for the reaction, and a tabular format to obtain the final concentrations of all species at equilibrium.

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9.6: THE DIRECTION OF CHANGE IN CHEMICAL REACTIONS- EMPIRICAL DESCRIPTION

LEARNING OBJECTIVES

- To predict in which direction a reaction will proceed.
- Describe the ways in which an equilibrium system can be stressed
- Predict the response of a stressed equilibrium using Le Chatelier's principle

We previously saw that knowing the magnitude of the equilibrium constant under a given set of conditions allows chemists to predict the extent of a reaction. Often, however, chemists must decide whether a system has reached equilibrium or if the composition of the mixture will continue to change with time. In this section, we describe how to quantitatively analyze the composition of a reaction mixture to make this determination.

9.6.1 THE REACTION QUOTIENT

To determine whether a system has reached equilibrium, chemists use a quantity called the Reaction Quotient (Q). The expression for the Reaction Quotient has precisely the same form as the equilibrium constant expression from the Law of Mass Action, except that Q may be derived from a set of values measured at any time during the reaction of any mixture of the reactants and the products, regardless of whether the system is at equilibrium. Therefore, for the following general reaction:

$$aA + bB \rightarrow cC + dD \tag{9.6.1}$$

the Reaction Quotient is defined as follows:

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{9.6.2}$$

To understand how information is obtained using a Reaction Quotient, consider the dissociation of dinitrogen tetroxide to nitrogen dioxide,

$$\mathrm{N_2O_4\,(g)} \rightleftharpoons \mathrm{2\,NO_2\,(g)}. \tag{9.6.3}$$

For this reaction, $K = 4.65 \times 10^{-3}$ at 298 K. We can write Q for this reaction as follows:

$$Q = \frac{[NO_2]^2}{[N_2O_4]} \tag{9.6.4}$$

The following table lists data from three experiments in which samples of the reaction mixture were obtained and analyzed at equivalent time intervals, and the corresponding values of Q were calculated for each. Each experiment begins with different proportions of product and reactant:

Table **9.6.1**: Three Conditions of the dissociation of dinitrogen tetroxide to nitrogen dioxide (Equation **9.6.1**)

Experiment	$[NO_2]\ (M)$	$[N_2O_4]\ (M)$	$Q = \frac{[NO^2]^2}{[N^2O^4]}$
1	0	0.0400	$\frac{0^2}{0.0400} = 0$
2	0.0600	0	$\frac{(0.0600)^2}{0} = \text{undefined}$
3	0.0200	0.0600	$\frac{(0.0200)^2}{0.0600} = 6.67 \times 10^{-3}$

As these calculations demonstrate, Q can have any numerical value between 0 and infinity (undefined); that is, Q can be greater than, less than, or equal to K.

Comparing the magnitudes of Q and K enables us to determine whether a reaction mixture is already at equilibrium and, if it is not, predict how its composition will change with time to reach equilibrium (i.e., whether the reaction will proceed to the right or to the left as written). All you need to remember is that the composition of a system not at equilibrium will change in a way that makes Q approach K. If $Q = K$, for example, then the system is already at equilibrium, and no further change in the composition of the system will occur unless the conditions are changed. If $Q < K$, then the ratio of the concentrations of products to the concentrations of reactants is less than the ratio at equilibrium. Therefore, the reaction will proceed to the right as written, forming products at the expense of reactants. Conversely, if $Q > K$, then the ratio of the concentrations of products to the concentrations of reactants is greater than at equilibrium, so the reaction will proceed to the left as written, forming reactants at the expense of products. These points are illustrated graphically in Figure **9.6.1**.

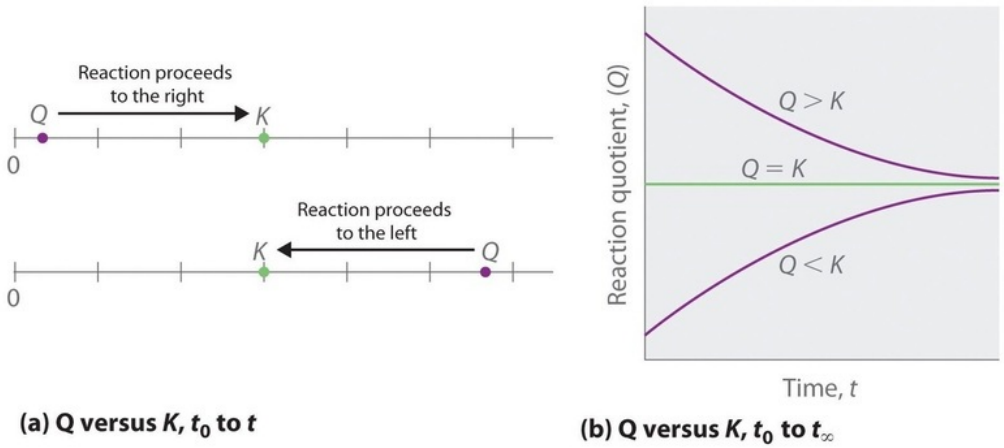


Figure **9.6.1**: Two Different Ways of Illustrating How the Composition of a System Will Change Depending on the Relative Values of Q and K.(a) Both Q and K are plotted as points along a number line: the system will always react in the way that causes Q to approach K. (b) The change in the composition of a system with time is illustrated for systems with initial values of $Q > K$, $Q < K$, and $Q = K$.

If $Q < K$, the reaction will proceed to the right as written. If $Q > K$, the reaction will proceed to the left as written. If $Q = K$, then the system is at equilibrium.

EXAMPLE 9.6.1: STEAM-REFORMING

At elevated temperatures, methane (CH_4) reacts with water to produce hydrogen and carbon monoxide in what is known as a steam-reforming reaction:

$$\mathrm{CH_4\,(g) + H_2O\,(g) \rightleftharpoons CO\,(g) + 3\,H_2\,(g)}$$

$K = 2.4 \times 10^{-4}$ at 900 K. Huge amounts of hydrogen are produced from natural gas in this way and are then used for the industrial synthesis of ammonia. If 1.2×10^{-2} mol of CH_4, 8.0×10^{-3} mol of H_2O, 1.6×10^{-2} mol of CO, and 6.0×10^{-3} mol of H_2 are placed in a 2.0 L steel reactor and heated to 900 K, will the reaction be at equilibrium or will it proceed to the right to produce CO and H_2 or to the left to form CH_4 and H_2O?

Given: balanced chemical equation, K, amounts of reactants and products, and volume

Asked for: direction of reaction

Strategy:

A. Calculate the molar concentrations of the reactants and the products.

B. Use Equation 9.6.2 to determine Q. Compare Q and K to determine in which direction the reaction will proceed.

Solution:

A: We must first find the initial concentrations of the substances present. For example, we have $1.2 \times 10^{-2} mol$ of CH_4 in a 2.0 L container, so

$$[CH_4] = \frac{1.2 \times 10^{-2} mol}{2.0\ L} = 6.0 \times 10^{-3} M$$

We can calculate the other concentrations in a similar way:

- $[H_2O] = 4.0 \times 10^{-3} M$,
- $[CO] = 8.0 \times 10^{-3} M$, and
- $[H_2] = 3.0 \times 10^{-3} M$.

B: We now compute Q and compare it with K:

$$Q = \frac{[CO][H_2]^3}{[CH_4][H_2O]}$$
$$= \frac{(8.0 \times 10^{-3})(3.0 \times 10^{-3})^3}{(6.0 \times 10^{-3})(4.0 \times 10^{-3})}$$
$$= 9.0 \times 10^{-6}$$

Because $K = 2.4 \times 10^{-4}$, we see that $Q < K$. Thus the ratio of the concentrations of products to the concentrations of reactants is less than the ratio for an equilibrium mixture. The reaction will therefore proceed to the right as written, forming H_2 and CO at the expense of H_2O and CH_4.

? EXERCISE 9.6.1

In the water–gas shift reaction introduced in Example 9.6.1, carbon monoxide produced by steam-reforming reaction of methane reacts with steam at elevated temperatures to produce more hydrogen:

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

$K = 0.64$ at 900 K. If 0.010 mol of both CO and H_2O, 0.0080 mol of CO_2, and 0.012 mol of H_2 are injected into a 4.0 L reactor and heated to 900 K, will the reaction proceed to the left or to the right as written?

Answer

$Q = 0.96$ (Q > K), so the reaction will proceed to the left, and CO and H_2O will form.

9.6.2 PREDICTING THE DIRECTION OF A REACTION WITH A GRAPH

By graphing a few equilibrium concentrations for a system at a given temperature and pressure, we can readily see the range of reactant and product concentrations that correspond to equilibrium conditions, for which $Q = K$. Such a graph allows us to predict what will happen to a reaction when conditions change so that Q no longer equals K, such as when a reactant concentration or a product concentration is increased or decreased.

Lead carbonate decomposes to lead oxide and carbon dioxide according to the following equation:

$$PbCO_3(s) \rightleftharpoons PbO(s) + CO_2(g) \tag{9.6.5}$$

Because $PbCO_3$ and PbO are solids, the equilibrium constant is simply $K = [CO_2]$. At a given temperature, therefore, any system that contains solid $PbCO_3$ and solid PbO will have exactly the same concentration of CO_2 at equilibrium, regardless of the ratio or the amounts of the solids present. This situation is represented in Figure 9.6.2, which shows a plot of $[CO_2]$ versus the amount of $PbCO_3$ added. Initially, the added $PbCO_3$ decomposes completely to CO_2 because the amount of $PbCO_3$ is not sufficient to give a CO_2 concentration equal to K. Thus the left portion of the graph represents a system that is not at equilibrium because it contains only CO2(g) and PbO(s). In contrast, when just enough $PbCO_3$ has been added to give $[CO_2] = K$, the system has reached equilibrium, and adding more $PbCO_3$ has no effect on the CO_2 concentration: the graph is a horizontal line. Thus any CO_2 concentration that is not on the horizontal line represents a nonequilibrium state, and the system will adjust its composition to achieve equilibrium, provided enough $PbCO_3$ and PbO are present. For example, the point labeled A in Figure 9.6.2 lies above the horizontal line, so it corresponds to a $[CO_2]$ that is greater than the equilibrium concentration of CO_2 (Q > K). To reach equilibrium, the system must decrease $[CO_2]$, which it can do only by reacting CO_2 with solid PbO to form solid $PbCO_3$. Thus the reaction in Equation 9.6.5 will proceed to the left as written, until $[CO_2] = K$. Conversely, the point labeled B in Figure 9.6.2 lies below the horizontal line, so it corresponds to a $[CO_2]$ that is less than the equilibrium concentration of CO_2 (Q < K). To reach equilibrium, the system must increase $[CO_2]$, which it can do only by decomposing solid $PbCO_3$ to form CO_2 and solid PbO. The reaction in Equation 9.6.5 will therefore proceed to the right as written, until $[CO_2] = K$.

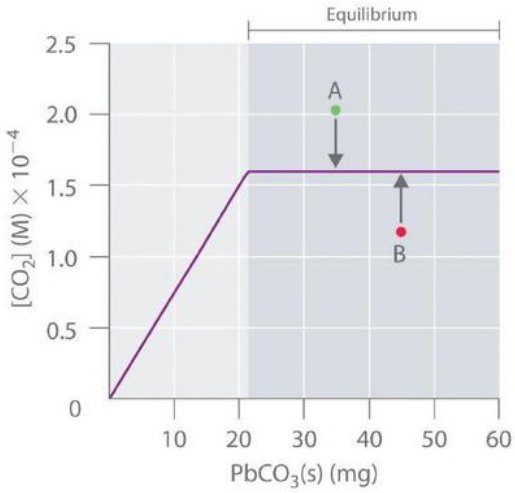


Figure **9.6.2**: The Concentration of Gaseous CO_2 in a Closed System at Equilibrium as a Function of the Amount of Solid $PbCO_3$ Added. Initially the concentration of CO2(g) increases linearly with the amount of solid $PbCO_3$ added, as $PbCO_3$ decomposes to CO2(g) and solid PbO. Once the CO_2 concentration reaches the value that corresponds to the equilibrium concentration, however, adding more solid $PbCO_3$ has no effect on $[CO_2]$, as long as the temperature remains constant.

In contrast, the reduction of cadmium oxide by hydrogen gives metallic cadmium and water vapor:

$$\mathrm{CdO\,(s) + H_2\,(g) \rightleftharpoons Cd\,(s) + H_2O\,(g)} \tag{9.6.6}$$

and the equilibrium constant K is $[H_2O]/[H_2]$. If $[H_2O]$ is doubled at equilibrium, then [H2] must also be doubled for the system to remain at equilibrium. A plot of $[H_2O]$ versus $[H_2]$ at equilibrium is a straight line with a slope of K (Figure **9.6.3**). Again, only those pairs of concentrations of H_2O and H_2 that lie on the line correspond to equilibrium states. Any point representing a pair of concentrations that does not lie on the line corresponds to a nonequilibrium state. In such cases, the reaction in Equation 9.6.6 will proceed in whichever direction causes the composition of the system to move toward the equilibrium line. For example, point A in Figure **9.6.3** lies below the line, indicating that the $[H_2O]/[H_2]$ ratio is less than the ratio of an equilibrium mixture (Q < K). Thus the reaction in Equation 9.6.6 will proceed to the right as written, consuming H_2 and producing H_2O, which causes the concentration ratio to move up and to the left toward the equilibrium line. Conversely, point B in Figure **9.6.3** lies above the line, indicating that the $[H_2O]/[H_2]$ ratio is greater than the ratio of an equilibrium mixture (Q > K). Thus the reaction in Equation 9.6.6 will proceed to the left as written, consuming H_2O and producing H_2, which causes the concentration ratio to move down and to the right toward the equilibrium line.

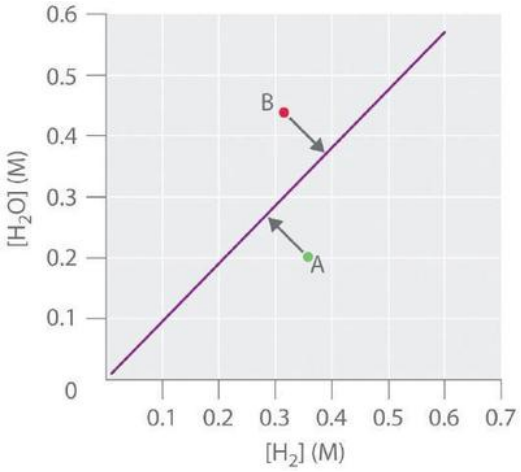


Figure **9.6.3**: The Concentration of Water Vapor versus the Concentration of Hydrogen for the $CdO_{(s)} + H_{2(g)} \rightleftharpoons Cd_{(s)} + H_2O_{(g)}$ System at Equilibrium. For any equilibrium concentration of $H_2O_{(g)}$, there is only one equilibrium concentration of H2(g). Because the magnitudes of the two concentrations are directly proportional, a large $[H_2O]$ at equilibrium requires a large $[H_2]$ and vice versa. In this case, the slope of the line is equal to K.

In another example, solid ammonium iodide dissociates to gaseous ammonia and hydrogen iodide at elevated temperatures:

$$NH_4I_{(s)} \rightleftharpoons NH_{3(g)} + HI_{(g)} \tag{9.6.7}$$

For this system, K is equal to the product of the concentrations of the two products: $[NH_3][HI]$. If we double the concentration of NH3, the concentration of HI must decrease by approximately a factor of 2 to maintain equilibrium, as shown in Figure **9.6.4**. As a result, for a given concentration of either HI or NH_3, only a single equilibrium composition that contains equal concentrations of both NH_3 and HI is possible, for which $[NH_3] = [HI] = K^{1/2}$. Any point that lies below and to the left of the equilibrium curve (such as point A in Figure **9.6.4**) corresponds to $Q < K$, and the reaction in Equation 9.6.7 will therefore proceed to the right as written, causing the composition of the system to move toward the equilibrium line. Conversely, any point that lies above and to the right of the equilibrium curve (such as point B in Figure **9.6.4**) corresponds to $Q > K$, and the reaction in Equation 9.6.7 will therefore proceed to the left as written, again causing the composition of the system to move toward the equilibrium line. By graphing equilibrium concentrations for a given system at a given temperature and pressure, we can predict the direction of reaction of that mixture when the system is not at equilibrium.

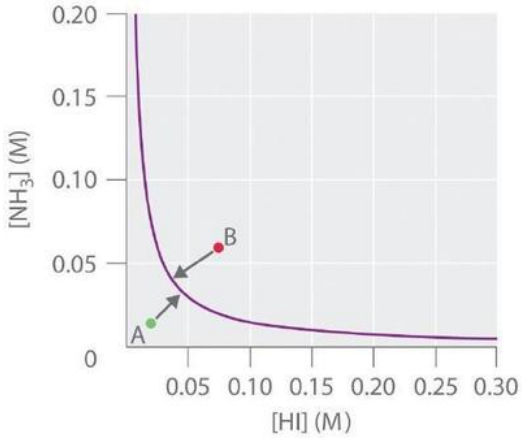


Figure **9.6.4**: The Concentration of $NH_{3(g)}$ versus the Concentration of $HI_{(g)}$ for the $NH_4I_{(s)} \rightleftharpoons NH_{3(g)} + HI_{(g)}$ System at Equilibrium. Only one equilibrium concentration of $NH_{3(g)}$ is possible for any given equilibrium concentration of HI(g). In this case, the two are inversely proportional. Thus a large $[HI]$ at equilibrium requires a small $[NH_3]$ at equilibrium and vice versa.

9.6.3 EFFECT OF CHANGE IN PRESSURE ON EQUILIBRIUM

Sometimes we can change the position of equilibrium by changing the pressure of a system. However, changes in pressure have a measurable effect only in systems in which gases are involved, and then only when the chemical reaction produces a change in the total number of gas molecules in the system. An easy way to recognize such a system is to look for different numbers of moles of gas on the reactant and product sides of the equilibrium. While evaluating pressure (as well as related factors like volume), it is important to remember that equilibrium constants are defined with regard to concentration (for K_c) or partial pressure (for K_p). Some changes to total pressure, like adding an inert gas that is not part of the equilibrium, will change the total pressure but not the partial pressures of the gases in the equilibrium constant expression. Thus, addition of a gas not involved in the equilibrium will not perturb the equilibrium.



Video **9.6.1**: See www.youtube.com/watch?v=pnU7ogsgUW8 to see a dramatic visual demonstration of how equilibrium changes with pressure changes.

As we increase the pressure of a gaseous system at equilibrium, either by decreasing the volume of the system or by adding more of one of the components of the equilibrium mixture, we introduce a stress by increasing the partial pressures of one or more of the components. In accordance with Le Chatelier's principle, a shift in the equilibrium that reduces the total number of molecules per unit of volume will be favored because this relieves the stress. The reverse reaction would be favored by a decrease in pressure.

Consider what happens when we increase the pressure on a system in which NO, O_2, and NO_2 are at equilibrium:

$$2\,NO_{(g)} + O_{2(g)} \rightleftharpoons 2\,NO_{2(g)} \tag{9.6.8}$$

The formation of additional amounts of NO_2 decreases the total number of molecules in the system because each time two molecules of NO_2 form, a total of three molecules of NO and O_2 are consumed. This reduces the total pressure exerted by the system and reduces, but does not completely relieve, the stress of the increased pressure. On the other hand, a decrease in the pressure on the system favors decomposition of NO_2 into NO and O_2, which tends to restore the pressure.

Now consider this reaction:

$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g) \tag{9.6.9}$$

Because there is no change in the total number of molecules in the system during reaction, a change in pressure does not favor either formation or decomposition of gaseous nitrogen monoxide.

9.6.4 EFFECT OF CHANGE IN TEMPERATURE ON EQUILIBRIUM

Changing concentration or pressure perturbs an equilibrium because the Reaction Quotient is shifted away from the equilibrium value. Changing the temperature of a system at equilibrium has a different effect: A change in temperature actually changes the value of the equilibrium constant. However, we can qualitatively predict the effect of the temperature change by treating it as a stress on the system and applying Le Chatelier's principle.

When hydrogen reacts with gaseous iodine, heat is evolved.

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g) \quad \Delta H = -9.4\ \text{kJ (exothermic)} \tag{9.6.10}$$

Because this reaction is exothermic, we can write it with heat as a product.

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g) + \text{heat} \tag{9.6.11}$$

Increasing the temperature of the reaction increases the internal energy of the system. Thus, increasing the temperature has the effect of increasing the amount of one of the products of this reaction. The reaction shifts to the left to relieve the stress, and there is an increase in the concentration of H_2 and I_2 and a reduction in the concentration of HI. Lowering the temperature of this system reduces the amount of energy present, favors the production of heat, and favors the formation of hydrogen iodide.

When we change the temperature of a system at equilibrium, the equilibrium constant for the reaction changes. Lowering the temperature in the HI system increases the equilibrium constant: At the new equilibrium the concentration of HI has increased and the concentrations of H_2 and I_2 decreased. Raising the temperature decreases the value of the equilibrium constant, from 67.5 at 357 °C to 50.0 at 400 °C.

Temperature affects the equilibrium between NO_2 and N_2O_4 in this reaction

$$N_2O_{4(g)} \rightleftharpoons 2\,NO_{2(g)} \quad \Delta H = 57.20\ \text{kJ} \tag{9.6.12}$$

The positive ΔH value tells us that the reaction is endothermic and could be written

$$\text{heat} + N_2O_{4(g)} \rightleftharpoons 2\,NO_{2(g)} \tag{9.6.13}$$

At higher temperatures, the gas mixture has a deep brown color, indicative of a significant amount of brown NO_2 molecules. If, however, we put a stress on the system by cooling the mixture (withdrawing energy), the equilibrium shifts to the left to supply some of the energy lost by cooling. The concentration of colorless N_2O_4 increases, and the concentration of brown NO_2 decreases, causing the brown color to fade.

TEMPERATURE IS NEITHER A REACTANT NOR PRODUCT

It is not uncommon that textbooks and instructors to consider heat as a independent "species" in a reaction. While this is rigorously incorrect because one cannot "add or remove heat" to a reaction as with species, it serves as a convenient mechanism to predict the shift of reactions with changing temperature. For example, if heat is a "reactant" ($\Delta H > 0$), then the reaction favors the formation of products at elevated temperature. Similarly, if heat is a "product" ($\Delta H < 0$), then the reaction favors the formation of reactants. A more accurate, and hence preferred, description is discussed below.

EXAMPLE 9.6.2: STEAM REFORMING OF METHANE

The commercial production of hydrogen is carried out by treating natural gas with steam at high temperatures and in the presence of a catalyst (“steam reforming of methane”):

$$CH_4 + H_2O \rightleftharpoons CH_3OH + H_2$$

Given the following boiling points: CH_4 (methane) = –161°C, H_2O = 100°C, CH_3OH = 65°, H_2 = –253°C, predict the effects of an increase in the total pressure on this equilibrium at 50°, 75° and 120°C.

Solution

To identify the influence of changing pressure on the three reaction conditions, we need to identify the correct reaction including the phase of each reactant and product. Calculate the change in the moles of gas for each process:

Temperature	Equation	Δn_g	shift
50°	$CH_4(g) + H_2O(l) \longrightarrow CH_3OH(l) + H_2(g)$	0	none
75°	$CH_4(g) + H_2O(l) \longrightarrow CH_3OH(g) + H_2(g)$	+1	to left
120°	$CH_4(g) + H_2O(g) \longrightarrow CH_3OH(g) + H_2(g)$	0	none

? EXERCISE 9.6.2

What will happen to the equilibrium when the volume of the system is decreased?

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

Answer

Decreasing the volume leads to an increase in pressure which will cause the equilibrium to shift towards the side with fewer moles. In this reaciton, there are three moles on the reactant side and two moles on the product side, so the new equilibrium will shift towards the products (to the right).

9.6.5 SUMMARY

The Reaction Quotient (Q) is used to determine whether a system is at equilibrium and if it is not, to predict the direction of reaction. Reaction Quotient:

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

The Reaction Quotient (Q or Q_p) has the same form as the equilibrium constant expression, but it is derived from concentrations obtained at any time. When a reaction system is at equilibrium, $Q = K$. Graphs derived by plotting a few equilibrium concentrations for a system at a given temperature and pressure can be used to predict the direction in which a reaction will proceed. Points that do not lie on the line or curve represent nonequilibrium states, and the system will adjust, if it can, to achieve equilibrium.

Systems at equilibrium can be disturbed by changes to temperature, concentration, and, in some cases, volume and pressure; volume and pressure changes will disturb equilibrium if the number of moles of gas is different on the reactant and product sides of the reaction. The system's response to these disturbances is described by Le Chatelier's principle: The system will respond in a way that counteracts the disturbance. Not all changes to the system result in a disturbance of the equilibrium. Adding a catalyst affects the rates of the reactions but does not alter the equilibrium, and changing pressure or volume will not significantly disturb systems with no gases or with equal numbers of moles of gas on the reactant and product side.

Effects of Disturbances of Equilibrium and K

Disturbance	Observed Change as Equilibrium is Restored	Direction of Shift	Effect on K
reactant added	added reactant is partially consumed	toward products	none
product added	added product is partially consumed	toward reactants	none
decrease in volume/increase in gas pressure	pressure decreases	toward side with fewer moles of gas	none
increase in volume/decrease in gas pressure	pressure increases	toward side with more moles of gas	none
temperature increase	heat is absorbed	toward products for endothermic, toward reactants for exothermic	changes
temperature decrease	heat is given off	toward reactants for endothermic, toward products for exothermic	changes

9.6.6 FOOTNOTES

1. 1 Herrlich, P. “The Responsibility of the Scientist: What Can History Teach Us About How Scientists Should Handle Research That Has the Potential to Create Harm?” *EMBO Reports* 14 (2013): 759–764.

9.6.7 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

9.6.8 CONTRIBUTORS AND ATTRIBUTIONS

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

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9.7: THE DIRECTION OF CHANGE IN CHEMICAL REACTIONS - THERMODYNAMIC EXPLANATION

LEARNING OBJECTIVES

- To know the relationship between free energy and the equilibrium constant.

We have identified three criteria for whether a given reaction will occur spontaneously:

- $\Delta S_{univ} > 0$ (2nd law of thermodynamics),
- $\Delta G_{sys} < 0$ (Gibbs Energy version), and
- the relative magnitude of the reaction quotient Q versus the equilibrium constant K.

Recall that if $Q < K$, then the reaction proceeds spontaneously to the right as written, resulting in the net conversion of reactants to products. Conversely, if $Q > K$, then the reaction proceeds spontaneously to the left as written, resulting in the net conversion of products to reactants. If $Q = K$, then the system is at equilibrium, and no net reaction occurs. Table **9.7.1** summarizes these criteria and their relative values for spontaneous, nonspontaneous, and equilibrium processes.

Table **9.7.1**: Criteria for the Spontaneity of a Process as Written

Spontaneous	Equilibrium	Nonspontaneous*
$\Delta S_{univ} > 0$	$\Delta S_{univ} = 0$	$\Delta S_{univ} < 0$
$\Delta G_{sys} < 0$	$\Delta G_{sys} = 0$	$\Delta G_{sys} > 0$
Q < K	Q = K	Q > K
*Spontaneous in the reverse direction.		

Because all three criteria assess the same thing—the spontaneity of the process—it would be most surprising indeed if they were not related. In this section, we explore the relationship between the standard free energy of reaction ($\Delta G°$) and the equilibrium constant (K).

9.7.1 FREE ENERGY AND THE EQUILIBRIUM CONSTANT

Because ΔH° and ΔS° determine the magnitude of ΔG° and because K is a measure of the ratio of the concentrations of products to the concentrations of reactants, we should be able to express K in terms of ΔG° and vice versa. "Free Energy", ΔG is equal to the maximum amount of work a system can perform on its surroundings while undergoing a spontaneous change. For a reversible process that does not involve external work, we can express the change in free energy in terms of volume, pressure, entropy, and temperature, thereby eliminating ΔH from the equation for ΔG. The general relationship can be shown as follow (derivation not shown):

$$\Delta G = V\Delta P - S\Delta T \tag{9.7.1}$$

If a reaction is carried out at constant temperature ($\Delta T = 0$), then Equation 9.7.1 simplifies to

$$\Delta G = V\Delta P \tag{9.7.2}$$

Under normal conditions, the pressure dependence of free energy is not important for solids and liquids because of their small molar volumes. For reactions that involve gases, however, the effect of pressure on free energy is very important.

Assuming ideal gas behavior, we can replace the V in Equation 9.7.2 by nRT/P (where n is the number of moles of gas and R is the ideal gas constant) and express ΔG in terms of the initial and final pressures (P_i and P_f, respectively):

$$\Delta G = \left(\frac{nRT}{P}\right)\Delta P \tag{9.7.3}$$

$$= nRT\frac{\Delta P}{P} = nRT\ln\left(\frac{P_f}{P_i}\right) \tag{9.7.4}$$

If the initial state is the standard state with P_i = 1 atm, then the change in free energy of a substance when going from the standard state to any other state with a pressure P can be written as follows:

$$G - G° = nRT\ln P \tag{9.7.5}$$

This can be rearranged as follows:

$$G = G° + nRT\ln P \tag{9.7.6}$$

As you will soon discover, Equation 9.7.6 allows us to relate ΔG^o and K_p. Any relationship that is true for K_p must also be true for K because K_p and K are simply different ways of expressing the equilibrium constant using different units.

Let's consider the following hypothetical reaction, in which all the reactants and the products are ideal gases and the lowercase letters correspond to the stoichiometric coefficients for the various species:

$$aA + bB \rightleftharpoons cC + dD \tag{9.7.7}$$

Because the free-energy change for a reaction is the difference between the sum of the free energies of the products and the reactants, we can write the following expression for ΔG:

$$\Delta G = \sum_m G_{products} - \sum_n G_{reactants} \tag{9.7.8}$$

$$= (cG_C + dG_D) - (aG_A + bG_B) \tag{9.7.9}$$

Substituting Equation 9.7.6 for each term into Equation 9.7.9,

$$\begin{aligned}\Delta G = &[(cG^o_C + cRT\ln P_C) + (dG^o_D + dRT\ln P_D)] \\ &- [(aG^o_A + aRT\ln P_A) + (bG^o_B + bRT\ln P_B)]\end{aligned} \tag{9.7.10}$$

Combining terms gives the following relationship between ΔG and the reaction quotient Q:

$$\Delta G = \Delta G^\circ + RT\ln\left(\frac{P_C^c P_D^d}{P_A^a P_B^b}\right) \tag{9.7.11}$$

$$= \Delta G^\circ + RT\ln Q \tag{9.7.12}$$

where ΔG° indicates that all reactants and products are in their standard states. For gases at equilibrium ($Q = K_p$,), and as you've learned in this chapter, $\Delta G = 0$ for a system at equilibrium. Therefore, we can describe the relationship between ΔG^o and K_p for gases as follows:

$$0 = \Delta G^\circ + RT\ln K_p \tag{9.7.13}$$

$$\Delta G^\circ = -RT\ln K_p \tag{9.7.14}$$

If the products and reactants are in their standard states and $\Delta G^\circ < 0$, then $K_p > 1$, and products are favored over reactants. Conversely, if $\Delta G^\circ > 0$, then $K_p < 1$, and reactants are favored over products. If $\Delta G^\circ = 0$, then $K_p = 1$, and neither reactants nor products are favored: the system is at equilibrium.

> *For a spontaneous process under standard conditions, K_{eq} and K_p are greater than 1.*

To further illustrate the relation between these two essential thermodynamic concepts, consider the observation that reactions spontaneously proceed in a direction that ultimately establishes equilibrium. As may be shown by plotting the free energy change versus the extent of the reaction (for example, as reflected in the value of Q), equilibrium is established when the system's free energy is minimized (Figure **9.7.3**). 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.

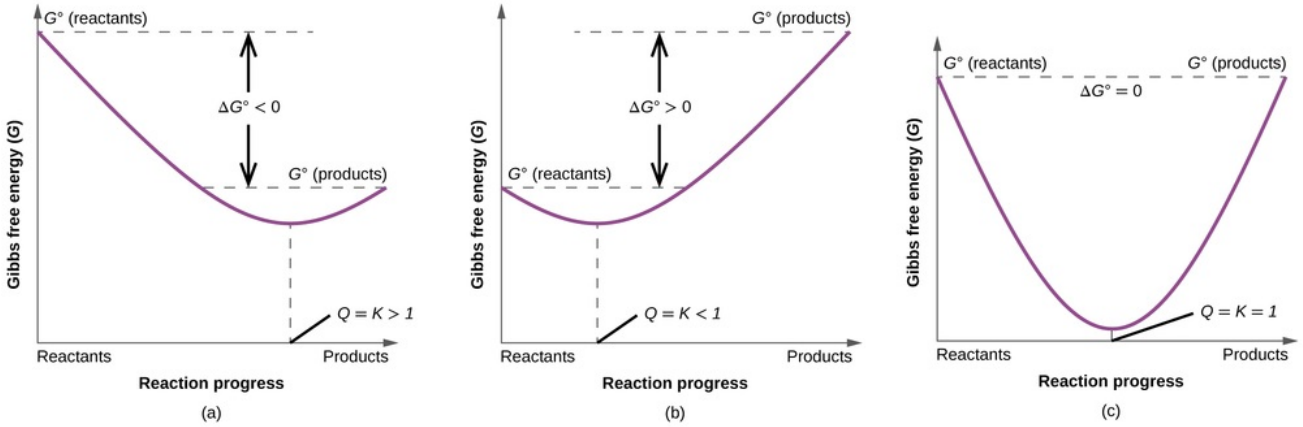


Figure **9.7.1**: These plots show the free energy versus reaction progress for systems whose standard free changes are (a) negative, (b) positive, and (c) zero. Nonequilibrium systems will proceed spontaneously in whatever direction is necessary to minimize free energy and establish equilibrium. (CC BY 4.0; OpenStax).

EXAMPLE 9.7.2

ΔG° is −32.7 kJ/mol of N_2 for the reaction

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

This calculation was for the reaction under standard conditions—that is, with all gases present at a partial pressure of 1 atm and a temperature of 25°C. Calculate ΔG for the same reaction under the following nonstandard conditions:

- P_{N_2} = 2.00 atm,
- P_{H_2} = 7.00 atm,
- P_{NH_3} = 0.021 atm,
- and T = 100°C.

Does the reaction favor products or reactants?

Given: balanced chemical equation, partial pressure of each species, temperature, and ΔG°

Asked for: whether products or reactants are favored

Strategy:

A. Using the values given and Equation 9.7.12, calculate Q.
B. Substitute the values of ΔG° and Q into Equation 9.7.12 to obtain ΔG for the reaction under nonstandard conditions.

Solution:

A The relationship between ΔG° and ΔG under nonstandard conditions is given in Equation 9.7.12. Substituting the partial pressures given, we can calculate Q:

$$Q = \frac{P_{NH_3}^2}{P_{N_2}P_{H_2}^3} = \frac{(0.021)^2}{(2.00)(7.00)^3} = 6.4 \times 10^{-7}$$

B Substituting the values of ΔG° and Q into Equation 9.7.12,

$$\begin{aligned}\Delta G &= \Delta G^\circ + RT\ln Q \\ &= -32.7\text{ kJ} + \left[(8.314\text{ J/K})(373\text{ K})\left(\frac{1\text{ kJ}}{1000\text{ J}}\right)\ln(6.4\times10^{-7})\right] \\ &= -32.7\text{ kJ} + (-44\text{ kJ}) \\ &= -77\text{ kJ/mol of } N_2\end{aligned}$$

Because ΔG < 0 and Q < 1.0, the reaction is spontaneous to the right as written, so products are favored over reactants.

EXERCISE 9.7.2

Calculate ΔG for the reaction of nitric oxide with oxygen to give nitrogen dioxide under these conditions: T = 50°C, P_{NO} = 0.0100 atm, P_{O_2} = 0.200 atm, and P_{NO_2} = 1.00 × 10^{-4} atm. The value of ΔG° for this reaction is −72.5 kJ/mol of O_2. Are products or reactants favored?

Answer

−92.9 kJ/mol of O_2; the reaction is spontaneous to the right as written, so products are favored.

EXAMPLE 9.7.3

Calculate K_p for the reaction of H_2 with N_2 to give NH_3 at 25°C. ΔG° for this reaction is −32.7 kJ/mol of N_2.

Given: balanced chemical equation from Example **9.7.2**, ΔG°, and temperature

Asked for: K_p

Strategy:

Substitute values for ΔG° and T (in kelvin) into Equation 9.7.14 to calculate K_p, the equilibrium constant for the formation of ammonia.

Solution

In Example 10, we used tabulated values of ΔG°_f to calculate ΔG° for this reaction (−32.7 kJ/mol of N_2). For equilibrium conditions, rearranging Equation 9.7.14,

$$\Delta G^\circ = -RT \ln K_p$$

$$\frac{-\Delta G^\circ}{RT} = \ln K_p$$

Inserting the value of ΔG° and the temperature (25°C = 298 K) into this equation,

$$\ln K_p = -\frac{(-32.7\ \text{kJ})(1000\ \text{J/kJ})}{(8.314\ \text{J/K})(298\ \text{K})} = 13.2$$

$$K_p = 5.4 \times 10^5$$

Thus the equilibrium constant for the formation of ammonia at room temperature is favorable. However, the rate at which the reaction occurs at room temperature is too slow to be useful.

? EXERCISE 9.7.3

Calculate K_p for the reaction of NO with O_2 to give NO_2 at 25°C. ΔG° for this reaction is −70.5 kJ/mol of O_2.

Answer

2.2×10^{12}

Although K_p is defined in terms of the partial pressures of the reactants and the products, the equilibrium constant K is defined in terms of the concentrations of the reactants and the products. We described the relationship between the numerical magnitude of \(K_{-p\}) and K previously and showed that they are related:

$$K_p = K(RT)^{\Delta n} \tag{9.7.15}$$

where Δn is the number of moles of gaseous product minus the number of moles of gaseous reactant. For reactions that involve only solutions, liquids, and solids, $\Delta n = 0$, so $K_p = K$. For all reactions that do not involve a change in the number of moles of gas present, the relationship in Equation 9.7.14 can be written in a more general form:

$$\Delta G^\circ = -RT \ln K \tag{9.7.16}$$

Only when a reaction results in a net production or consumption of gases is it necessary to correct Equation 9.7.16 for the difference between K_p and K. Although we typically use concentrations or pressures in our equilibrium calculations, recall that equilibrium constants are generally expressed as unitless numbers because of the use of **activities** or **fugacities** in precise thermodynamic work. Systems that contain gases at high pressures or concentrated solutions that deviate substantially from ideal behavior require the use of fugacities or activities, respectively.

Combining Equations 9.7.16 with $\Delta G^o = \Delta H^o - T\Delta S^o$ provides insight into how the components of ΔG° influence the magnitude of the equilibrium constant:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln K \tag{9.7.17}$$

Notice that K becomes larger as ΔS° becomes more positive, indicating that the magnitude of the equilibrium constant is directly influenced by the tendency of a system to move toward maximum disorder. Moreover, K increases as ΔH° decreases. Thus the magnitude of the equilibrium constant is also directly influenced by the tendency of a system to seek the lowest energy state possible.

> *The magnitude of the equilibrium constant is directly influenced by the tendency of a system to move toward maximum disorder and seek the lowest energy state possible.*

9.7.2 TEMPERATURE DEPENDENCE OF THE EQUILIBRIUM CONSTANT

The fact that ΔG° and K are related provides us with another explanation of why equilibrium constants are temperature dependent. This relationship is shown explicitly in Equation 9.7.17, which can be rearranged as follows:

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{9.7.18}$$

Assuming ΔH° and ΔS° are temperature independent, for an exothermic reaction (ΔH° < 0), the magnitude of K decreases with increasing temperature, whereas for an endothermic reaction (ΔH° > 0), the magnitude of K increases with increasing temperature. The quantitative relationship expressed in Equation 9.7.18 agrees with the qualitative predictions made by applying Le Chatelier's principle. Because heat is produced in an exothermic reaction, adding heat (by increasing the temperature) will shift the equilibrium to the left, favoring the reactants and decreasing the magnitude of K. Conversely, because heat is consumed in an endothermic reaction, adding heat will shift the equilibrium to the right, favoring the products and increasing the magnitude of K. Equation 9.7.18 also shows that the magnitude of ΔH° dictates how rapidly K changes as a function of temperature. In contrast, the magnitude and sign of ΔS° affect the magnitude of K but not its temperature dependence.

If we know the value of K at a given temperature and the value of ΔH° for a reaction, we can estimate the value of K at any other temperature, even in the absence of information on ΔS°. Suppose, for example, that K_1 and K_2 are the equilibrium constants for a reaction at temperatures T_1 and T_2, respectively. Applying Equation 9.7.18 gives the following relationship at each temperature:

$$\ln K_1 = \frac{-\Delta H^\circ}{RT_1} + \frac{\Delta S^\circ}{R} \tag{9.7.19}$$

$$\ln K_2 = \frac{-\Delta H^\circ}{RT_2} + \frac{\Delta S^\circ}{R} \tag{9.7.20}$$

Subtracting $\ln K_1$ from $\ln K_2$,

$$\ln K_2 - \ln K_1 = \ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{9.7.21}$$

Thus calculating ΔH° from tabulated enthalpies of formation and measuring the equilibrium constant at one temperature (K_1) allow us to calculate the value of the equilibrium constant at any other temperature (K_2), assuming that ΔH° and ΔS° are independent of temperature. Equation 9.7.21 is often referred to as the **van 't Hoff equation** after Dutch chemist Jacobus Henricus van 't Hoff in 1884 in his book Études de Dynamique chimique (Studies in dynamic chemistry).

EXAMPLE 9.7.4

The equilibrium constant for the formation of NH_3 from H_2 and N_2 at 25°C was calculated to be $K_p = 5.4 \times 10^5$ in Example **9.7.2**. What is K_p at 500°C? (Use the data from Example **9.7.1**)

Given: balanced chemical equation, ΔH°, initial and final T, and K_p at 25°C

Asked for: K_p at 500°C

Strategy:

Convert the initial and final temperatures to kelvin. Then substitute appropriate values into Equation 9.7.21 to obtain K_2, the equilibrium constant at the final temperature.

Solution:

The value of ΔH° for the reaction obtained using Hess's law is −91.8 kJ/mol of N_2. If we set T_1 = 25°C = 298 K and T_2 = 500°C = 773 K, then from Equation 9.7.21 we obtain the following:

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$= \frac{(-91.8\ \text{kJ})(1000\ \text{J/kJ})}{8.314\ \text{J/K}}\left(\frac{1}{298\ \text{K}} - \frac{1}{773\ \text{K}}\right) = -22.8$$

$$\frac{K_2}{K_1} = 1.3 \times 10^{-10}$$

$$K_2 = (5.4 \times 10^5)(1.3 \times 10^{-10}) = 7.0 \times 10^{-5}$$

Thus at 500°C, the equilibrium strongly favors the reactants over the products.

EXERCISE 9.7.4

The equilibrium constant for the reaction of **NO** with O_2 to give NO_2 at 25°C is $K_p = 2.2 \times 1012$. Use the ΔH_f° values in the exercise in Example **9.7.4** to calculate K_p for this reaction at 1000°C.

Answer

5.6×10^{-4}

9.7.3 SUMMARY

For a reversible process that does not involve external work, we can express the change in free energy in terms of volume, pressure, entropy, and temperature. If we assume ideal gas behavior, the ideal gas law allows us to express ΔG in terms of the partial pressures of the reactants and products, which gives us a relationship between ΔG and K_p, the equilibrium constant of a reaction involving gases, or K, the equilibrium constant expressed in terms of concentrations. If $\Delta G° < 0$, then K or $K_p > 1$, and products are favored over reactants. If $\Delta G° > 0$, then K or $K_p < 1$, and reactants are favored over products. If $\Delta G° = 0$, then K or $K_p = 1$, and the system is at equilibrium. We can use the measured equilibrium constant K at one temperature and $\Delta H°$ to estimate the equilibrium constant for a reaction at any other temperature.

9.7.4 CONTRIBUTORS AND ATTRIBUTIONS

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9.8: DISTRIBUTION BETWEEN IMMISCIBLE PHASES - EXTRACTION AND SEPARATION PROCESSES

A partitioning of a compound exist between a mixture of two immiscible phases at equilibrium, which is a measure of the difference in solubility of the compound in these two phases. If one of the solvents is a gas and the other a liquid, the "gas/liquid partition coefficient" is the same as the dimensionless form of the Henry's law constant. A solute can partition when one or both solvents is a solid (e.g., solid solution).

9.8.1 LIQUID-LIQUID EXTRACTIONS

We call the process of moving a species from one phase to another phase an **extraction**. Simple extractions are particularly useful for separations where only one component has a favorable partition coefficient. Several important separation techniques are based on a simple extraction, including liquid–liquid, liquid–solid, solid–liquid, and gas–solid extractions. The most important group of separation techniques uses a selective partitioning of the solute between two immiscible phases. If we bring a phase containing a solute, S, into contact with a second phase, the solute partitions itself between the two phases, as shown by the following equilibrium reaction.

$$\mathrm{S_{phase\ 1}} \rightleftharpoons \mathrm{S_{phase\ 2}} \tag{9.8.1}$$

The equilibrium constant for this equilbrium is

$$K_\mathrm{D} = \frac{[\mathrm{S_{phase\ 2}}]}{[\mathrm{S_{phase\ 1}}]} \tag{9.8.2}$$

is called the distribution constant or **partition coefficient**. If K_D is sufficiently large, then the solute moves from phase 1 to phase 2. The solute remains in phase 1 if the partition coefficient is sufficiently small. When we bring a phase containing two solutes into contact with a second phase, if K_D is favorable for only one of the solutes a separation of the solutes is possible. The physical states of the phases are identified when describing the separation process, with the phase containing the sample listed first. For example, if the sample is in a liquid phase and the second phase is a solid, then the separation involves liquid–solid partitioning.

It often happens that two immiscible liquid phases are in contact, one of which contains a solute. How will the solute tend to distribute itself between the two phases? One’s first thought might be that some of the solute will migrate from one phase into the other until it is distributed equally between the two phases, since this would correspond to the maximum dispersion (randomness) of the solute. This, however, does not take into the account the differing solubilities the solute might have in the two liquids; if such a difference does exist, the solute will preferentially migrate into the phase in which it is more soluble (Figure 9.8.1).

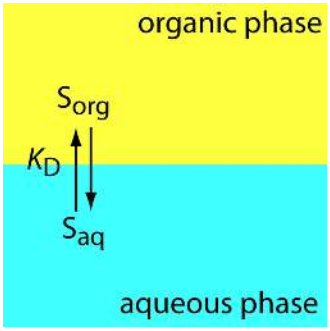


Figure 9.8.1: Scheme for a simple liquid–liquid extraction in which the solute’s partitioning depends only on the K_D equilibrium.

BIOMAGNIFICATION

The transport of substances between different phases is of immense importance in such diverse fields as pharmacology and environmental science. For example, if a drug is to pass from the aqueous phase with the stomach into the bloodstream, it must pass through the lipid (oil-like) phase of the epithelial cells that line the digestive tract. Similarly, a pollutant such as a pesticide residue that is more soluble in oil than in water will be preferentially taken up and retained by marine organism, especially fish, whose bodies contain more oil-like substances; this is basically the mechanism whereby such residues as DDT can undergo *biomagnification* as they become more concentrated at higher levels within the food chain. For this reason, environmental regulations now require that oil-water distribution ratios be established for any new chemical likely to find its way into natural waters. The standard “oil” phase that is almost universally used is octanol, $C_8H_{17}OH$.

In preparative chemistry it is frequently necessary to recover a desired product present in a reaction mixture by extracting it into another liquid in which it is more soluble than the unwanted substances. On the laboratory scale this operation is carried out in a **separatory funnel** as shown below. The two immiscible liquids are poured into the funnel through the opening at the top. The funnel is then shaken to bring the two phases into intimate contact, and then set aside to allow the two liquids to separate into layers, which are then separated by allowing the more dense liquid to exit through the stopcock at the bottom.



Figure **9.8.2**: A separatory funnel with two solvents.

If the distribution ratio is too low to achieve efficient separation in a single step, it can be repeated; there are automated devices that can carry out hundreds of successive extractions, each yielding a product of higher purity. In these applications our goal is to exploit the Le Chatelier principle by repeatedly upsetting the phase distribution equilibrium that would result if two phases were to remain in permanent contact.



Video **9.8.1**: How to perform a liquid-liquid extraction using a separating funnel.

EXAMPLE 9.8.1

The distribution ratio for iodine between water and carbon disulfide is 650. Calculate the concentration of I_2 remaining in the aqueous phase after 50.0 mL of 0.10M I_2 in water is shaken with 10.0 mL of CS_2.

Solution

The equilibrium constant is

$$K_d = \frac{C_{CS_2}}{C_{H_2O}} = 650$$

Let m_1 and m_2 represent the numbers of millimoles of solute in the water and CS_2 layers, respectively. K_d can then be written as (m_2/10 mL) ÷ (m_1/50 mL) = 650. The number of moles of solute is (50 mL) × (0.10 mmol mL^{-1}) = 5.00 mmol, and mass conservation requires that m_1 +

m_2 = 5.00 mmol, so m_2 = (5.00 – m_1) mmol and we now have only the single unknown m_1. The equilibrium constant then becomes

$$\frac{(5.00–m_1)\,mmol/10\,mL}{m_1\,mmol/50\,mL} = 650$$

Simplifying and solving for m_1 yields

$$\frac{(0.50–0.1)m_1}{0.02\,m_1} = 650$$

with m_1 = 0.0382 mmol.

The concentration of solute in the water layer is (0.0382 mmol) / (50 mL) = **0.000763 M**, showing that almost all of the iodine has moved into the CS_2 layer.

9.8.2 CHROMATOGRAPHIC SEPARATIONS

In an extraction, the sample is one phase and we extract the analyte or the interferent into a second phase. We also can separate the analyte and interferents by continuously passing one sample-free phase, called the mobile phase, over a second sample-free phase that remains fixed or stationary. The sample is injected into the mobile phase and the sample's components partition themselves between the mobile phase and the stationary phase. Those components with larger partition coefficients are more likely to move into the stationary phase, taking a longer time to pass through the system. This is the basis of all chromatographic separations. Chromatography provides both a separation of analytes and interferents, and a means for performing a qualitative or quantitative analysis for the analyte.

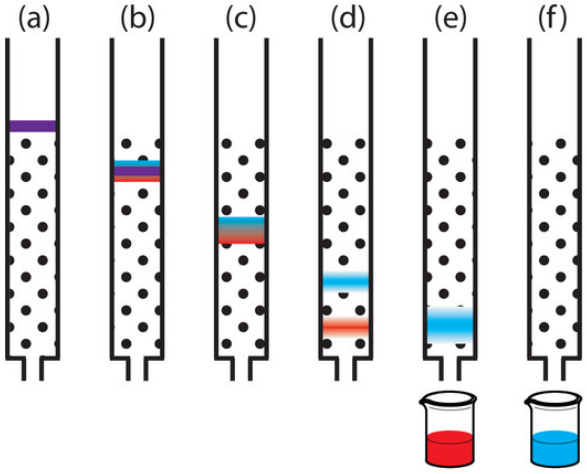


Figure **9.8.3**: Progress of a column chromatographic separation of a two-component mixture. In (a) the sample is layered on top of the stationary phase. As mobile phase passes through the column, the sample separates into two solute bands (b–d). In (e) and (f), we collect each solute as it elutes from the column.

Of the two methods for bringing the stationary phase and the mobile phases into contact, the most important is column chromatography. In this section we develop a general theory that we may apply to any form of column chromatography. Figure **9.8.3** provides a simple view of a liquid–solid column chromatography experiment. The sample is introduced at the top of the column as a narrow band. Ideally, the solute's initial concentration profile is rectangular (Figure **9.8.1***a*). As the sample moves down the column the solutes begin to separate (Figures **9.8.1***b*, *c*), and the individual solute bands begin to broaden and develop a Gaussian profile. If the strength of each solute's interaction with the stationary phase is sufficiently different, then the solutes separate into individual bands (Figure **9.8.1***d*).

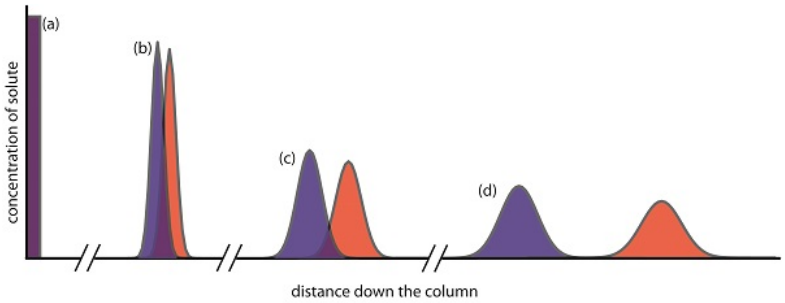


Figure **9.8.4**: An alternative view of the separation in Figure **9.8.3** showing the concentration of each solute as a function of distance down the column.

We can follow the progress of the separation either by collecting fractions as they elute from the column (Figure **9.8.4**), or by placing a suitable detector at the end of the column. A plot of the detector's response as a function of elution time, or as a function of the volume of mobile phase, is known as a **chromatogram** (Figure **9.8.5**), and consists of a peak for each solute.

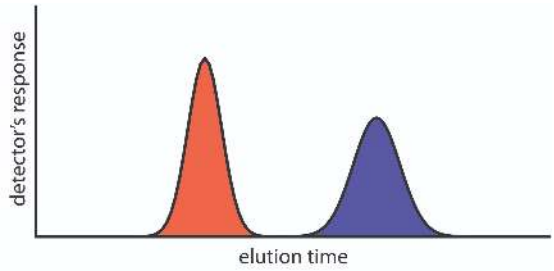


Figure **9.8.5**: Chromatogram for the separation shown in Figure **9.8.3** showing the detector's response as a function of the elution time.

9.8.3 CONTRIBUTORS AND ATTRIBUTIONS

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9.E: CHEMICAL EQUILIBRIUM (EXERCISES)

These are homework exercises to accompany the Textmap created for "Principles of Modern Chemistry" by Oxtoby et al. Complementary General Chemistry question banks can be found for other Textmaps and can be accessed here.

9.E.1 Q1

Write an expression for the equilibrium constant K_c for each reaction below.

a. $2\,NO\,(g) + O_2\,(g) \rightleftharpoons 2\,NO_2\,(g)$
b. $N_2H_4\,(g) + 3\,O_2\,(g) \rightleftharpoons 2\,NO_2\,(g) + H_2O\,(g)$
c. $O_3\,(g) + H_2O\,(l) \rightleftharpoons H_2\,(g) + 2\,O_2\,(g)$

9.E.2 Q3

Gaseous chlorine reacts with water vapor to form hydrogen chloride and oxygen gas. Write down the equilibrium expression (K_p) for the reaction.

9.E.3 Q11

For each thermodynamics equilibrium expressions outlined below, determine one possible chemical reaction related to each.

a. $$K = \frac{a\{CO\}^2}{a\{CO_2\}}$$

b. $$K = \frac{a\{H_2O\}^2}{a\{H_2\}^2 a\{O_2\}}$$

c. $$K = \frac{a\{Cl_2O\}^2}{a\{Cl_2\}^2 a\{O_2\}}$$

d. $$K = \frac{a\{COCl_2\}}{a\{CO\} \cdot a\{Cl_2\}}$$

9.E.4 Q15A

Based on the following data, calculate the equilibrium constant and the value of ΔG° at 273 K.

a. $CO_2\,(g) + H_2\,(g) \rightleftharpoons CO\,(g) + H_2O\,(g)$ with

- $[CO_2]_{eq} = 0.0954\,M$
- $[H_2]_{eq} = 0.0454\,M$
- $[CO]_{eq} = 0.0046\,M$
- $[H_2O]_{eq} = 0.0046\,M$

b. $2\,NO\,(g) + 2\,H_2\,(g) \rightleftharpoons N_2\,(g) + 2\,H_2O\,(g)$ with

- $[NO]_{eq} = 0.45\,M$
- $[H_2]_{eq} = 0.63\,M$
- $[N_2]_{eq} = 0.95\,M$
- $[H_2O]_{eq} = 1.3\,M$

9.E.5 Q15B

Calculate the appropriate K value for the following reactions using the information provided. Assume that they are preformed under standard conditions (and 298.15 K).

a. $$2\,NO_2\,(g) \rightleftharpoons 2\,NO\,(g) + O_2\,(g)$$

b. $$NH_4^+\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + NH_3\,(aq)$$

c. Jim's brother, Txeltoqlztop, goes to the bathroom only to find out that his sibling did not refill the toilet paper roll! To get revenge, Txeltoqlztop decides to fill his brother's room with carbon monoxide, via the following reaction:

$$2\,CH_4\,(g) + 3\,O_2\,(g) \rightleftharpoons 2\,CO\,(g) + 4\,H_2O\,(g)$$

Calculate the K value for this equation under standard conditions, interpret what it means in regards to the direction this equation will go, and compare it to the other two.

9.E.6 Q15C

Use the thermodynamic data in Tables T1 and T2 to calculate the equilibrium constants for the following equations at 25°C.

a. $\mathrm{H_2(g) + F_2(g) \rightleftharpoons 2\,HF(g)}$
b. $\mathrm{FeCl_3(s) \rightleftharpoons FeCl_2(s) + Cl(g)}$
c. $\mathrm{CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)}$

9.E.7 Q17

To ignite this house on fire, you dowsed the house in some ethanol and used a combustion reaction:

$$\mathrm{C_2H_5OH(l) + O_2(g) \rightleftharpoons H_2O(l) + CO_2(g)}$$

This reaction has an equilibrium constant of K_1. If you multiply this equation by 5, will the equilibrium constant change? If so, write this new equilibrium constant, K_2, in terms of K_1.

9.E.8 Q21

An unknown gas B_5D_{10} reacts at room temperature and becomes $B_{10}D_{20}$, the reaction is illustrated with the equation

$$\mathrm{2\,B_5D_{10}(g) \rightleftharpoons B_{10}D_{20}(g)}$$

At room temperature the equilibrium partial pressure of B_5D_{10} is $\mathrm{1.23 \times 10^{-4}\ atm}$ and that of $B_{10}D_{20}$ is $\mathrm{3.14 \times 10^{-16}\ atm}$. Given these constants, what is K_p of this reaction at room temperature.

9.E.9 Q23A

Suppose there exists a compound that can be found in two forms, red and blue, such that

$$\mathrm{X_{red} \rightleftharpoons X_{blue}}$$

During equilibrium at 25.0°C, 17% of the substance is determined to be in blue form. What is the equilibrium constant for this reaction?

9.E.10 Q23B

1,2-dimethylcyclohexane can exist in both boat and chair conformation. There is equilibrium between the two forms. What is the equilibrium constant for the reaction of boat conformation to chair conformation if the molecules in the boat form are 68.7%?

9.E.11 Q28

The K_p for the following reaction is 3.0 at 1000 K.

$$\mathrm{CO_2(g) + C(s) \rightleftharpoons 2\,CO(g)}$$

a. If the pressure in the container where the reaction occurs was initially 0.48 bar, calculate the partial pressures of $\mathrm{CO_2}$ and CO at equilibrium.
b. Calculate the percentage of $\mathrm{CO_2}$ that has been dissociated.

9.E.12 Q29

A 100.0 mL glass bulb was filled which a weighed sample of solid $\mathrm{XO_3}$, where X is an unknown element. The bulb was then attached to a pressure gauge and heated to 325 K, at which, the pressure was read to be 0.891 atm. Given that all of the $\mathrm{XO_3}$ in the bulb at 325 K was in the gas phase, and it also partially dissociated into $\mathrm{O_2(g)}$ and $\mathrm{XO(g)}$:

$$\mathrm{XO_3(g) \rightleftharpoons O_2(g) + XO(g)}$$

At 325 K, K_p = 3.14 for this reaction. Calculate the partial pressures of all three species in the bulb at equilibrium.

9.E.13 Q31

The equilibrium constant K_c for the reaction

$$\mathrm{F_2(g) + H_2(g) \rightleftharpoons 2\,HF(g)}$$

at 298 K is $\mathrm{5.07 \times 10^4}$. Hydrogen with a partial pressure of 0.03500 atm is mixed with fluorine with a partial pressure of 0.06800 atm, and allowed to reach the equilibrium. What is the partial pressure of each of the gasses at the equilibrium?

9.E.14 Q33

At 25 °C, the equilibrium constant for the reaction below has the value of 1.7×10^{-13}:

$$N_2O\,(g) + \tfrac{1}{2}\,O_2\,(g) \rightleftharpoons 2\,NO\,(g)$$

In a container where N_2O has an initial partial pressure of 0.62 atm, O_2 has a pressure of 0.24 atm, and NO has an initial pressure of 0.08 atm, what will the partial pressure of the three gases be after reaching equilibrium at the same temperature?

9.E.15 Q35

The reaction:

$$2\,HI\,(g) \rightleftharpoons H_2\,(g) + I_2\,(g)$$

has an equilibrium constant $K_c = 1.82 \times 10^{-2}$ at 698 K. If the reaction took place in a tank at 698 K and started off with HI having a partial pressure of 1 atm, what would the partial pressures of all the gases be at equilibrium?

9.E.16 Q37

What is the concentration of a XY that will be found in equilibrium at room temperature, given that X_2 has a concentration of $3.14 \times 10^{-15}\,M$, Y_2 has a concentration of $1.23 \times 10^{-4}\,M$, and the K_c of the reaction is $2.22 \times 10^{-7}\,M$.

9.E.17 Q41

Hydrogen and oxygen gas react with each other to form gaseous water with an equilibrium constant for the reaction is $K_c = 1.33 \times 10^{20}$ at 1000 K.

a. Consider a system at 1000.0 K in which 4.00 atm of oxygen is mixed with 0.500 atm of hydrogen and no water is initially present. What is the concentration of hydrogen gas after equilibration.
b. Consider a system, also at 1000.0 K, where 0.250 atm of oxygen is mixed with 0.500 atm of hydrogen and 2.000 atm of water. What is the concentration of hydrogen and oxygen gas after equilibration.

9.E.18 Q43

If you decompose ammonium nitrate into water and nitrous oxide, which further decomposes into oxygen and nitrogen gas, making the final reaction:

$$2\,NH_4NO_3\,(s) \rightleftharpoons 2\,N_2\,(g) + O_2\,(g) + 4\,H_2O\,(g)$$

This reaction takes place only in the molten salt, above its melting point of 169.6°C (for the anhydrous product). So, you get your 170°C blow torch and begin decomposing the ammonium nitrate under a sealed hood. Upon decomposition, all of the ammonium nitrate is gone, i.e. the reaction goes to completion.

a. What can be said of the equilibrium constant of this reaction at 170°C?
b. Now, in another universe, the partial pressure of N_2(g) is 0.3 atm initially. Will the reaction still go to, essentially, completion?

9.E.19 Q45

Al_2Cl_6 at a partial pressure of 0.600 atm is placed in a closed container at 454 K. Al_3Cl_9 (partial pressure 1.98×10^{-3} atm) is also placed in it as well. Argon is added to raise the total pressure up to 1.00 atm.

Find whether if there is going to be net production or consumption of Al_3Cl_9 given $K_p = 1.04 \times 10^{-4}$. Then find the final pressure of Al_3Cl_9.

9.E.20 Q46

The thermal decomposition of NH_4Cl solid proceeds as follows:

$$NH_4Cl\,(s) \rightleftharpoons NH_3\,(g) + HCl\,(g)$$

the equilibrium constant at 275°C is 1.04×10^{-2}. If the partial pressures of $NH_3\,(g)$ and $HCl\,(g)$ are equal, and the total partial pressure of the system is 0.200 atm, in what direction does the reaction proceed? What will be formed?

9.E.21 Q47

A tube contains a mixture of NO_2 and N_2O_4 gas is set at 298K, in which the initial partial pressure NO_2 is 0.38 atm, and the initial partial pressure of N_2O_4 is 0.59 atm. NO_2 is a brownish gas, while N_2O_4 is a colorless gas.

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

a. What is the reaction quotient at the start of this reaction?
b. As the reaction shown above reaches equilibrium, the mixture becomes more brown. With this in mind, is the equilibrium constant, K_p, greater than or less than the Q calculated in part a?

9.E.22 Q49

At 500 K the equilibrium constant for the reaction:

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

is $K_{eq} = 2.1$. Suppose the equilibrium is disturbed and shifts, while temperature remains constant. Calculate the reaction quotient for each one of the possible changes in equilibrium concentration given below and evaluate in what direction the reaction will shift to reestablish equilibrium.

a. [PCl_3]= 0.0563, [Cl_2]= 0.0784, [PCl_5]= 0.8934.
b. [PCl_3]=0.4390 , [Cl_2]= 0.3547, [PCl_5]= 0.1048.
c. [PCl_3]= 0.4018, [Cl_2]= 0.8690, [PCl_5]= 0.7205.

9.E.23 Q48

NO_2 has a brownish color. At elevated temperatures, NO_2 reacts with CO

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

The other gases in this equation are colorless. When a gas mixture is prepared at 600K, in which 9.6 atm is the initial partial pressure of both NO_2 and CO, and 5.4 atm is the partial pressure of both NO and CO_2, the brown color of the mixture observed begins to get stronger as the reaction progresses toward equilibrium. Give a condition that must be satisfied by the equilibrium constant K.

9.E.24 Q51

The equilibrium constant (K_p) for the reaction

$$As_4(g) \rightleftharpoons 2\,As_2(g)$$

is 5.5837×10^{-4} at 1090 K.

a. The initial molarity of [As_4] is 2.3 M and the initial molarity of [As_2] is 0.001 M. Calculate the reaction quotient Q and determine which way the reaction proceeds.
b. Calculate the molarity of each compound at the equilibrium.
c. Which direction will the reaction proceed if the pressure on the reaction decreases? Explain your answer.

9.E.25 Q55

Consider a reaction involving only gaseous compounds. The product yield at equilibrium decreases when the temperature and volume increase.

a. Is this reaction endothermic or exothermic?
b. Does the number of gas molecules in this reaction increase or decrease?

9.E.26 Q57

the Haber process, also called the Haber–Bosch process, is an artificial nitrogen fixation process and is the main industrial procedure for the production of ammonia today.

$$N_3 + 3\,H_2 \rightleftharpoons 2\,NH_3 \quad (\Delta H = -92.4\,kJ/mol)$$

Determine the best condition of temperature and pressure to yield the most ammonia.

9.E.27 Q59

At room temperature, a vessel is filled with gaseous carbon dioxide. Some water is added at 2.00 atm. It is well-shaken, integrating carbon dioxide gas into the water. 0.5 kg of the solution is taken out and boiled to extract 2.50 L of carbon dioxide. The system is at 10 degree Celsius and 1.00 atm. What is the Henry's Law constant for carbon dioxide in water?

9.E.28 Q61

The equilibrium constant for a reaction increases from $K = 4.5 \times 10^{-2}$ to $K = 4.5$ as the temperature increases from 0.00°C to 300.0°C. Assuming the change in enthalpy (ΔH) and change in entropy (ΔS) are constant over this range of temperatures, what is ΔS for this

reaction? Is this reaction endothermic or exothermic?

9.E.29 Q63A

The equilibrium constant for the reaction $2\,NO_2\,(g) \rightleftharpoons N_2O_4\,(g)$ is measured to be 5.9×10^{-3} at $298\ K$ and 1.3×10^{-6} at $398\ K$

a. Calculate $\Delta G°$ at 298 K for the reaction.
b. Calculate $\Delta H°$ and $\Delta S°$, assuming the enthalpy and entropy changes are independent of temperature between 298 K and 398 K.

9.E.30 Q63B

For the reaction: $Br_2\,(g) \rightleftharpoons 2\,Br\,(g)$, the equilibrium constant is 4.64×10^{-29} at 25°C and 1.1×10^{-3} at 1280 K.

a. What is $\Delta G°$ of the reaction at 298 K?
b. Assuming that $\Delta H°$ and $\Delta S°$ are independent of temperature, what are the values of enthalpy and entropy when the temperature changes to 1280 K?

9.E.31 Q65

Calculate the equilibrium constant for the reaction,

$$2\ NO_2\ (g) \rightleftharpoons N_2O_4\ (g) \text{ at } 500\ K,$$

given the equilibrium constant K = 4.65 x 10^{-3} at 298 K, and ΔH° = -57.2 kJ mol^{-1}. Assume that ΔH° does not change between 298 K and 500 K

9.E.32 Q69

The equilibrium constant for the following reaction was experientially calculated at different temperatures.

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

Temperature (°C)	300	400	450	500	550	600
Equilibrium Constant (K_{eq})	4.34 x 10^{-3}	1.64 x 10^{-4}	4.51 x 10^{-5}	1.45 x 10^{-5}	5.38 x 10^{-6}	2.25 x 10^{-6}

a. Plot $\ln K$ as a function of $1/T$ (K^{-1})
b. What is $\Delta H°$ of the equilibrium reaction with ammonia? HINT: use the slope to find the $\Delta H°$

9.E.33 Q71

At a certain temperature, $0.5\ mol\ I_{2\,(aq)}$ is dissolved in $2\ L\ H_2O$ and shaken vigorously in a container with $2\ L$ of CCl_4, an immiscible liquid. The container is then left to equilibrate during which time the iodine redistributes itself between the layers of H_2O and CCl_4 as indicated by the following reaction:

$$I_{2\,(aq)} \rightleftharpoons I_2\ (CCl_4)$$

The final concentration of $I_{2\,(aq)}$ is determined to be $0.0710\ M$. What is the partition coefficient (K) for this process?

9.E.34 Q73

At 25°C, 0.130 g/L of chloroacetic acid ($C_2H_3ClO_2$) dissolve in of water, and at the same temperature 0.2834 g/L of chloroacetic acid dissolve in 1-octanol.

a. Calculate the following equilibrium constants

$$C_2H_2ClO_2H\,(s) \rightleftharpoons C_2H_2ClO_2H_{(aq)}$$

$$C_2H_2ClO_2H\,(s) \rightleftharpoons C_2H_2ClO_2H_{(octanol)}$$

b. Calculate the *participation coefficient*, K, of the combined reactions.

$$C_2H_2ClO_2H\,(aq) \rightleftharpoons C_2H_2ClO_2H_{(octanol)}$$

9.E.35 Q75

At 298 K, the two gases NOBr and Br_2 have the number of moles of 1.25 and 8.5 x 10^{-5} at equilibrium with a sufficient amount of solid NO. Determine the equilibrium constant of the reaction:

$$2NOBr_{(g)} \rightleftharpoons 2NO_{(s)} + Br_{2(g)}$$

9.E.36 Q79

At 300 K and 1 atm, N_2O_4 is partly dissociated into NO_2. The density of the equilibrium mixture was 2.076 g/L. What is the degree of dissociation of N_2O_4 under these circumstances?

9.E.37 Q85

The decompressions of calcium carbonate ($\mathbf{CaCO_3}$) occurs according to the following reaction:

$$\mathbf{CaCO_3\,(s)} \rightleftharpoons \mathbf{CaO\,(s) + CO_2\,(g)}$$

100 g of solid calcium carbonate ($\mathbf{CaCO_3}$) and 50 g of calcium oxide ($\mathbf{CaO}$) are placed in an evacuated round bottom flask that is heated up to 35°C. At this temperature the pressure in the round bottom flask is found to be 0.5 atm.

a. What is the equilibrium constant of the decompressions of calcium carbonate ($\mathbf{CaCO_3}$) at 35°C?
b. If 100 g of calcium oxide (CaO) at 35°C was added to the flask what would be the new total pressure of the flask and why?
c. If the pressure in the round bottom flask would to increase to 1.0 atm, then what would would be the new equilibrium constant?

9.E.38 Q87

Let's say you have the reaction:

$$A(s) + B(g) \leftrightharpoons C(s) + D(g)$$

At 25°C, this reaction has an equilibrium constant of 157.2. Find the partial pressures of $B(g)$ and $D(g)$ when the total pressure of the system is equal to 4.3 atm.

9.E.39 Q91

Given the reaction

$$C_3H_5N(g) + 3\ H_2(g) \leftrightharpoons C_5H_{11}N(g)$$

whose equilibrium constant is solved by this equation

$$log_{10}(K) = -20.28 + \frac{10.56\ K}{T}$$

a. Solve for K when $T = 200\ K$
b. What is partial pressure of $C_3H_5N(g)$ when $T = 200\ K$ and the partial pressure of hydrogen is 1.0 atm and the partial pressure of $C_5H_{11}N(g)$ is 2.0×10^{-5} atm.

9.E.40 Q93

Two equal volume solutions of 2M $HCOO^-$ and 2M HCOOH are mixed together. Assume that the volumes are additive. The value of the equilibrium constant Ka for HCOOH is 1.77 x 10^{-4}. What is the ratio between the amounts of HCOOH and $HCOO^-$ in the solution at equilibrium?

9.E.41 Q101

The \(ΔG_f^o\) of $\mathbf{PbO\,(s)}$ is -188.95 kJ mol^{-1}. Calculate the equilibrium pressure of O_2(g) over a sample of pure PbO(s) in contact with pure Pb(s) at 25°C. PbO(s) decomposes according to the equation

$$\mathbf{PbO_{(s)} \rightleftharpoons Pb\,(s) + \tfrac{1}{2}\,O_2\,(g)}$$

9.E.42 Q105

If that weren't enough, Jim's sister, ., knocked his grass juice (a mixture of 1-Hexanol, Cl_2, $CaCl_2$, and cyclohexane) into the family's benzene-ethanol vat! Assume that the two solvents in the vat are immiscible with each other but are miscible with the grass juice components. Jim separates the benzene and ethanol, and drinks the one with the greater amount of 1-Hexanol. Which one does he drink? Which of the two solvents have the highest concentration of the other components of the grass juice?

9.E.43 Q107

Calculate the pH of a 0.5 M H_3PO_4 acid solution given that $K_{a1} = 7.1 \times 10^{-3}$, $K_{a2} = 6.3 \times 10^{-8}$ and $K_{a3} = 4.2 \times 10^{-13}$.

9.E.44 Q107

The Haber-Bosch process is a method invented in the 20th century as a method for hydrogen fixation. It is widely used in industry today, and involves reacting nitrogen and hydrogen in the following manner:

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

Calculate ΔG°_{rxn}. If the pressure of the products and reaction are all kept constant at the same value, in which direction will the reaction go?

Relevant information:

$\Delta G^\circ_f\ NH_{2\,(g)} = 199.83 \frac{kJ}{mol}$

9.E.45 Q109

At 273 K, the equation: $H_2(g) + I_2(g) \rightarrow 2HI(g)$ has an equilibrium constant of 60.2

a. Solve for ΔG^o at 273 K
b. How does G change when the pressure of HI is 2 atm, I_2 is 4 atm and H_2 is 6 atm?
c. Is this reaction spontaneous?

9.E.46 Q109

At 773 K the equilibrium constant for the Haber-Bosch process is 1.45×10^{-5}. The chemical reaction involved in the Haber-Bosch process is:

$$N_{2\,(g)} + 3H_{2\,(g)} \rightleftharpoons 2NH_{3\,(g)}$$

a. What is $\Delta G^\circ(773)$ for this reaction?
b. What is ΔG at 773 K for transforming 1 mole of N_2 and 3 moles H_2 held at 30 atm to 2 moles of NH_3 held at 1 atm?
c. In which direction would the previous reaction run spontaneously?

9.E.47 Q111

The following reaction is exothermic

$$\mathrm{SnO_2\,(s) + 2\,H_2\,(g) \longrightarrow Sn\,(g) + 2\,H_2O\,(l)}$$

a. What is the equilibrium expression based on this chemical equation?
b. What happens to the reaction if more H_2 is added? SnO_2 is added into the system?
c. What effect would an increase in temperature have on the system?
d. What affect would an increase in pressure have on the system?

9.E.48 Q112

Given the chemical reaction

$$\mathrm{SnO_2\,(s) \rightleftharpoons Sn\,(s) + O_2\,(g)}$$

a. Formulate the equilibrium expression using activities
b. State the effect on $\mathrm{pO_2}$ at equilibrium if more $\mathrm{SnCl_4\,(l)}$ is added to the system
c. State the effect on $\mathrm{pO_2}$ at equilibrium if more $\mathrm{O_2\,(g)}$ is added to the system

9.E.49 Q113

Arrange the following solutions in order of most acidic to basic: NaOH, NaCN, H_2SO_4, NH_4NO_3, NaCl

9.E.50 Q115

Given that the K_b values for $\mathrm{NH_3}$ and $\mathrm{NH_2NH_2}$ are 1.8×10^{-5} and 8.5×10^{-7}, respectively. Which is the stronger acid?

9.E.51 Q119

Calculate the pH of the following solutions.

a. 0.5 M NaCN (K_a of $\mathrm{HCN} = 6.2 \times 10^{-10}$)
b. 0.01 M $\mathrm{NH_4Cl}$ (K_b of $\mathrm{NH_3} = 1.8 \times 10^{-5}$)

9.E.52 Q131

Identify the stronger acid in each of the following combination. Explain.

a. HF and HBr
b. H_2SO_4 and H_2SO_3
c. HOCl and HOBr

9.E.53 Q137

Identify the Lewis acid and Lewis base for each of the following reaction.

a. $\mathbf{H^+(aq) + NH_3(aq) \rightleftharpoons NH_4{}^+(aq)}$
b. $\mathbf{Al^{3+}(aq) + 6\,H_2O(l) \rightleftharpoons Al(H_2O)_6{}^{3+}(aq)}$
c. $\mathbf{CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)}$

9.E.54 Q139

Beryllium hydroxide is an amphoteric compound. It can react as an acid as well as a base. Please write the reactions of $Be(OH)_2$ and describe its role base on Brønsted-Lowry and Lewis theories.

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CHAPTER OVERVIEW

10: ELECTROCHEMISTRY (SUPPLEMENTARY)

Electrochemistry is the study of chemical processes that cause electrons to move. This movement of electrons is called electricity, which can be generated by movements of electrons from one element to another in a reaction known as an oxidation-reduction ("redox") reaction. In this chapter, the married subjects of thermodynamics and equilibrium will be expanded to a troika by including electrochemistry. The ability to "steal" and "donate" electrons will be introduced and discussed in the context of free energies, enthalpies, entropies and equilibrium constants.

10.1: Electrochemical Cells

10.2: The Gibbs Free Energy and Cell Voltage

10.3: Concentration Effects and the Nernst Equation

10.4: Batteries and Fuel Cells

10.5: Corrosion and Its Prevention

10.6: Electrolysis - A Deeper Look

10.E: Electrochemistry (Exercises)

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10.1: Electrochemical Cells

Learning Objectives

- To understand the basics of voltaic cells
- To connect voltage from a voltaic cell to underlying redox chemistry

In any electrochemical process, electrons flow from one chemical substance to another, driven by an oxidation–reduction (redox) reaction. A redox reaction occurs when electrons are transferred from a substance that is oxidized to one that is being reduced. The **reductant** is the substance that loses electrons and is oxidized in the process; the **oxidant** is the species that gains electrons and is reduced in the process. The associated potential energy is determined by the potential difference between the valence electrons in atoms of different elements.

Because it is impossible to have a reduction without an oxidation and vice versa, a redox reaction can be described as two **half-reactions**, one representing the oxidation process and one the reduction process. For the reaction of zinc with bromine, the overall chemical reaction is as follows:

$$\mathrm{Zn(s) + Br_2(aq) \rightarrow Zn^{2+}(aq) + 2\,Br^-(aq)}$$

The half-reactions are as follows:

reduction half-reaction:

$$\mathrm{Br_2(aq) + 2\,e^- \rightarrow 2\,Br^-(aq)}$$

oxidation half-reaction:

$$\mathrm{Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^-}$$

Each half-reaction is written to show what is actually occurring in the system; Zn is the *reductant* in this reaction (it loses electrons), and $\mathrm{Br_2}$ is the *oxidant* (it gains electrons). Adding the two half-reactions gives the overall chemical reaction (Equation 10.1.1). A redox reaction is balanced when the number of electrons lost by the reductant equals the number of electrons gained by the oxidant. Like any balanced chemical equation, the overall process is electrically neutral; that is, the net charge is the same on both sides of the equation.

> *In any redox reaction, the number of electrons lost by the oxidation reaction(s) equals the number of electrons gained by the reduction reaction(s).*

In most of our discussions of chemical reactions, we have assumed that the reactants are in intimate physical contact with one another. Acid–base reactions, for example, are usually carried out with the acid and the base dispersed in a single phase, such as a liquid solution. With redox reactions, however, it is possible to physically separate the oxidation and reduction half-reactions in space, as long as there is a complete circuit, including an external electrical connection, such as a wire, between the two half-reactions. As the reaction progresses, the electrons flow from the reductant to the oxidant over this electrical connection, producing an electric current that can be used to do work. An apparatus that is used to generate electricity from a spontaneous redox reaction or, conversely, that uses electricity to drive a nonspontaneous redox reaction is called an **electrochemical cell**.

There are two types of electrochemical cells: galvanic cells and electrolytic cells. Galvanic cells are named for the Italian physicist and physician Luigi Galvani (1737–1798), who observed that dissected frog leg muscles twitched when a small electric shock was applied, demonstrating the electrical nature of nerve impulses. A **galvanic (voltaic) cell** uses the energy released during a spontaneous redox reaction ($\Delta G < 0$) to generate electricity. This type of electrochemical cell is often called a voltaic cell after its inventor, the Italian physicist Alessandro Volta (1745–1827). In contrast, an **electrolytic cell** consumes electrical energy from an external source, using it to cause a nonspontaneous redox reaction to occur ($\Delta G > 0$). Both types contain two **electrodes**, which are solid metals connected to an external circuit that provides an electrical connection between the two parts of the system (Figure 10.1.1). The oxidation half-reaction occurs at one electrode (the **anode**), and the reduction half-reaction occurs at the other (the **cathode**). When the circuit is closed, electrons flow from the anode to the cathode. The electrodes are also connected by an

electrolyte, an ionic substance or solution that allows ions to transfer between the electrode compartments, thereby maintaining the system's electrical neutrality. In this section, we focus on reactions that occur in galvanic cells.

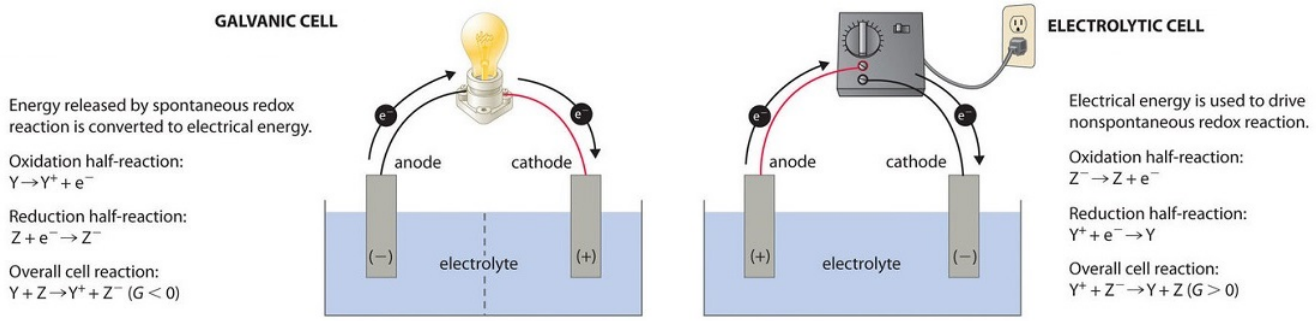


Figure **10.1.1**: Electrochemical Cells. A galvanic cell (left) transforms the energy released by a spontaneous redox reaction into electrical energy that can be used to perform work. The oxidative and reductive half-reactions usually occur in separate compartments that are connected by an external electrical circuit; in addition, a second connection that allows ions to flow between the compartments (shown here as a vertical dashed line to represent a porous barrier) is necessary to maintain electrical neutrality. The potential difference between the electrodes (voltage) causes electrons to flow from the reductant to the oxidant through the external circuit, generating an electric current. In an electrolytic cell (right), an external source of electrical energy is used to generate a potential difference between the electrodes that forces electrons to flow, driving a nonspontaneous redox reaction; only a single compartment is employed in most applications. In both kinds of electrochemical cells, the anode is the electrode at which the oxidation half-reaction occurs, and the cathode is the electrode at which the reduction half-reaction occurs.

Voltaic (Galvanic) Cells

To illustrate the basic principles of a galvanic cell, let's consider the reaction of metallic zinc with cupric ion (Cu^{2+}) to give copper metal and Zn^{2+} ion. The balanced chemical equation is as follows:

$$\mathrm{Zn\,(s) + Cu^{2+}\,(aq) \rightarrow Zn^{2+}\,(aq) + Cu\,(s)} \tag{10.1.1}$$

We can cause this reaction to occur by inserting a zinc rod into an aqueous solution of copper(II) sulfate. As the reaction proceeds, the zinc rod dissolves, and a mass of metallic copper forms. These changes occur spontaneously, but all the energy released is in the form of heat rather than in a form that can be used to do work.



Figure **10.1.2**: The Reaction of Metallic Zinc with Aqueous Copper(II) Ions in a Single Compartment. When a zinc rod is inserted into a beaker that contains an aqueous solution of copper(II) sulfate, a spontaneous redox reaction occurs: the zinc electrode dissolves to give $\mathrm{Zn^{2+}\,(aq)}$ ions, while $\mathrm{Cu^{2+}\,(aq)}$ ions are simultaneously reduced to metallic copper. The reaction occurs so rapidly that the copper is deposited as very fine particles that appear black, rather than the usual reddish color of copper. (youtu.be/2gPRK0HmYu4)

This same reaction can be carried out using the galvanic cell illustrated in Figure **10.1.3***a*. To assemble the cell, a copper strip is inserted into a beaker that contains a 1 M solution of $\mathrm{Cu^{2+}}$ ions, and a zinc strip is inserted into a different beaker that contains a 1 M solution of $\mathrm{Zn^{2+}}$ ions. The two metal strips, which serve as electrodes, are connected by a wire, and the compartments are connected by a **salt bridge**, a U-shaped tube inserted into both solutions that contains a concentrated liquid or gelled electrolyte.

The ions in the salt bridge are selected so that they do not interfere with the electrochemical reaction by being oxidized or reduced themselves or by forming a precipitate or complex; commonly used cations and anions are Na^+ or K^+ and NO_3^- or SO_4^{2-}, respectively. (The ions in the salt bridge do not have to be the same as those in the redox couple in either compartment.) When the circuit is closed, a spontaneous reaction occurs: zinc metal is oxidized to Zn^{2+} ions at the zinc electrode (the anode), and Cu^{2+} ions are reduced to Cu metal at the copper electrode (the cathode). As the reaction progresses, the zinc strip dissolves, and the concentration of Zn^{2+} ions in the solution increases; simultaneously, the copper strip gains mass, and the concentration of Cu^{2+} ions in the solution decreases (Figure 10.1.3*b*). Thus we have carried out the same reaction as we did using a single beaker, but this time the oxidative and reductive half-reactions are physically separated from each other. The electrons that are released at the anode flow through the wire, producing an electric current. Galvanic cells therefore transform chemical energy into electrical energy that can then be used to do work.

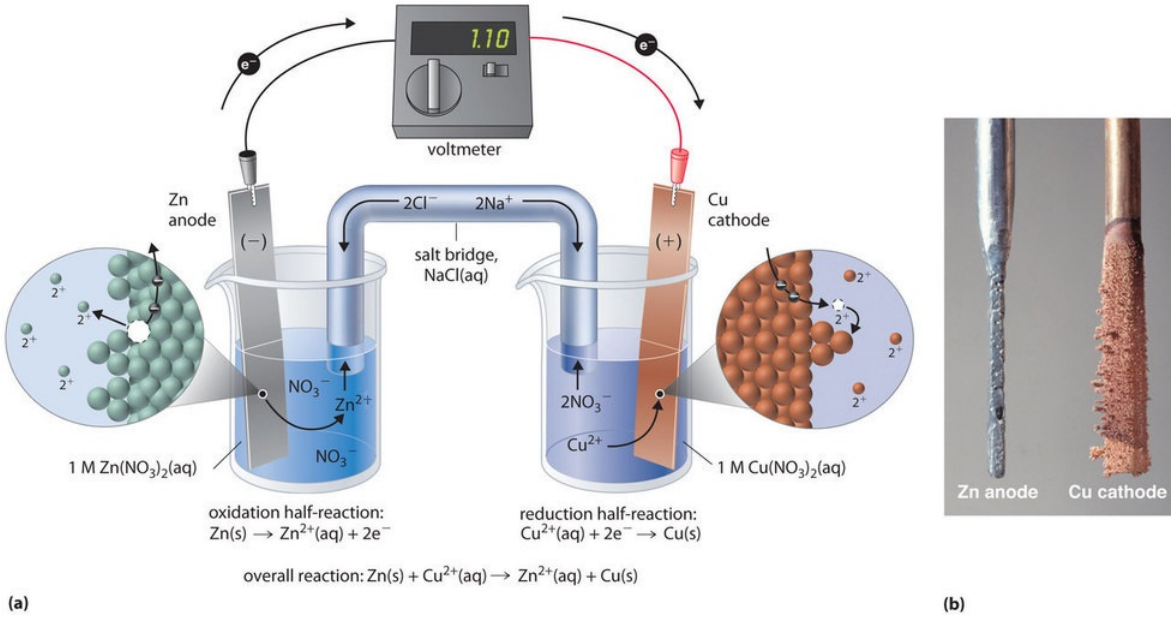


Figure 10.1.3: The Reaction of Metallic Zinc with Aqueous Copper(II) Ions in a Galvanic Cell. (a) A galvanic cell can be constructed by inserting a copper strip into a beaker that contains an aqueous 1 M solution of Cu^{2+} ions and a zinc strip into a different beaker that contains an aqueous 1 M solution of Zn^{2+} ions. The two metal strips are connected by a wire that allows electricity to flow, and the beakers are connected by a salt bridge. When the switch is closed to complete the circuit, the zinc electrode (the anode) is spontaneously oxidized to Zn^{2+} ions in the left compartment, while Cu^{2+} ions are simultaneously reduced to copper metal at the copper electrode (the cathode). (b) As the reaction progresses, the Zn anode loses mass as it dissolves to give Zn^{2+}(aq) ions, while the Cu cathode gains mass as Cu^{2+}(aq) ions are reduced to copper metal that is deposited on the cathode. (CC BY-SA-NC; anonymous)

The electrolyte in the salt bridge serves two purposes: it completes the circuit by carrying electrical charge and maintains electrical neutrality in both solutions by allowing ions to migrate between them. The identity of the salt in a salt bridge is unimportant, as long as the component ions do not react or undergo a redox reaction under the operating conditions of the cell. Without such a connection, the total positive charge in the Zn^{2+} solution would increase as the zinc metal dissolves, and the total positive charge in the Cu^{2+} solution would decrease. The salt bridge allows charges to be neutralized by a flow of anions into the Zn^{2+} solution and a flow of cations into the Cu^{2+} solution. In the absence of a salt bridge or some other similar connection, the reaction would rapidly cease because electrical neutrality could not be maintained.

A voltmeter can be used to measure the difference in electrical potential between the two compartments. Opening the switch that connects the wires to the anode and the cathode prevents a current from flowing, so no chemical reaction occurs. With the switch closed, however, the external circuit is closed, and an electric current can flow from the anode to the cathode. The **potential** (E_{cell}) of the cell, measured in volts, is the difference in electrical potential between the two half-reactions and is related to the energy needed to move a charged particle in an electric field. In the cell we have described, the voltmeter indicates a potential of 1.10 V (Figure 10.1.3*a*). Because electrons from the oxidation half-reaction are released at the anode, the anode in a galvanic cell is negatively charged. The cathode, which attracts electrons, is positively charged.

Not all electrodes undergo a chemical transformation during a redox reaction. The electrode can be made from an inert, highly conducting metal such as platinum to prevent it from reacting during a redox process, where it does not appear in the overall electrochemical reaction. This phenomenon is illustrated in Example **10.1.1**.

> *A galvanic (voltaic) cell converts the energy released by a **spontaneous** chemical reaction to electrical energy. An electrolytic cell consumes electrical energy from an external source to drive a **nonspontaneous** chemical reaction.*

Example 10.1.1

A chemist has constructed a galvanic cell consisting of two beakers. One beaker contains a strip of tin immersed in aqueous sulfuric acid, and the other contains a platinum electrode immersed in aqueous nitric acid. The two solutions are connected by a salt bridge, and the electrodes are connected by a wire. Current begins to flow, and bubbles of a gas appear at the platinum electrode. The spontaneous redox reaction that occurs is described by the following balanced chemical equation:

$$3\,Sn\,(s) + 2\,NO_3^-\,(aq) + 8\,H^+\,(aq) \rightarrow 3\,Sn^{2+}\,(aq) + 2\,NO\,(g) + 4\,H_2O\,(l)$$

For this galvanic cell,

a. write the half-reaction that occurs at each electrode.
b. indicate which electrode is the cathode and which is the anode.
c. indicate which electrode is the positive electrode and which is the negative electrode.

Given: galvanic cell and redox reaction

Asked for: half-reactions, identity of anode and cathode, and electrode assignment as positive or negative

Strategy:

A. Identify the oxidation half-reaction and the reduction half-reaction. Then identify the anode and cathode from the half-reaction that occurs at each electrode.
B. From the direction of electron flow, assign each electrode as either positive or negative.

Solution

A In the reduction half-reaction, nitrate is reduced to nitric oxide. (The nitric oxide would then react with oxygen in the air to form NO_2, with its characteristic red-brown color.) In the oxidation half-reaction, metallic tin is oxidized. The half-reactions corresponding to the actual reactions that occur in the system are as follows:

reduction:

$$NO_3^-\,(aq) + 4\,H^+\,(aq) + 3\,e^- \longrightarrow NO\,(g) + 2\,H_2O\,(l)$$

oxidation:

$$Sn\,(s) \longrightarrow Sn^{2+}\,(aq) + 2\,e^-$$

Thus nitrate is reduced to NO, while the tin electrode is oxidized to Sn^{2+}.

Because the reduction reaction occurs at the Pt electrode, it is the cathode. Conversely, the oxidation reaction occurs at the tin electrode, so it is the anode.

B Electrons flow from the tin electrode through the wire to the platinum electrode, where they transfer to nitrate. The electric circuit is completed by the salt bridge, which permits the diffusion of cations toward the cathode and anions toward the anode. Because electrons flow from the tin electrode, it must be electrically negative. In contrast, electrons flow toward the Pt electrode, so that electrode must be electrically positive.

? Exercise 10.1.1

Consider a simple galvanic cell consisting of two beakers connected by a salt bridge. One beaker contains a solution of MnO_4^- in dilute sulfuric acid and has a Pt electrode. The other beaker contains a solution of Sn^{2+} in dilute sulfuric acid, also with a Pt electrode. When the two electrodes are connected by a wire, current flows and a spontaneous reaction occurs that is described by the following balanced chemical equation:

$$2\,MnO_4^-(aq) + 5\,Sn^{2+}(aq) + 16\,H^+(aq) \rightarrow 2\,Mn^{2+}(aq) + 5\,Sn^{4+}(aq) + 8\,H_2O(l)$$

For this galvanic cell,

a. write the half-reaction that occurs at each electrode.
b. indicate which electrode is the cathode and which is the anode.
c. indicate which electrode is positive and which is negative.

Answer a

$$MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \rightarrow Mn^{2+}(aq) + 4\,H_2O(l)$$
$$Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2\,e^-$$

Answer b

The Pt electrode in the permanganate solution is the cathode; the one in the tin solution is the anode.

Answer c

The cathode (electrode in beaker that contains the permanganate solution) is positive, and the anode (electrode in beaker that contains the tin solution) is negative.



Electrochemical Cells: Electrochemical Cells(opens in new window) [youtu.be]

Constructing Cell Diagrams (Cell Notation)

Because it is somewhat cumbersome to describe any given galvanic cell in words, a more convenient notation has been developed. In this line notation, called a cell diagram, the identity of the electrodes and the chemical contents of the compartments are indicated by their chemical formulas, with the anode written on the far left and the cathode on the far right. Phase boundaries are shown by single vertical lines, and the salt bridge, which has two phase boundaries, by a double vertical line. Thus the cell diagram for the **Zn/Cu** cell shown in Figure **10.1.3*a*** is written as follows:

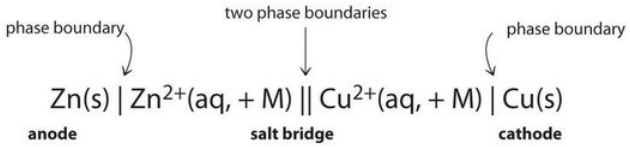


Figure 10.1.4: A cell diagram includes solution concentrations when they are provided. The + M term is meant to indicate the applicable concentration of the species. If the species is a gas, then you substitute the pressure instead.

At the anode is solid zinc. after the phase boundary is aq Zinc two plus and plus M. After the two phase boundary is aq copper two plus and plus M. At the cathode is solid copper.

Galvanic cells can have arrangements other than the examples we have seen so far. For example, the voltage produced by a redox reaction can be measured more accurately using two electrodes immersed in a single beaker containing an electrolyte that completes the circuit. This arrangement reduces errors caused by resistance to the flow of charge at a boundary, called the **junction potential**. One example of this type of galvanic cell is as follows:

$$\mathrm{Pt(s)\ |\ H_2(g)\ |\ HCl(aq,\ 1\,M)\ |\ AgCl(s)\ Ag(s)}$$

This cell diagram does not include a double vertical line representing a salt bridge because there is no salt bridge providing a junction between two dissimilar solutions. Moreover, solution concentrations have not been specified, so they are not included in the cell diagram. The half-reactions and the overall reaction for this cell are as follows:

cathode reaction:

$$\mathrm{AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)}$$

anode reaction:

$$\mathrm{\tfrac{1}{2}\,H_2(g) \longrightarrow H^+(aq) + e^-}$$

overall:

$$\mathrm{AgCl(s) + \tfrac{1}{2}\,H_2(g) \longrightarrow Ag(s) + Cl^- + H^+(aq)}$$

A single-compartment galvanic cell will initially exhibit the same voltage as a galvanic cell constructed using separate compartments, but it will discharge rapidly because of the direct reaction of the reactant at the anode with the oxidized member of the cathodic redox couple. Consequently, cells of this type are not particularly useful for producing electricity.

Example 10.1.2

Draw a cell diagram for the galvanic cell described in Example 10.1.1. The balanced chemical reaction is as follows:

$$\mathrm{3\,Sn(s) + 2\,NO_3^-(aq) + 8\,H^+(aq) \rightarrow 3\,Sn^{2+}(aq) + 2\,NO(g) + 4\,H_2O(l)}$$

Given: galvanic cell and redox reaction

Asked for: cell diagram

Strategy:

Using the symbols described, write the cell diagram beginning with the oxidation half-reaction on the left.

Solution

The anode is the tin strip, and the cathode is the Pt electrode. Beginning on the left with the anode, we indicate the phase boundary between the electrode and the tin solution by a vertical bar. The anode compartment is thus $\mathrm{Sn(s)\,|\,Sn^{2+}(aq)}$. We could include $\mathrm{H_2SO_4(aq)}$ with the contents of the anode compartment, but the sulfate ion (as $\mathrm{HSO_4^-}$) does not participate in the overall reaction, so it does not need to be specifically indicated. The cathode compartment contains aqueous nitric acid, which does participate in the overall reaction, together with the product of the reaction (NO) and the Pt electrode. These are written as $\mathrm{HNO_3(aq)\,|\,NO(g)\,|\,Pt(s)}$, with single vertical bars indicating the phase boundaries. Combining the two compartments and using a double vertical bar to indicate the salt bridge,

$$\mathrm{Sn(s)\ |\,Sn^{2+}(aq)\,||\,HNO_3(aq)\,|\,NO(g)\,|\,Pt_{(s)}}$$

The solution concentrations were not specified, so they are not included in this cell diagram.

? Exercise 10.1.2

Draw the cell diagram for the following reaction, assuming the concentration of Ag^+ and Mg^{2+} are each 1 M:

$$Mg(s) + 2\,Ag^+(aq) \rightarrow Mg^{2+}(aq) + 2\,Ag(s)$$

Answer

$$Mg(s)\ \left|Mg^{2+}(aq,\ 1\,M)\right|\left|Ag^+(aq,\ 1\ M)\right|\ Ag(s)$$



Cell Diagrams: Cell Diagrams(opens in new window) [youtu.be]

Summary

A galvanic (voltaic) cell uses the energy released during a spontaneous redox reaction to generate electricity, whereas an electrolytic cell consumes electrical energy from an external source to force a reaction to occur. Electrochemistry is the study of the relationship between electricity and chemical reactions. The oxidation–reduction reaction that occurs during an electrochemical process consists of two half-reactions, one representing the oxidation process and one the reduction process. The sum of the half-reactions gives the overall chemical reaction. The overall redox reaction is balanced when the number of electrons lost by the reductant equals the number of electrons gained by the oxidant. An electric current is produced from the flow of electrons from the reductant to the oxidant. An electrochemical cell can either generate electricity from a spontaneous redox reaction or consume electricity to drive a nonspontaneous reaction. In a galvanic (voltaic) cell, the energy from a spontaneous reaction generates electricity, whereas in an electrolytic cell, electrical energy is consumed to drive a nonspontaneous redox reaction. Both types of cells use two electrodes that provide an electrical connection between systems that are separated in space. The oxidative half-reaction occurs at the anode, and the reductive half-reaction occurs at the cathode. A salt bridge connects the separated solutions, allowing ions to migrate to either solution to ensure the system's electrical neutrality. A voltmeter is a device that measures the flow of electric current between two half-reactions. The potential of a cell, measured in volts, is the energy needed to move a charged particle in an electric field. An electrochemical cell can be described using line notation called a cell diagram, in which vertical lines indicate phase boundaries and the location of the salt bridge. Resistance to the flow of charge at a boundary is called the junction potential.

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10.2: The Gibbs Free Energy and Cell Voltage

Learning Objectives

- To understand the relationship between cell potential and the equilibrium constant.
- To use cell potentials to calculate solution concentrations.

Changes in reaction conditions can have a tremendous effect on the course of a redox reaction. For example, under standard conditions, the reaction of $\mathrm{Co(s)}$ with $\mathrm{Ni^{2+}(aq)}$ to form $\mathrm{Ni(s)}$ and $\mathrm{Co^{2+}(aq)}$ occurs spontaneously, but if we reduce the concentration of $\mathrm{Ni^{2+}}$ by a factor of 100, so that $[\mathrm{Ni^{2+}}]$ is 0.01 M, then the reverse reaction occurs spontaneously instead. The relationship between voltage and concentration is one of the factors that must be understood to predict whether a reaction will be spontaneous.

The Relationship between Cell Potential & Gibbs Energy

Electrochemical cells convert chemical energy to electrical energy and vice versa. The total amount of energy produced by an electrochemical cell, and thus the amount of energy available to do electrical work, depends on both the cell potential and the total number of electrons that are transferred from the reductant to the oxidant during the course of a reaction. The resulting electric current is measured in **coulombs (C)**, an SI unit that measures the number of electrons passing a given point in 1 s. A coulomb relates energy (in joules) to electrical potential (in volts). Electric current is measured in **amperes (A)**; 1 A is defined as the flow of 1 C/s past a given point (1 C = 1 A·s):

$$\frac{1\ \mathrm{J}}{1\ \mathrm{V}} = 1\ \mathrm{C} = \mathrm{A \cdot s}$$

In chemical reactions, however, we need to relate the coulomb to the charge on a mole of electrons. Multiplying the charge on the electron by Avogadro's number gives us the charge on 1 mol of electrons, which is called the **faraday (F)**, named after the English physicist and chemist Michael Faraday (1791–1867):

$$\begin{aligned} F &= (1.60218 \times 10^{-19}\ \mathrm{C}) \left(\frac{6.02214 \times 10^{23}\ J}{1\ \mathrm{mol\ e^-}} \right) \\ &= 9.64833212 \times 10^{4}\ \mathrm{C/mol\ e^-} \\ &\simeq 96,485\ J/(\mathrm{V \cdot mol\ e^-}) \end{aligned}$$

The total charge transferred from the reductant to the oxidant is therefore nF, where n is the number of moles of electrons.

Michael Faraday (1791–1867)

Faraday was a British physicist and chemist who was arguably one of the greatest experimental scientists in history. The son of a blacksmith, Faraday was self-educated and became an apprentice bookbinder at age 14 before turning to science. His experiments in electricity and magnetism made electricity a routine tool in science and led to both the electric motor and the electric generator. He discovered the phenomenon of electrolysis and laid the foundations of electrochemistry. In fact, most of the specialized terms introduced in this chapter (electrode, anode, cathode, and so forth) are due to Faraday. In addition, he discovered benzene and invented the system of oxidation state numbers that we use today. Faraday is probably best known for "The Chemical History of a Candle," a series of public lectures on the chemistry and physics of flames.

The maximum amount of work that can be produced by an electrochemical cell (w_{max}) is equal to the product of the cell potential (E°_{cell}) and the total charge transferred during the reaction (nF):

$$w_{max} = nFE_{cell}$$

Work is expressed as a negative number because work is being done by a system (an electrochemical cell with a positive potential) on its surroundings.

The change in free energy (ΔG) is also a measure of the maximum amount of work that can be performed during a chemical process ($\Delta G = w_{max}$). Consequently, there must be a relationship between the potential of an electrochemical cell and ΔG; this relationship is as follows:

$$\Delta G = -nFE_{cell}$$

A spontaneous redox reaction is therefore characterized by a negative value of ΔG and a positive value of E°_{cell}, consistent with our earlier discussions. When both reactants and products are in their standard states, the relationship between ΔG° and E°_{cell} is as follows:

$$\Delta G^\circ = -nFE^\circ_{cell} \tag{10.2.1}$$

A spontaneous redox reaction is characterized by a negative value of ΔG°, which corresponds to a positive value of E°_{cell}.

Example 10.2.1

Suppose you want to prepare elemental bromine from bromide using the dichromate ion as an oxidant. Using the data in Table P2, calculate the free-energy change (ΔG°) for this redox reaction under standard conditions. Is the reaction spontaneous?

Given: redox reaction

Asked for: ΔG^o for the reaction and spontaneity

Strategy:

A. From the relevant half-reactions and the corresponding values of E^o, write the overall reaction and calculate E°_{cell}.

B. Determine the number of electrons transferred in the overall reaction. Then use Equation 10.2.1 to calculate ΔG^o. If ΔG^o is negative, then the reaction is spontaneous.

Solution

A

As always, the first step is to write the relevant half-reactions and use them to obtain the overall reaction and the magnitude of E^o. From Table P2, we can find the reduction and oxidation half-reactions and corresponding E^o values:

cathode:	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	$E^\circ_{cathode} = 1.36\ V$
anode:	$2Br^-(aq) \rightarrow Br_2(aq) + 2e^-$	$E^\circ_{anode} = 1.09\ V$

To obtain the overall balanced chemical equation, we must multiply both sides of the oxidation half-reaction by 3 to obtain the same number of electrons as in the reduction half-reaction, remembering that the magnitude of E^o is not affected:

cathode:	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	$E^\circ_{cathode} = 1.36\ V$
anode:	$6Br^-(aq) \rightarrow 3Br_2(aq) + 6e^-$	$E^\circ_{anode} = 1.09\ V$
overall:	$Cr_2O_7^{2-}(aq) + 6Br^-(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 3Br_2(aq) + 7H_2O(l)$	$E^\circ_{cell} = 0.27\ V$

B

We can now calculate ΔG° using Equation 10.2.1. Because six electrons are transferred in the overall reaction, the value of n is 6:

$$\begin{aligned}\Delta G^\circ &= -(n)(F)(E^\circ_{cell}) \\ &= -(6\ \text{mole})[96,485\ \text{J}/(\text{V}\cdot\text{mol})(0.27\ \text{V})] \\ &= -15.6 \times 10^4\ \text{J} \\ &= -156\ \text{kJ/mol}\ Cr_2O_7^{2-}\end{aligned}$$

Thus ΔG^o is −168 kJ/mol for the reaction as written, and the reaction is spontaneous.

Exercise 10.2.1

Use the data in Table P2 to calculate ΔG^o for the reduction of ferric ion by iodide:

$$2\,Fe^{3+}(aq) + 2\,I^-(aq) \longrightarrow 2\,Fe^{2+}(aq) + I_2(s)$$

Is the reaction spontaneous?

Answer

−44 kJ/mol I_2; yes

Potentials for the Sums of Half-Reactions

Although Table P2 list several half-reactions, many more are known. When the standard potential for a half-reaction is not available, we can use relationships between standard potentials and free energy to obtain the potential of any other half-reaction that can be written as the sum of two or more half-reactions whose standard potentials are available. For example, the potential for the reduction of $\mathrm{Fe^{3+}(aq)}$ to $\mathrm{Fe(s)}$ is not listed in the table, but two related reductions are given:

$$\mathrm{Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)} \quad E^\circ = +0.77V$$

$$\mathrm{Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s)} \quad E^\circ = -0.45V$$

Although the sum of these two half-reactions gives the desired half-reaction, we cannot simply add the potentials of two reductive half-reactions to obtain the potential of a third reductive half-reaction because E^o is not a state function. However, because ΔG^o is a state function, the sum of the ΔG^o values for the individual reactions gives us ΔG^o for the overall reaction, which is proportional to both the potential and the number of electrons (n) transferred. To obtain the value of E^o for the overall half-reaction, we first must add the values of $\Delta G^o (= -nFE^o)$ for each individual half-reaction to obtain ΔG^o for the overall half-reaction:

Extra close brace or missing open brace

Solving the last expression for ΔG° for the overall half-reaction,

$$\Delta G^\circ = F[(-0.77V) + (-2)(-0.45V)] = F(0.13V)$$

Three electrons ($n = 3$) are transferred in the overall reaction, so substituting into Equation 10.2.1 and solving for E^o gives the following:

$$\begin{aligned} \Delta G^\circ &= -nFE^\circ_{\text{cell}} \\ F(0.13\text{ V}) &= -(3)(F)(E^\circ_{\text{cell}}) \\ E^\circ &= -\frac{0.13\text{ V}}{3} = -0.043\text{ V} \end{aligned}$$

This value of E^o is very different from the value that is obtained by simply adding the potentials for the two half-reactions (0.32 V) and even has the opposite sign.

> *Values of E^o for half-reactions cannot be added to give E^o for the sum of the half-reactions; only values of $\Delta G^o = -nFE^\circ_{cell}$ for half-reactions can be added.*

The Relationship between Cell Potential & the Equilibrium Constant

We can use the relationship between ΔG° and the equilibrium constant K, to obtain a relationship between E°_{cell} and K. Recall that for a general reaction of the type $aA + bB \rightarrow cC + dD$, the standard free-energy change and the equilibrium constant are related by the following equation:

$$\Delta G^\circ = -RT \ln K$$

Given the relationship between the standard free-energy change and the standard cell potential (Equation 10.2.1), we can write

$$-nFE^\circ_{cell} = -RT \ln K$$

Rearranging this equation,

$$E^\circ_{\text{cell}} = \left(\frac{RT}{nF}\right) \ln K \tag{10.2.2}$$

For $T = 298\,K$, Equation 10.2.2 can be simplified as follows:

$$E^\circ_{\text{cell}} = \left(\frac{RT}{nF}\right) \ln K$$
$$= \left[\frac{[8.314\ \text{J/(mol} \cdot \text{K)}(298\ \text{K})]}{n[96,485\ \text{J/(V} \cdot \text{mol)}]}\right] 2.303 \log K$$
$$= \left(\frac{0.0592\ \text{V}}{n}\right) \log K \tag{10.2.3}$$

Thus E°_{cell} is directly proportional to the logarithm of the equilibrium constant. This means that large equilibrium constants correspond to large positive values of E°_{cell} and vice versa.

Example 10.2.2

Use the data in Table P2 to calculate the equilibrium constant for the reaction of metallic lead with PbO_2 in the presence of sulfate ions to give $PbSO_4$ under standard conditions. (This reaction occurs when a car battery is discharged.) Report your answer to two significant figures.

Given: redox reaction

Asked for: K

Strategy:

A. Write the relevant half-reactions and potentials. From these, obtain the overall reaction and E^o_{cell}.

B. Determine the number of electrons transferred in the overall reaction. Use Equation 10.2.3 to solve for $\log K$ and then K.

Solution

A The relevant half-reactions and potentials from Table P2 are as follows:

cathode:	$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$	$E^\circ_{\text{cathode}} = 1.69\ \text{V}$
anode:	$Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$	$E^\circ_{\text{anode}} = -0.36\ \text{V}$
overall:	$Pb(s) + PbO_2(s) + 2SO_4^{2-}(aq) + 4H^+(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$	$E^\circ_{\text{cell}} = 2.05\ \text{V}$

B Two electrons are transferred in the overall reaction, so $n = 2$. Solving Equation 10.2.3 for log K and inserting the values of n and E^o,

$$\log K = \frac{nE^\circ}{0.0591\ \text{V}} = \frac{2(2.05\ \text{V})}{0.0591\ \text{V}} = 69.37$$
$$K = 2.3 \times 10^{69}$$

Thus the equilibrium lies far to the right, favoring a discharged battery (as anyone who has ever tried unsuccessfully to start a car after letting it sit for a long time will know).

Exercise 10.2.2

Use the data in Table P2 to calculate the equilibrium constant for the reaction of $Sn^{2+}(aq)$ with oxygen to produce $Sn^{4+}(aq)$ and water under standard conditions. Report your answer to two significant figures. The reaction is as follows:

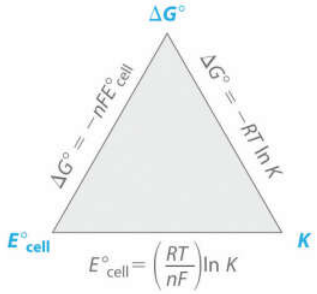
$$2\,Sn^{2+}(aq) + O_2(g) + 4\,H^+(aq) \rightleftharpoons 2\,Sn^{4+}(aq) + 2\,H_2O(l)$$

Answer

5.7×10^{72}

Figure 10.2.1 summarizes the relationships that we have developed based on properties of the system—that is, based on the equilibrium constant, standard free-energy change, and standard cell potential—and the criteria for spontaneity ($\Delta G^\circ < 0$). Unfortunately, these criteria apply only to systems in which all reactants and products are present in their standard states, a situation

that is seldom encountered in the real world. A more generally useful relationship between cell potential and reactant and product concentrations, as we are about to see, uses the relationship between ΔG and the reaction quotient Q.



$\Delta G°$	$E°_{cell}$	K	Direction of Reaction
<0	>0	>1	spontaneous in forward direction
>0	<0	<1	spontaneous in reverse direction
0	0	1	no net reaction: system at equilibrium

Figure **10.2.1**: The Relationships among Criteria for Thermodynamic Spontaneity. The three properties of a system that can be used to predict the spontaneity of a redox reaction under standard conditions are K, ΔG°, and $E°_{cell}$. If we know the value of one of these quantities, then these relationships enable us to calculate the value of the other two. The signs of ΔG° and $E°_{cell}$ and the magnitude of K determine the direction of spontaneous reaction under standard conditions. (CC BY-NC-SA; Anonymous by request)

If ΔG is less than zero, E^o is greater than zero and K is greater than 1 then the direction of the reaction is spontaneous in forward direction. If ΔG is greater than zero, E^o is less than zero and K is less than one then the direction of reaction is spontaneous in reverse direction. If ΔG is zero, E is zero and K is one that there is no net reaction and the system is at equilibrium .

Summary

A coulomb (C) relates electrical potential, expressed in volts, and energy, expressed in joules. The current generated from a redox reaction is measured in amperes (A), where 1 A is defined as the flow of 1 C/s past a given point. The faraday (F) is Avogadro's number multiplied by the charge on an electron and corresponds to the charge on 1 mol of electrons. The product of the cell potential and the total charge is the maximum amount of energy available to do work, which is related to the change in free energy that occurs during the chemical process. Adding together the ΔG values for the half-reactions gives ΔG for the overall reaction, which is proportional to both the potential and the number of electrons (n) transferred. Spontaneous redox reactions have a negative ΔG and therefore a positive E_{cell}. Because the equilibrium constant K is related to ΔG, $E°_{cell}$ and K are also related. Large equilibrium constants correspond to large positive values of E°.

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10.3: Concentration Effects and the Nernst Equation

Learning Objectives

- Relate cell potentials to Gibbs energy changes
- Use the Nernst equation to determine cell potentials at nonstandard conditions
- Perform calculations that involve converting between cell potentials, free energy changes, and equilibrium constants

The *Nernst Equation* enables the determination of cell potential under non-standard conditions. It relates the measured cell potential to the reaction quotient and allows the accurate determination of equilibrium constants (including solubility constants).

The Effect of Concentration on Cell Potential: The Nernst Equation

Recall that the actual free-energy change for a reaction under nonstandard conditions, ΔG, is given as follows:

$$\Delta G = \Delta G^\circ + RT \ln Q \tag{10.3.1}$$

We also know that $\Delta G = -nFE_{cell}$ (under non-standard conditions) and $\Delta G^o = -nFE^o_{cell}$ (under standard conditions). Substituting these expressions into Equation 10.3.1, we obtain

$$-nFE_{cell} = -nFE^o_{cell} + RT \ln Q \tag{10.3.2}$$

Dividing both sides of this equation by $-nF$,

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{RT}{nF}\right) \ln Q \tag{10.3.3}$$

Equation 10.3.3 is called the **Nernst equation**, after the German physicist and chemist Walter Nernst (1864–1941), who first derived it. The Nernst equation is arguably the most important relationship in electrochemistry. When a redox reaction is at equilibrium ($\Delta G = 0$), then Equation 10.3.3 reduces to Equation 10.3.4 and 10.3.5 because $Q = K$, and there is no net transfer of electrons (i.e., $E_{cell} = 0$).

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{RT}{nF}\right) \ln K = 0 \tag{10.3.4}$$

since

$$E^\circ_{\text{cell}} = \left(\frac{RT}{nF}\right) \ln K \tag{10.3.5}$$

Substituting the values of the constants into Equation 10.3.3 with $T = 298\ K$ and converting to base-10 logarithms give the relationship of the actual cell potential (E_{cell}), the standard cell potential ($E°_{cell}$), and the reactant and product concentrations at room temperature (contained in Q):

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right) \log Q \tag{10.3.6}$$

The Power of the Nernst Equation

The Nernst Equation (10.3.3) can be used to determine the value of E_{cell}, and thus the direction of spontaneous reaction, for any redox reaction under any conditions.

Equation 10.3.6 allows us to calculate the potential associated with any electrochemical cell at 298 K for any combination of reactant and product concentrations under any conditions. We can therefore determine the spontaneous direction of any redox reaction under any conditions, as long as we have tabulated values for the relevant standard electrode potentials. Notice in Equation 10.3.6 that the cell potential changes by 0.0591/n V for each 10-fold change in the value of Q because log 10 = 1.

Example 10.3.1

The following reaction proceeds spontaneously under standard conditions because $E°_{cell} > 0$ (which means that $\Delta G° < 0$):

$$2\,Ce^{4+}(aq) + 2\,Cl^-(aq) \longrightarrow 2\,Ce^{3+}(aq) + Cl_2(g) \qquad E°_{cell} = 0.25\,V$$

Calculate E_{cell} for this reaction under the following nonstandard conditions and determine whether it will occur spontaneously: $[Ce^{4+}] = 0.013$ M, $[Ce^{3+}] = 0.60$ M, $[Cl^-] = 0.0030$ M, $P_{Cl_2} = 1.0$ atm, and T = 25°C.

Given: balanced redox reaction, standard cell potential, and nonstandard conditions

Asked for: cell potential

Strategy:

Determine the number of electrons transferred during the redox process. Then use the Nernst equation to find the cell potential under the nonstandard conditions.

Solution

We can use the information given and the Nernst equation to calculate E_{cell}. Moreover, because the temperature is 25°C (298 K), we can use Equation 10.3.6 instead of Equation 10.3.3. The overall reaction involves the net transfer of two electrons:

$$2Ce^{4+}_{(aq)} + 2e^- \rightarrow 2Ce^{3+}_{(aq)}$$

$$2Cl^-_{(aq)} \rightarrow Cl_{2(g)} + 2e^-$$

so n = 2. Substituting the concentrations given in the problem, the partial pressure of Cl_2, and the value of $E°_{cell}$ into Equation 10.3.6,

$$\begin{aligned} E_{cell} &= E°_{cell} - \left(\frac{0.0591\ \text{V}}{n}\right)\log Q \\ &= 0.25\ \text{V} - \left(\frac{0.0591\ \text{V}}{2}\right)\log\left(\frac{[Ce^{3+}]^2 P_{Cl_2}}{[Ce^{4+}]^2[Cl^-]^2}\right) \\ &= 0.25\ \text{V} - [(0.0296\ \text{V})(8.37)] = 0.00\ \text{V} \end{aligned}$$

Thus the reaction will not occur spontaneously under these conditions (because E = 0 V and $\Delta G = 0$). The composition specified is that of an equilibrium mixture

Exercise 10.3.1

Molecular oxygen will not oxidize MnO_2 to permanganate via the reaction

$$4\,MnO_2(s) + 3\,O_2(g) + 4\,OH^-(aq) \longrightarrow 4\,MnO_4^-(aq) + 2\,H_2O(l) \quad E°_{cell} = -0.20\,V$$

Calculate E_{cell} for the reaction under the following nonstandard conditions and decide whether the reaction will occur spontaneously: pH 10, P_{O_2} = 0.20 atm, $[MNO_4^-] = 1.0 \times 10^{-4}$ M, and T = 25°C.

Answer

$E_{cell} = -0.22$ V; the reaction will not occur spontaneously.

Applying the Nernst equation to a simple electrochemical cell such as the Zn/Cu cell allows us to see how the cell voltage varies as the reaction progresses and the concentrations of the dissolved ions change. Recall that the overall reaction for this cell is as follows:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s) \quad E°cell = 1.10V \tag{10.3.7}$$

The reaction quotient is therefore $Q = [Zn^{2+}]/[Cu^{2+}]$. Suppose that the cell initially contains 1.0 M Cu^{2+} and 1.0×10^{-6} M Zn^{2+}. The initial voltage measured when the cell is connected can then be calculated from Equation 10.3.6:

$$E_{cell} = E^\circ_{cell} - \left(\frac{0.0591\ V}{n}\right) \log \frac{[Zn^{2+}]}{[Cu^{2+}]} \tag{10.3.8}$$

$$= 1.10\ V - \left(\frac{0.0591\ V}{2}\right) \log \left(\frac{1.0 \times 10^{-6}}{1.0}\right) = 1.28\ V \tag{10.3.9}$$

Thus the initial voltage is greater than E° because $Q < 1$. As the reaction proceeds, $[Zn^{2+}]$ in the anode compartment increases as the zinc electrode dissolves, while $[Cu^{2+}]$ in the cathode compartment decreases as metallic copper is deposited on the electrode. During this process, the ratio Q = $[Zn^{2+}]/[Cu^{2+}]$ steadily increases, and the cell voltage therefore steadily decreases. Eventually, $[Zn^{2+}] = [Cu^{2+}]$, so Q = 1 and $E_{cell} = E°_{cell}$. Beyond this point, $[Zn^{2+}]$ will continue to increase in the anode compartment, and $[Cu^{2+}]$ will continue to decrease in the cathode compartment. Thus the value of Q will increase further, leading to a further decrease in E_{cell}. When the concentrations in the two compartments are the opposite of the initial concentrations (i.e., 1.0 M Zn^{2+} and 1.0×10^{-6} M Cu^{2+}), Q = 1.0×10^6, and the cell potential will be reduced to 0.92 V.

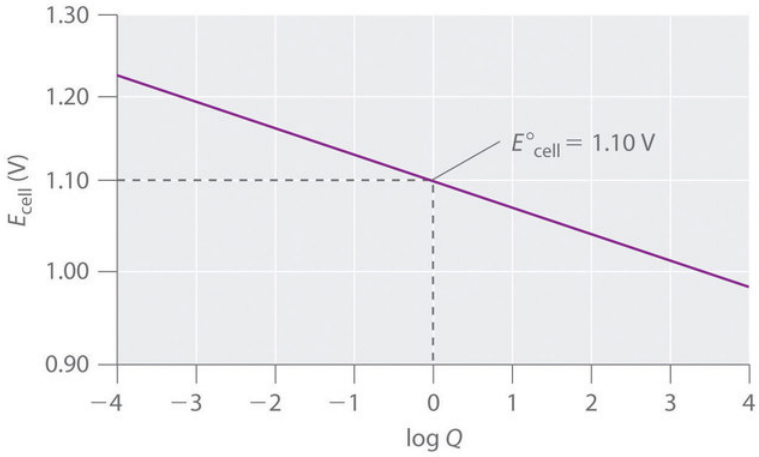


Figure **10.3.1**: The Variation of E_{cell} with Log Q for a Zn/Cu Cell. Initially, log Q < 0, and the voltage of the cell is greater than $E°_{cell}$. As the reaction progresses, log Q increases, and E_{cell} decreases. When $[Zn^{2+}] = [Cu^{2+}]$, log Q = 0 and $E_{cell} = E°_{cell}$ = 1.10 V. As long as the electrical circuit remains intact, the reaction will continue, and log Q will increase until Q = K and the cell voltage reaches zero. At this point, the system will have reached equilibrium.

The variation of E_{cell} with $\log Q$ over this range is linear with a slope of −0.0591/n, as illustrated in Figure **10.3.1**. As the reaction proceeds still further, Q continues to increase, and E_{cell} continues to decrease. If neither of the electrodes dissolves completely, thereby breaking the electrical circuit, the cell voltage will eventually reach zero. This is the situation that occurs when a battery is "dead." The value of Q when E_{cell} = 0 is calculated as follows:

$$E_{cell} = E^\circ_{cell} - \left(\frac{0.0591\ V}{n}\right) \log Q = 0 \tag{10.3.10}$$

$$E^\circ = \left(\frac{0.0591\ V}{n}\right) \log Q \tag{10.3.11}$$

$$\log Q = \frac{E°n}{0.0591\ V} = \frac{(1.10\ V)(2)}{0.0591\ V} = 37.23 \tag{10.3.12}$$

$$Q = 10^{37.23} = 1.7 \times 10^{37} \tag{10.3.13}$$

Recall that at equilibrium, $Q = K$. Thus the equilibrium constant for the reaction of Zn metal with Cu^{2+} to give Cu metal and Zn^{2+} is 1.7×10^{37} at 25°C.



The Nernst Equation: The Nernst Equation (opens in new window) [youtu.be]

Concentration Cells

A voltage can also be generated by constructing an electrochemical cell in which each compartment contains the same redox active solution but at different concentrations. The voltage is produced as the concentrations equilibrate. Suppose, for example, we have a cell with 0.010 M $AgNO_3$ in one compartment and 1.0 M $AgNO_3$ in the other. The cell diagram and corresponding half-reactions are as follows:

$$\mathrm{Ag(s)\,|\,Ag^+}(aq, 0.010\ M)\ ||\ \mathrm{Ag^+}(aq, 1.0\ M)\,|\,\mathrm{Ag\,(s)} \tag{10.3.14}$$

cathode:

$$\mathrm{Ag^+}(aq, 1.0\ M) + \mathrm{e^-} \rightarrow \mathrm{Ag\,(s)} \tag{10.3.15}$$

anode:

$$\mathrm{Ag\,(s)} \rightarrow \mathrm{Ag^+}(aq, 0.010\ M) + \mathrm{e^-} \tag{10.3.16}$$

Overall

$$\mathrm{Ag^+}(aq, 1.0\ M) \rightarrow \mathrm{Ag^+}(aq, 0.010\ M) \tag{10.3.17}$$

As the reaction progresses, the concentration of Ag^+ will increase in the left (oxidation) compartment as the silver electrode dissolves, while the Ag^+ concentration in the right (reduction) compartment decreases as the electrode in that compartment gains mass. The total mass of $Ag(s)$ in the cell will remain constant, however. We can calculate the potential of the cell using the Nernst equation, inserting 0 for $E°_{cell}$ because $E°_{cathode} = -E°_{anode}$:

$$\begin{aligned} E_{\text{cell}} &= E°_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right)\log Q \\ &= 0 - \left(\frac{0.0591\ \text{V}}{1}\right)\log\left(\frac{0.010}{1.0}\right) \\ &= 0.12\ \text{V} \end{aligned}$$

An electrochemical cell of this type, in which the anode and cathode compartments are identical except for the concentration of a reactant, is called a **concentration cell**. As the reaction proceeds, the difference between the concentrations of Ag^+ in the two compartments will decrease, as will E_{cell}. Finally, when the concentration of Ag^+ is the same in both compartments, equilibrium will have been reached, and the measured potential difference between the two compartments will be zero ($E_{cell} = 0$).

Example 10.3.2

Calculate the voltage in a galvanic cell that contains a manganese electrode immersed in a 2.0 M solution of $MnCl_2$ as the cathode, and a manganese electrode immersed in a 5.2×10^{-2} M solution of $MnSO_4$ as the anode (T = 25°C).

Given: galvanic cell, identities of the electrodes, and solution concentrations

Asked for: voltage

Strategy:

A. Write the overall reaction that occurs in the cell.

B. Determine the number of electrons transferred. Substitute this value into the Nernst equation to calculate the voltage.

Solution

A This is a concentration cell, in which the electrode compartments contain the same redox active substance but at different concentrations. The anions (Cl^- and SO_4^{2-}) do not participate in the reaction, so their identity is not important. The overall reaction is as follows:

$$\mathrm{Mn^{2+}}(aq, 2.0\,M) \rightarrow \mathrm{Mn^{2+}}(aq, 5.2 \times 10^{-2}\,M)$$

B For the reduction of Mn^{2+}(aq) to Mn(s), n = 2. We substitute this value and the given Mn^{2+} concentrations into Equation 10.3.6:

$$\begin{aligned} E_{\text{cell}} &= E^\circ_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right) \log Q \\ &= 0\ \text{V} - \left(\frac{0.0591\ \text{V}}{2}\right) \log\left(\frac{5.2 \times 10^{-2}}{2.0}\right) \\ &= 0.047\ \text{V} \end{aligned}$$

Thus manganese will dissolve from the electrode in the compartment that contains the more dilute solution and will be deposited on the electrode in the compartment that contains the more concentrated solution.

? Exercise 10.3.2

Suppose we construct a galvanic cell by placing two identical platinum electrodes in two beakers that are connected by a salt bridge. One beaker contains 1.0 M HCl, and the other a 0.010 M solution of Na_2SO_4 at pH 7.00. Both cells are in contact with the atmosphere, with P_{O_2} = 0.20 atm. If the relevant electrochemical reaction in both compartments is the four-electron reduction of oxygen to water:

$$\mathrm{O_2\,(g) + 4\,H^+\,(aq) + 4\,e^- \rightarrow 2\,H_2O\,(l)}$$

What will be the potential when the circuit is closed?

Answer

0.41 V

Using Cell Potentials to Measure Solubility Products

Because voltages are relatively easy to measure accurately using a voltmeter, electrochemical methods provide a convenient way to determine the concentrations of very dilute solutions and the solubility products (K_{sp}) of sparingly soluble substances. As you learned previously, solubility products can be very small, with values of less than or equal to 10^{-30}. Equilibrium constants of this magnitude are virtually impossible to measure accurately by direct methods, so we must use alternative methods that are more sensitive, such as electrochemical methods.

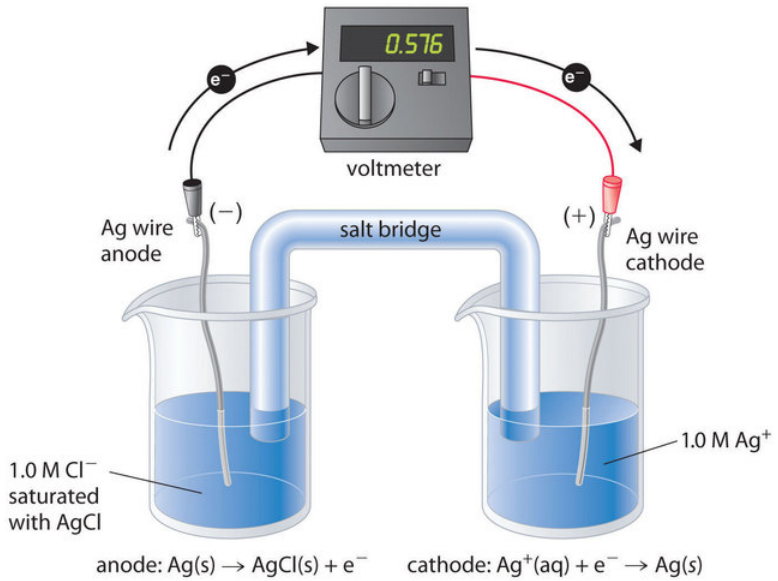


Figure **10.3.1**: A Galvanic ("Concentration") Cell for Measuring the Solubility Product of AgCl. One compartment contains a silver wire inserted into a 1.0 M solution of Ag^+, and the other compartment contains a silver wire inserted into a 1.0 M Cl^- solution saturated with AgCl. The potential due to the difference in $[Ag^+]$ between the two cells can be used to determine K_{sp}. (CC BY-NC-SA; Anonymous by request)

To understand how an electrochemical cell is used to measure a solubility product, consider the cell shown in Figure **10.3.1**, which is designed to measure the solubility product of silver chloride:

$$K_{sp} = [Ag^+][Cl^-].$$

In one compartment, the cell contains a silver wire inserted into a 1.0 M solution of Ag^+; the other compartment contains a silver wire inserted into a 1.0 M Cl^- solution saturated with AgCl. In this system, the Ag^+ ion concentration in the first compartment equals K_{sp}. We can see this by dividing both sides of the equation for K_{sp} by $[Cl^-]$ and substituting:

$$\begin{aligned}[Ag^+] &= \frac{K_{sp}}{[Cl^-]} \\ &= \frac{K_{sp}}{1.0} = K_{sp}.\end{aligned}$$

The overall cell reaction is as follows:

$$Ag^+(aq, \text{concentrated}) \rightarrow Ag^+(aq, \text{dilute})$$

Thus the voltage of the concentration cell due to the difference in $[Ag^+]$ between the two cells is as follows:

$$\begin{aligned}E_{cell} &= 0\ V - \left(\frac{0.0591\ V}{1}\right) \log\left(\frac{[Ag^+]_{dilute}}{[Ag^+]_{concentrated}}\right) \\ &= -0.0591\ V\ \log\left(\frac{K_{sp}}{1.0}\right) \\ &= -0.0591\ V\ \log K_{sp} \qquad (10.3.18)\end{aligned}$$

By closing the circuit, we can measure the potential caused by the difference in [Ag+] in the two cells. In this case, the experimentally measured voltage of the concentration cell at 25°C is 0.580 V. Solving Equation 10.3.18 for K_{sp},

$$\log K_{sp} = \frac{-E_{cell}}{0.0591\ V} = \frac{-0.580\ V}{0.0591\ V} = -9.81$$

$$K_{sp} = 1.5 \times 10^{-10}$$

Thus a single potential measurement can provide the information we need to determine the value of the solubility product of a sparingly soluble salt.

Example 10.3.3: Solubility of lead(II) sulfate

To measure the solubility product of lead(II) sulfate ($PbSO_4$) at 25°C, you construct a galvanic cell like the one shown in Figure **10.3.1**, which contains a 1.0 M solution of a very soluble Pb^{2+} salt [lead(II) acetate trihydrate] in one compartment that is connected by a salt bridge to a 1.0 M solution of Na_2SO_4 saturated with $PbSO_4$ in the other. You then insert a Pb electrode into each compartment and close the circuit. Your voltmeter shows a voltage of 230 mV. What is K_{sp} for $PbSO_4$? Report your answer to two significant figures.

Given: galvanic cell, solution concentrations, electrodes, and voltage

Asked for: K_{sp}

Strategy:

A. From the information given, write the equation for K_{sp}. Express this equation in terms of the concentration of Pb^{2+}.

B. Determine the number of electrons transferred in the electrochemical reaction. Substitute the appropriate values into Equation ??? and solve for K_{sp}.

Solution

A You have constructed a concentration cell, with one compartment containing a 1.0 M solution of $\mathbf{Pb^{2+}}$ and the other containing a dilute solution of Pb^{2+} in 1.0 M Na_2SO_4. As for any concentration cell, the voltage between the two compartments can be calculated using the Nernst equation. The first step is to relate the concentration of Pb^{2+} in the dilute solution to K_{sp}:

$$[Pb^{2+}][SO_4^{2-}] = K_{sp}$$

$$[Pb^{2+}] = \frac{K_{sp}}{[SO_4^{2-}]} = \frac{K_{sp}}{1.0\ M} = K_{sp}$$

B The reduction of Pb^{2+} to Pb is a two-electron process and proceeds according to the following reaction:

$$Pb^{2+}(aq, concentrated) \rightarrow Pb^{2+}(aq, dilute)$$

so

$$E_{cell} = E^\circ_{cell} - \left(\frac{0.0591}{n}\right) \log Q$$

$$0.230\ V = 0\ V - \left(\frac{0.0591\ V}{2}\right) \log \left(\frac{[Pb^{2+}]_{dilute}}{[Pb^{2+}]_{concentrated}}\right) = -0.0296\ V \log \left(\frac{K_{sp}}{1.0}\right)$$

$$-7.77 = \log K_{sp}$$

$$1.7 \times 10^{-8} = K_{sp}$$

Exercise 10.3.3

A concentration cell similar to the one described in Example **10.3.3** contains a 1.0 M solution of lanthanum nitrate [$La(NO_3)_3$] in one compartment and a 1.0 M solution of sodium fluoride saturated with LaF_3 in the other. A metallic La strip is inserted into each compartment, and the circuit is closed. The measured potential is 0.32 V. What is the K_{sp} for LaF_3? Report your answer to two significant figures.

Answer

5.7×10^{-17}

Using Cell Potentials to Measure Concentrations

Another use for the Nernst equation is to calculate the concentration of a species given a measured potential and the concentrations of all the other species. We saw an example of this in Example **10.3.3**, in which the experimental conditions were defined in such a way that the concentration of the metal ion was equal to K_{sp}. Potential measurements can be used to obtain the concentrations of dissolved species under other conditions as well, which explains the widespread use of electrochemical cells in many analytical devices. Perhaps the most common application is in the determination of $[H^+]$ using a pH meter, as illustrated below.

Example 10.3.4: Measuring pH

Suppose a galvanic cell is constructed with a standard Zn/Zn^{2+} couple in one compartment and a modified hydrogen electrode in the second compartment. The pressure of hydrogen gas is 1.0 atm, but $[H^+]$ in the second compartment is unknown. The cell diagram is as follows:

$$\mathrm{Zn\,(s)\,|Zn^{2+}}(aq, 1.0\,M)\,|\,|\mathrm{H^+}(aq, ?\,M)\,|\,\mathrm{H_2}(g, 1.0\,atm)|Pt(s)$$

What is the pH of the solution in the second compartment if the measured potential in the cell is 0.26 V at 25°C?

Given: galvanic cell, cell diagram, and cell potential

Asked for: pH of the solution

Strategy:

A. Write the overall cell reaction.

B. Substitute appropriate values into the Nernst equation and solve for $-\log[H^+]$ to obtain the pH.

Solution

A Under standard conditions, the overall reaction that occurs is the reduction of protons by zinc to give H_2 (note that Zn lies below H_2 in Table P2):

$$Zn(s) + 2H^{2+}(aq) \rightarrow Zn^{2+}(aq) + H_2(g) \quad E°=0.76\ V$$

B By substituting the given values into the simplified Nernst equation (Equation 10.3.6), we can calculate $[H^+]$ under nonstandard conditions:

$$E_{cell} = E^\circ_{cell} - \left(\frac{0.0591\ V}{n}\right)\log\left(\frac{[Zn^{2+}]P_{H_2}}{[H^+]^2}\right)$$

$$0.26\ V = 0.76\ V - \left(\frac{0.0591\ V}{2}\right)\log\left(\frac{(1.0)(1.0)}{[H^+]^2}\right)$$

$$16.9 = \log\left(\frac{1}{[H^+]^2}\right) = \log[H^+]^{-2} = (-2)\log[H^+]$$

$$8.46 = -\log[H^+]$$

$$8.5 = pH$$

Thus the potential of a galvanic cell can be used to measure the pH of a solution.

Exercise 10.3.4

Suppose you work for an environmental laboratory and you want to use an electrochemical method to measure the concentration of Pb^{2+} in groundwater. You construct a galvanic cell using a standard oxygen electrode in one compartment ($E°_{cathode}$ = 1.23 V). The other compartment contains a strip of lead in a sample of groundwater to which you have added sufficient acetic acid, a weak organic acid, to ensure electrical conductivity. The cell diagram is as follows:

$$Pb_{(s)}\ |\ Pb^{2+}(aq, ?M)\ \|\ H^+(aq), 1.0M\ |\ O_2(g, 1.0atm)\ |\ Pt_{(s)}$$

When the circuit is closed, the cell has a measured potential of 1.62 V. Use Table P2 to determine the concentration of Pb^{2+} in the groundwater.

Answer

$1.2 \times 10^{-9}\ M$

Summary

The Nernst equation can be used to determine the direction of spontaneous reaction for any redox reaction in aqueous solution. The Nernst equation allows us to determine the spontaneous direction of any redox reaction under any reaction conditions from values of the relevant standard electrode potentials. Concentration cells consist of anode and cathode compartments that are identical

except for the concentrations of the reactant. Because $\Delta G = 0$ at equilibrium, the measured potential of a concentration cell is zero at equilibrium (the concentrations are equal). A galvanic cell can also be used to measure the solubility product of a sparingly soluble substance and calculate the concentration of a species given a measured potential and the concentrations of all the other species.

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10.4: Batteries and Fuel Cells

Because galvanic cells can be self-contained and portable, they can be used as batteries and fuel cells. A **battery (storage cell)** is a galvanic cell (or a series of galvanic cells) that contains all the reactants needed to produce electricity. In contrast, a **fuel cell** is a galvanic cell that requires a constant external supply of one or more reactants to generate electricity. In this section, we describe the chemistry behind some of the more common types of batteries and fuel cells.

Batteries

There are two basic kinds of batteries: disposable, or primary, batteries, in which the electrode reactions are effectively irreversible and which cannot be recharged; and rechargeable, or secondary, batteries, which form an insoluble product that adheres to the electrodes. These batteries can be recharged by applying an electrical potential in the reverse direction. The recharging process temporarily converts a rechargeable battery from a galvanic cell to an electrolytic cell.

Batteries are cleverly engineered devices that are based on the same fundamental laws as galvanic cells. The major difference between batteries and the galvanic cells we have previously described is that commercial batteries use solids or pastes rather than solutions as reactants to maximize the electrical output per unit mass. The use of highly concentrated or solid reactants has another beneficial effect: the concentrations of the reactants and the products do not change greatly as the battery is discharged; consequently, the output voltage remains remarkably constant during the discharge process. This behavior is in contrast to that of the Zn/Cu cell, whose output decreases logarithmically as the reaction proceeds (Figure **10.4.1**). When a battery consists of more than one galvanic cell, the cells are usually connected in series—that is, with the positive (+) terminal of one cell connected to the negative (−) terminal of the next, and so forth. The overall voltage of the battery is therefore the sum of the voltages of the individual cells.

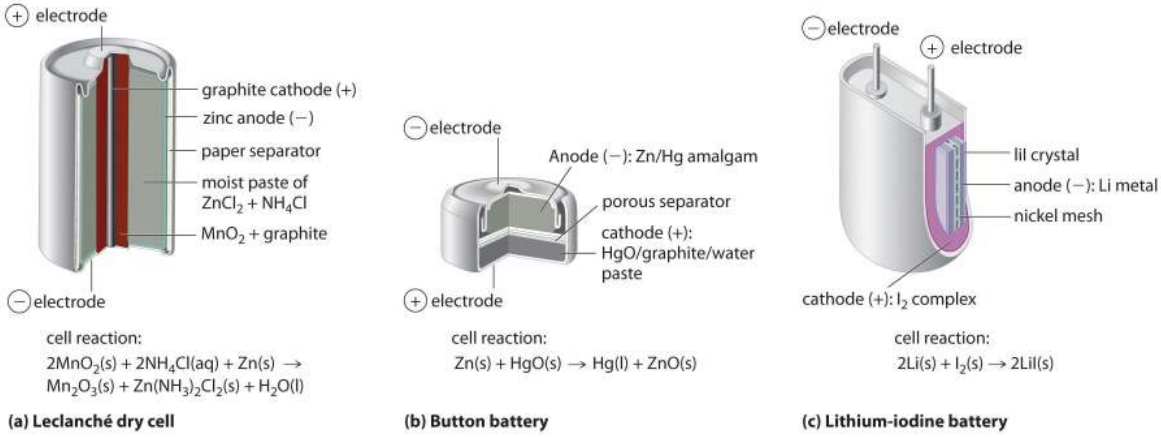


Figure **10.4.1**: Three Kinds of Primary (Nonrechargeable) Batteries. (a) A Leclanché dry cell is actually a "wet cell," in which the electrolyte is an acidic water-based paste containing MnO_2, NH_4Cl, $ZnCl_2$, graphite, and starch. Though inexpensive to manufacture, the cell is not very efficient in producing electrical energy and has a limited shelf life. (b) In a button battery, the anode is a zinc–mercury amalgam, and the cathode can be either HgO (shown here) or Ag_2O as the oxidant. Button batteries are reliable and have a high output-to-mass ratio, which allows them to be used in applications such as calculators and watches, where their small size is crucial. (c) A lithium–iodine battery consists of two cells separated by a metallic nickel mesh that collects charge from the anodes. The anode is lithium metal, and the cathode is a solid complex of I_2. The electrolyte is a layer of solid LiI that allows Li^+ ions to diffuse from the cathode to the anode. Although this type of battery produces only a relatively small current, it is highly reliable and long-lived.

> The major difference between batteries and the galvanic cells is that commercial typically batteries use solids or pastes rather than solutions as reactants to maximize the electrical output per unit mass. An obvious exception is the standard car battery which used solution phase chemistry.

Leclanché Dry Cell

The dry cell, by far the most common type of battery, is used in flashlights, electronic devices such as the Walkman and Game Boy, and many other devices. Although the dry cell was patented in 1866 by the French chemist Georges Leclanché and more than 5 billion such cells are sold every year, the details of its electrode chemistry are still not completely understood. In spite of its name, the **Leclanché dry cell** is actually a "wet cell": the electrolyte is an acidic water-based paste containing MnO_2, NH_4Cl, $ZnCl_2$, graphite, and starch (part (a) in Figure **10.4.1**). The half-reactions at the anode and the cathode can be summarized as follows:

- cathode (reduction):

$$2\,MnO_2(s) + 2\,NH_4^+(aq) + 2\,e^- \longrightarrow Mn_2O_3(s) + 2\,NH_3(aq) + H_2O(l)$$

- anode (oxidation):

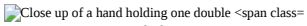
$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$$

The Zn^{2+} ions formed by the oxidation of $Zn(s)$ at the anode react with NH_3 formed at the cathode and Cl^- ions present in solution, so the overall cell reaction is as follows:

- overall reaction:

$$2MnO_2(s) + 2NH_4Cl(aq) + Zn(s) \longrightarrow Mn_2O_3(s) + Zn(NH_3)_2Cl_2(s) + H_2O(l) \quad (10.4.1)$$

The dry cell produces about 1.55 V and is inexpensive to manufacture. It is not, however, very efficient in producing electrical energy because only the relatively small fraction of the MnO_2 that is near the cathode is actually reduced and only a small fraction of the zinc cathode is actually consumed as the cell discharges. In addition, dry cells have a limited shelf life because the Zn anode reacts spontaneously with NH_4Cl in the electrolyte, causing the case to corrode and allowing the contents to leak out.



AA

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Source: Photo courtesy of Mitchclanky2008, www.flickr.com/photos/25597837@N05/2422765479/.

The **alkaline battery** is essentially a Leclanché cell adapted to operate under alkaline, or basic, conditions. The half-reactions that occur in an alkaline battery are as follows:

- cathode (reduction)

$$2MnO_2(s) + H_2O(l) + 2e^- \longrightarrow Mn_2O_3(s) + 2OH^-(aq)$$

- anode (oxidation):

$$Zn(s) + 2OH^-(aq) \longrightarrow ZnO(s) + H_2O(l) + 2e^-$$

- overall reaction:

$$Zn(s) + 2MnO_2(s) \longrightarrow ZnO(s) + Mn_2O_3(s)$$

This battery also produces about 1.5 V, but it has a longer shelf life and more constant output voltage as the cell is discharged than the Leclanché dry cell. Although the alkaline battery is more expensive to produce than the Leclanché dry cell, the improved performance makes this battery more cost-effective.

Button Batteries

Although some of the small button batteries used to power watches, calculators, and cameras are miniature alkaline cells, most are based on a completely different chemistry. In these "button" batteries, the anode is a zinc–mercury amalgam rather than pure zinc, and the cathode uses either HgO or Ag_2O as the oxidant rather than MnO_2 in Figure 10.4.1*b*).



Button batteries. (Gerhard H Wrodnigg via Wikipedia)

The cathode, anode and overall reactions and cell output for these two types of button batteries are as follows (two half-reactions occur at the anode, but the overall oxidation half-reaction is shown):

- cathode (mercury battery):

$$HgO(s) + H_2O(l) + 2e^- \longrightarrow Hg(l) + 2OH^-(aq)$$

- Anode (mercury battery):

$$Zn + 2OH^- \longrightarrow ZnO + H_2O + 2e^-$$

- overall reaction (mercury battery):

$$Zn(s) + 2HgO(s) \longrightarrow 2Hg(l) + ZnO(s)$$

with $E_{cell} = 1.35\,V$.

- cathode reaction (silver battery):

$$Ag_2O(s) + H_2O(l) + 2e^- \longrightarrow 2Ag(s) + 2OH^-(aq)$$

- anode (silver battery):

$$Zn + 2OH^- \longrightarrow ZnO + H_2O + 2e^-$$

- Overall reaction (silver battery):

$$Zn(s) + 2Ag_2O(s) \longrightarrow 2Ag(s) + ZnO(s)$$

with $E_{cell} = 1.6\,V$.

The major advantages of the mercury and silver cells are their reliability and their high output-to-mass ratio. These factors make them ideal for applications where small size is crucial, as in cameras and hearing aids. The disadvantages are the expense and the environmental problems caused by the disposal of heavy metals, such as **Hg** and **Ag**.

Lithium–Iodine Battery

None of the batteries described above is actually "dry." They all contain small amounts of liquid water, which adds significant mass and causes potential corrosion problems. Consequently, substantial effort has been expended to develop water-free batteries. One of the few commercially successful water-free batteries is the **lithium–iodine battery**. The anode is lithium metal, and the cathode is a solid complex of I_2. Separating them is a layer of solid LiI, which acts as the electrolyte by allowing the diffusion of Li^+ ions. The electrode reactions are as follows:

- cathode (reduction):

$$I_{2(s)} + 2e^- \rightarrow 2I^-_{(LiI)} \tag{10.4.2}$$

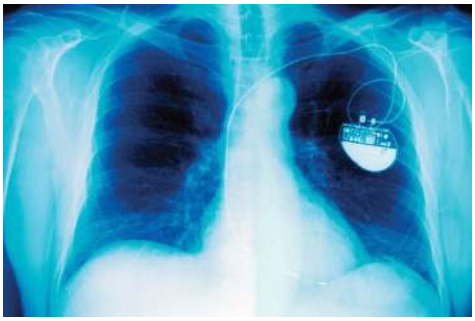
- anode (oxidation):

$$2Li_{(s)} \rightarrow 2Li^+_{(LiI)} + 2e^- \tag{10.4.3}$$

- overall:

$$2Li_{(s)} + I_{2(s)} \rightarrow 2LiI_{(s)} \tag{10.4.4}$$

with $E_{cell} = 3.5\,V$



Cardiac pacemaker: An x-ray of a patient showing the location and size of a pacemaker powered by a lithium–iodine battery.

As shown in part (c) in Figure **10.4.1**, a typical lithium–iodine battery consists of two cells separated by a nickel metal mesh that collects charge from the anode. Because of the high internal resistance caused by the solid electrolyte, only a low current can be drawn. Nonetheless, such batteries have proven to be long-lived (up to 10 yr) and reliable. They are therefore used in applications where frequent replacement is difficult or undesirable, such as in cardiac pacemakers and other medical implants and in computers for memory protection. These batteries are also used in security transmitters and smoke alarms. Other batteries based on lithium anodes and solid electrolytes are under development, using TiS_2, for example, for the cathode.

Dry cells, button batteries, and lithium–iodine batteries are disposable and cannot be recharged once they are discharged. Rechargeable batteries, in contrast, offer significant economic and environmental advantages because they can be recharged and discharged numerous times. As a result, manufacturing and disposal costs drop dramatically for a given number of hours of battery usage. Two common rechargeable batteries are the nickel–cadmium battery and the lead–acid battery, which we describe next.

Nickel–Cadmium (NiCad) Battery

The **nickel–cadmium**, or NiCad, battery is used in small electrical appliances and devices like drills, portable vacuum cleaners, and AM/FM digital tuners. It is a water-based cell with a cadmium anode and a highly oxidized nickel cathode that is usually described as the nickel(III) oxo-hydroxide, NiO(OH). As shown in Figure **10.4.2**, the design maximizes the surface area of the electrodes and minimizes the distance between them, which decreases internal resistance and makes a rather high discharge current possible.

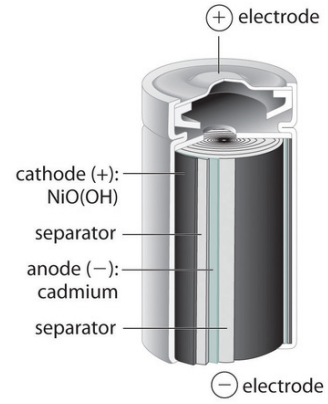


Figure 10.4.2: The Nickel–Cadmium (NiCad) Battery, a Rechargeable Battery. NiCad batteries contain a cadmium anode and a highly oxidized nickel cathode. This design maximizes the surface area of the electrodes and minimizes the distance between them, which gives the battery both a high discharge current and a high capacity.

The electrode reactions during the discharge of a ***NiCad*** battery are as follows:

- cathode (reduction):

$$2NiO(OH)_{(s)} + 2H_2O_{(l)} + 2e^- \rightarrow 2Ni(OH)_{2(s)} + 2OH^-_{(aq)} \tag{10.4.5}$$

- anode (oxidation):

$$Cd_{(s)} + 2OH^-_{(aq)} \rightarrow Cd(OH)_{2(s)} + 2e^- \tag{10.4.6}$$

- overall:

$$Cd_{(s)} + 2NiO(OH)_{(s)} + 2H_2O_{(l)} \rightarrow Cd(OH)_{2(s)} + 2Ni(OH)_{2(s)} \tag{10.4.7}$$

$$E_{cell} = 1.4V$$

Because the products of the discharge half-reactions are solids that adhere to the electrodes [$Cd(OH)_2$ and $2Ni(OH)_2$], the overall reaction is readily reversed when the cell is recharged. Although NiCad cells are lightweight, rechargeable, and high capacity, they have certain disadvantages. For example, they tend to lose capacity quickly if not allowed to discharge fully before recharging, they do not store well for long periods when fully charged, and they present significant environmental and disposal problems because of the toxicity of cadmium.

A variation on the NiCad battery is the nickel–metal hydride battery (NiMH) used in hybrid automobiles, wireless communication devices, and mobile computing. The overall chemical equation for this type of battery is as follows:

\[NiO(OH)_{(s)} + MH \rightarrow Ni(OH)_{2(s)} + M_{(s)} \label{Eq16} \]

The NiMH battery has a 30%–40% improvement in capacity over the NiCad battery; it is more environmentally friendly so storage, transportation, and disposal are not subject to environmental control; and it is not as sensitive to recharging memory. It is, however, subject to a 50% greater self-discharge rate, a limited service life, and higher maintenance, and it is more expensive than the NiCad battery.

> Directive 2006/66/EC of the European Union prohibits the placing on the market of portable batteries that contain more than 0.002% of cadmium by weight. The aim of this directive was to improve "the environmental performance of batteries and accumulators"

Lead–Acid (Lead Storage) Battery

The **lead–acid battery** is used to provide the starting power in virtually every automobile and marine engine on the market. Marine and car batteries typically consist of multiple cells connected in series. The total voltage generated by the battery is the potential per cell ($E°_{cell}$) times the number of cells.

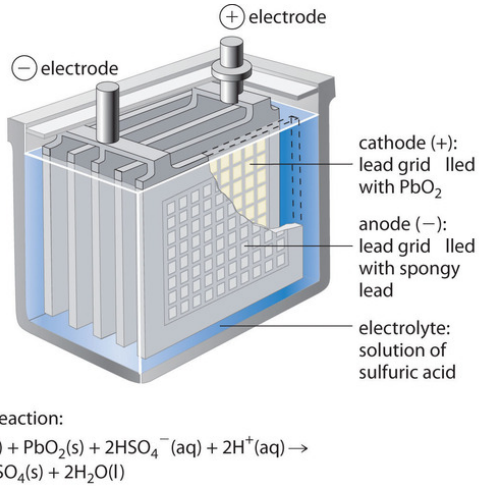


Figure **10.4.3**: One Cell of a Lead–Acid Battery. The anodes in each cell of a rechargeable battery are plates or grids of lead containing spongy lead metal, while the cathodes are similar grids containing powdered lead dioxide (PbO_2). The electrolyte is an aqueous solution of sulfuric acid. The value of E° for such a cell is about 2 V. Connecting three such cells in series produces a 6 V battery, whereas a typical 12 V car battery contains six cells in series. When treated properly, this type of high-capacity battery can be discharged and recharged many times over.

As shown in Figure **10.4.3**, the anode of each cell in a lead storage battery is a plate or grid of spongy lead metal, and the cathode is a similar grid containing powdered lead dioxide (***PbO_2***). The electrolyte is usually an approximately 37% solution (by mass) of sulfuric acid in water, with a density of 1.28 g/mL (about 4.5 M ***H_2SO_4***). Because the redox active species are solids, there is no need to separate the electrodes. The electrode reactions in each cell during discharge are as follows:

- cathode (reduction):

\[PbO_{2(s)} + HSO^-_{4(aq)} + 3H^+_{(aq)} + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O_{(l)} \label{Eq17} \]

with $E^\circ_{cathode} = 1.685\ V$

- anode (oxidation):

$$Pb_{(s)} + HSO^-_{4(aq)} \rightarrow PbSO_{4(s)} + H^+_{(aq)} + 2e^- \tag{10.4.8}$$

with $E^\circ_{anode} = -0.356\ V$

- overall:

$$Pb_{(s)} + PbO_{2(s)} + 2HSO^-_{4(aq)} + 2H^+_{(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(l)} \tag{10.4.9}$$

and $E^\circ_{cell} = 2.041\ V$

As the cell is discharged, a powder of ***$PbSO_4$*** forms on the electrodes. Moreover, sulfuric acid is consumed and water is produced, decreasing the density of the electrolyte and providing a convenient way of monitoring the status of a battery by simply measuring the density of the electrolyte. This is often done with the use of a hydrometer.



A hydrometer can be used to test the specific gravity of each cell as a measure of its state of charge (www.youtube.com/watch?v=SRcOqfL6GqQ).

When an external voltage in excess of 2.04 V per cell is applied to a lead–acid battery, the electrode reactions reverse, and $PbSO_4$ is converted back to metallic lead and PbO_2. If the battery is recharged too vigorously, however, electrolysis of water can occur:

$$2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2(g)} \tag{10.4.10}$$

This results in the evolution of potentially explosive hydrogen gas. The gas bubbles formed in this way can dislodge some of the $PbSO_4$ or PbO_2 particles from the grids, allowing them to fall to the bottom of the cell, where they can build up and cause an internal short circuit. Thus the recharging process must be carefully monitored to optimize the life of the battery. With proper care, however, a lead–acid battery can be discharged and recharged thousands of times. In automobiles, the alternator supplies the electric current that causes the discharge reaction to reverse.

Fuel Cells

A fuel cell is a galvanic cell that requires a constant external supply of reactants because the products of the reaction are continuously removed. Unlike a battery, it does not store chemical or electrical energy; a fuel cell allows electrical energy to be extracted directly from a chemical reaction. In principle, this should be a more efficient process than, for example, burning the fuel to drive an internal combustion engine that turns a generator, which is typically less than 40% efficient, and in fact, the efficiency of a fuel cell is generally between 40% and 60%. Unfortunately, significant cost and reliability problems have hindered the wide-scale adoption of fuel cells. In practice, their use has been restricted to applications in which mass may be a significant cost factor, such as US manned space vehicles.

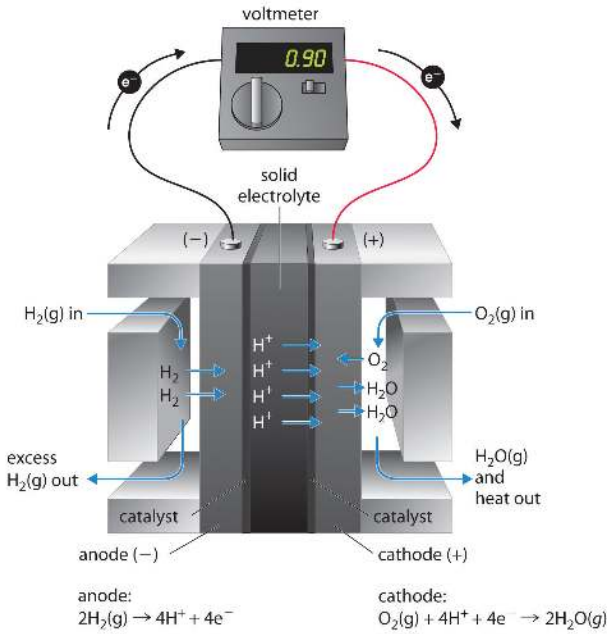


Figure **10.4.4**: A Hydrogen Fuel Cell Produces Electrical Energy Directly from a Chemical Reaction. Hydrogen is oxidized to protons at the anode, and the electrons are transferred through an external circuit to the cathode, where oxygen is reduced and combines with H^+ to form water. A solid electrolyte allows the protons to diffuse from the anode to the cathode. Although fuel cells are an essentially pollution-free means of obtaining electrical energy, their expense and technological complexity have thus far limited their applications.

These space vehicles use a hydrogen/oxygen fuel cell that requires a continuous input of $H_2(g)$ and $O_2(g)$, as illustrated in Figure **10.4.4**. The electrode reactions are as follows:

- cathode (reduction):

$$O_{2(g)} + 4H^+ + 4e^- \rightarrow 2H_2O_{(g)} \tag{10.4.11}$$

- anode (oxidation):

$$2H_{2(g)} \rightarrow 4H^+ + 4e^- \tag{10.4.12}$$

- overall:

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)} \tag{10.4.13}$$

The overall reaction represents an essentially pollution-free conversion of hydrogen and oxygen to water, which in space vehicles is then collected and used. Although this type of fuel cell should produce 1.23 V under standard conditions, in practice the device achieves only about 0.9 V. One of the major barriers to achieving greater efficiency is the fact that the four-electron reduction of $O_2(g)$ at the cathode is intrinsically rather slow, which limits current that can be achieved. All major automobile manufacturers have major research programs involving fuel cells: one of the most important goals is the development of a better catalyst for the reduction of $O_2(g)$.

Summary

Commercial batteries are galvanic cells that use solids or pastes as reactants to maximize the electrical output per unit mass. A battery is a contained unit that produces electricity, whereas a fuel cell is a galvanic cell that requires a constant external supply of one or more reactants to generate electricity. One type of battery is the Leclanché dry cell, which contains an electrolyte in an acidic water-based paste. This battery is called an alkaline battery when adapted to operate under alkaline conditions. Button batteries have a high output-to-mass ratio; lithium–iodine batteries consist of a solid electrolyte; the nickel–cadmium (NiCad) battery is rechargeable; and the lead–acid battery, which is also rechargeable, does not require the electrodes to be in separate compartments. A fuel cell requires an external supply of reactants as the products of the reaction are continuously removed. In a fuel cell, energy is not stored; electrical energy is provided by a chemical reaction.

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10.5: Corrosion and Its Prevention

Learning Objectives

- To understand the process of corrosion.

Corrosion is a galvanic process by which metals deteriorate through oxidation—usually but not always to their oxides. For example, when exposed to air, iron rusts, silver tarnishes, and copper and brass acquire a bluish-green surface called a patina. Of the various metals subject to corrosion, iron is by far the most important commercially. An estimated $100 billion per year is spent in the United States alone to replace iron-containing objects destroyed by corrosion. Consequently, the development of methods for protecting metal surfaces from corrosion constitutes a very active area of industrial research. In this section, we describe some of the chemical and electrochemical processes responsible for corrosion. We also examine the chemical basis for some common methods for preventing corrosion and treating corroded metals.

> *Corrosion is a REDOX process.*

Under ambient conditions, the oxidation of most metals is thermodynamically spontaneous, with the notable exception of gold and platinum. Hence it is actually somewhat surprising that any metals are useful at all in Earth's moist, oxygen-rich atmosphere. Some metals, however, are resistant to corrosion for kinetic reasons. For example, aluminum in soft-drink cans and airplanes is protected by a thin coating of metal oxide that forms on the surface of the metal and acts as an impenetrable barrier that prevents further destruction. Aluminum cans also have a thin plastic layer to prevent reaction of the oxide with acid in the soft drink. Chromium, magnesium, and nickel also form protective oxide films. Stainless steels are remarkably resistant to corrosion because they usually contain a significant proportion of chromium, nickel, or both.

In contrast to these metals, when iron corrodes, it forms a red-brown hydrated metal oxide ($\mathbf{Fe_2O_3 \cdot \mathit{x}\, H_2O}$), commonly known as rust, that does not provide a tight protective film (Figure **10.5.1**). Instead, the rust continually flakes off to expose a fresh metal surface vulnerable to reaction with oxygen and water. Because both oxygen and water are required for rust to form, an iron nail immersed in deoxygenated water will not rust—even over a period of several weeks. Similarly, a nail immersed in an organic solvent such as kerosene or mineral oil will not rust because of the absence of water even if the solvent is saturated with oxygen.

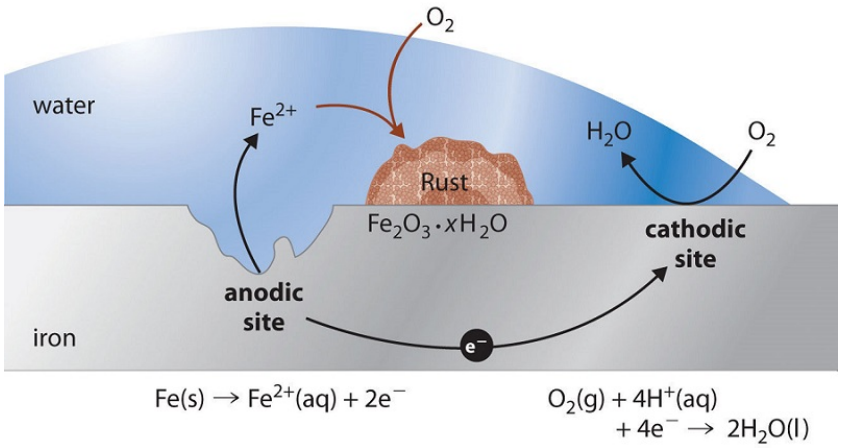


Figure **10.5.1**: Rust, the Result of Corrosion of Metallic Iron. Iron is oxidized to Fe^{2+}(aq) at an anodic site on the surface of the iron, which is often an impurity or a lattice defect. Oxygen is reduced to water at a different site on the surface of the iron, which acts as the cathode. Electrons are transferred from the anode to the cathode through the electrically conductive metal. Water is a solvent for the Fe^{2+} that is produced initially and acts as a salt bridge. Rust (Fe_2O_3•xH_2O) is formed by the subsequent oxidation of Fe^{2+} by atmospheric oxygen. (CC BY-NC-SA; anonymous)

In the corrosion process, iron metal acts as the anode in a galvanic cell and is oxidized to Fe^{2+}; oxygen is reduced to water at the cathode. The relevant reactions are as follows:

- at cathode:

$$\mathbf{O_2\,(g) + 4\,H^+\,(aq) + 4\,e^- \longrightarrow 2\,H_2O\,(l)}$$

with $E^o_{SRP} = 1.23\ V$.

- at anode:

$$\mathrm{Fe\,(s) \longrightarrow Fe^{2+}\,(aq) + 2\,e^-}$$

with $E^o_{SRP} = -0.45\ V$.

- overall:

$$\mathrm{2\,Fe\,(s) + O_2\,(g) + 4\,H^+\,(aq) \longrightarrow 2\,Fe^{2+}\,(aq) + 2\,H_2O\,(l)} \tag{10.5.1}$$

with $E^o_{cell} = 1.68\ V$.

The $\mathrm{Fe^{2+}}$ ions produced in the initial reaction are then oxidized by atmospheric oxygen to produce the insoluble hydrated oxide containing $\mathrm{Fe^{3+}}$, as represented in the following equation:

$$\mathrm{4\,Fe^{2+}\,(aq) + O_2\,(g) + (2 + 4\,x)H_2O \ \rightarrow 2\,Fe_2O_3 \ \cdot x\,H_2O + 4\,H^+\,(aq)} \tag{10.5.2}$$

The sign and magnitude of E^o_{cell} for the corrosion process (Equation 10.5.1) indicate that there is a strong driving force for the oxidation of iron by O_2 under standard conditions (1 M H^+). Under neutral conditions, the driving force is somewhat less but still appreciable (E = 1.25 V at pH 7.0). Normally, the reaction of atmospheric CO_2 with water to form H^+ and HCO_3^- provides a low enough pH to enhance the reaction rate, as does acid rain. Automobile manufacturers spend a great deal of time and money developing paints that adhere tightly to the car's metal surface to prevent oxygenated water, acid, and salt from coming into contact with the underlying metal. Unfortunately, even the best paint is subject to scratching or denting, and the electrochemical nature of the corrosion process means that two scratches relatively remote from each other can operate together as anode and cathode, leading to sudden mechanical failure (Figure **10.5.2**).

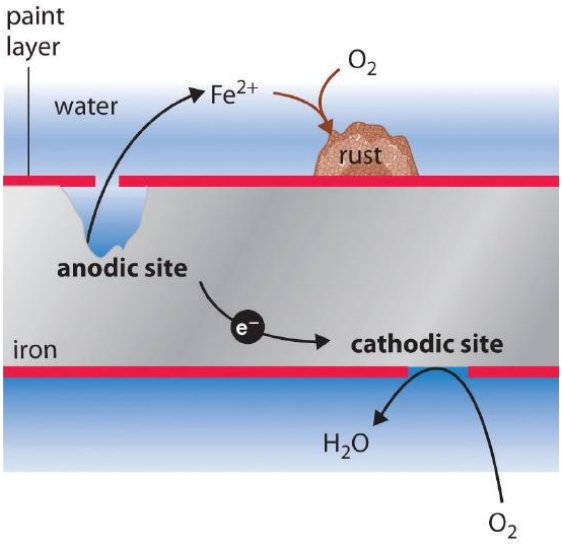


Figure **10.5.2**: Small Scratches in a Protective Paint Coating Can Lead to the Rapid Corrosion of Iron. Holes in a protective coating allow oxygen to be reduced at the surface with the greater exposure to air (the cathode), while metallic iron is oxidized to Fe^{2+}(aq) at the less exposed site (the anode). Rust is formed when Fe^{2+}(aq) diffuses to a location where it can react with atmospheric oxygen, which is often remote from the anode. The electrochemical interaction between cathodic and anodic sites can cause a large pit to form under a painted surface, eventually resulting in sudden failure with little visible warning that corrosion has occurred.

Prophylactic Protection

One of the most common techniques used to prevent the corrosion of iron is applying a protective coating of another metal that is more difficult to oxidize. Faucets and some external parts of automobiles, for example, are often coated with a thin layer of chromium using an electrolytic process. With the increased use of polymeric materials in cars, however, the use of chrome-plated steel has diminished in recent years. Similarly, the "tin cans" that hold soups and other foods are actually consist of steel container that is coated with a thin layer of tin. While neither chromium nor tin metals are intrinsically resistant to corrosion, they both form protective oxide coatings that hinder access of oxygen and water to the underlying steel (iron alloy).

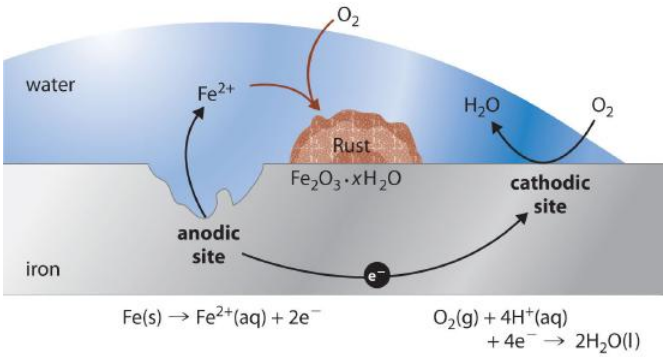


Figure 10.5.3: Galvanic Corrosion. If iron is in contact with a more corrosion-resistant metal such as tin, copper, or lead, the other metal can act as a large cathode that greatly increases the rate of reduction of oxygen. Because the reduction of oxygen is coupled to the oxidation of iron, this can result in a dramatic increase in the rate at which iron is oxidized at the anode. Galvanic corrosion is likely to occur whenever two dissimilar metals are connected directly, allowing electrons to be transferred from one to the other.

As with a protective paint, scratching a protective metal coating will allow corrosion to occur. In this case, however, the presence of the second metal can actually increase the rate of corrosion. The values of the standard electrode potentials for $\mathbf{Sn^{2+}}$ ($E° = -0.14$ V) and Fe^{2+} ($E° = -0.45$ V) in Table P2 show that **Fe** is more easily oxidized than **Sn**. As a result, the more corrosion-resistant metal (in this case, tin) accelerates the corrosion of iron by acting as the cathode and providing a large surface area for the reduction of oxygen (Figure 10.5.3). This process is seen in some older homes where copper and iron pipes have been directly connected to each other. The less easily oxidized copper acts as the cathode, causing iron to dissolve rapidly near the connection and occasionally resulting in a catastrophic plumbing failure.

Cathodic Protection

One way to avoid these problems is to use a more easily oxidized metal to protect iron from corrosion. In this approach, called cathodic protection, a more reactive metal such as **Zn** ($E° = -0.76$ V for $\mathbf{Zn^{2+} + 2\,e^- \longrightarrow Zn}$) becomes the anode, and iron becomes the cathode. This prevents oxidation of the iron and protects the iron object from corrosion. The reactions that occur under these conditions are as follows:

$$\underbrace{O_{2(g)} + 4e^- + 4H^+_{(aq)} \rightarrow 2H_2O_{(l)}}_{\text{reduction at cathode}} \tag{10.5.3}$$

$$\underbrace{Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-}_{\text{oxidation at anode}} \tag{10.5.4}$$

$$\underbrace{2Zn_{(s)} + O_{2(g)} + 4H^+_{(aq)} \rightarrow 2Zn^{2+}_{(aq)} + 2H_2O_{(l)}}_{\text{overall}} \tag{10.5.5}$$

The more reactive metal reacts with oxygen and will eventually dissolve, “sacrificing” itself to protect the iron object. Cathodic protection is the principle underlying galvanized steel, which is steel protected by a thin layer of zinc. Galvanized steel is used in objects ranging from nails to garbage cans.



Crystalline surface of a hot-dip galvanized steel surface. This served both as prophylactic protection (protecting the underlying steel from the oxygen in the air) and cathodic protection (once exposed, the zinc will oxidize before the underlying steel).

In a similar strategy, **sacrificial electrodes** using magnesium, for example, are used to protect underground tanks or pipes (Figure 10.5.4). Replacing the sacrificial electrodes is more cost-effective than replacing the iron objects they are protecting.

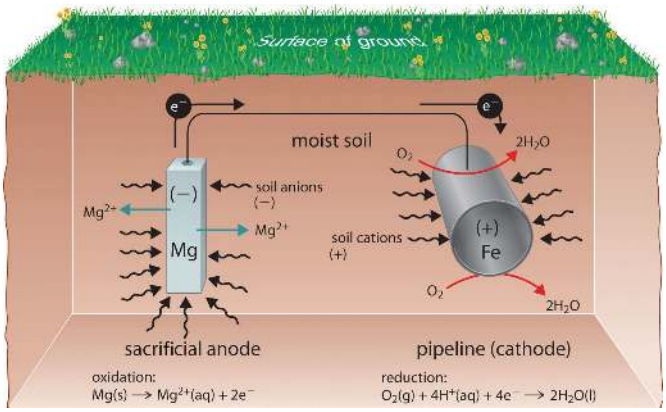


Figure **10.5.4**: The Use of a Sacrificial Electrode to Protect Against Corrosion. Connecting a magnesium rod to an underground steel pipeline protects the pipeline from corrosion. Because magnesium (E° = −2.37 V) is much more easily oxidized than iron (E° = −0.45 V), the Mg rod acts as the anode in a galvanic cell. The pipeline is therefore forced to act as the cathode at which oxygen is reduced. The soil between the anode and the cathode acts as a salt bridge that completes the electrical circuit and maintains electrical neutrality. As Mg(s) is oxidized to Mg^{2+} at the anode, anions in the soil, such as nitrate, diffuse toward the anode to neutralize the positive charge. Simultaneously, cations in the soil, such as H^+ or NH_4^+, diffuse toward the cathode, where they replenish the protons that are consumed as oxygen is reduced. A similar strategy uses many miles of somewhat less reactive zinc wire to protect the Alaska oil pipeline.

Example 10.5.1

Suppose an old wooden sailboat, held together with iron screws, has a bronze propeller (recall that bronze is an alloy of copper containing about 7%–10% tin).

a. If the boat is immersed in seawater, what corrosion reaction will occur? What is $E°°_{cell}$?
b. How could you prevent this corrosion from occurring?

Given: identity of metals

Asked for: corrosion reaction, $E°°_{cell}$, and preventive measures

Strategy:

A. Write the reactions that occur at the anode and the cathode. From these, write the overall cell reaction and calculate $E°°_{cell}$.
B. Based on the relative redox activity of various substances, suggest possible preventive measures.

Solution

a. **A** According to Table P2, both copper and tin are less active metals than iron (i.e., they have higher positive values of $E°°_{cell}$ than iron). Thus if tin or copper is brought into electrical contact by seawater with iron in the presence of oxygen, corrosion will occur. We therefore anticipate that the bronze propeller will act as the cathode at which O_2 is reduced, and the iron screws will act as anodes at which iron dissolves:

cathode:	$O_2(s) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$	$E°_{cathode} = 1.23$ V
anode:	$Fe(s) \rightarrow Fe^{2+} + 2e^-$	$E°_{anode} = -0.45$ V
overall:	$2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l)$	$E°_{overall} = 1.68$ V

Over time, the iron screws will dissolve, and the boat will fall apart.

b. **B** Possible ways to prevent corrosion, in order of decreasing cost and inconvenience, are as follows: disassembling the boat and rebuilding it with bronze screws; removing the boat from the water and storing it in a dry place; or attaching an inexpensive piece of zinc metal to the propeller shaft to act as a sacrificial electrode and replacing it once or twice a year. Because zinc is a more active metal than iron, it will act as the sacrificial anode in the electrochemical cell and dissolve (Equation 10.5.5).



Zinc sacrificial anode (rounded object screwed to underside of hull) used to prevent corrosion on the screw in a boat via cathodic protection. Image by Rémi Kaupp and used with permission.

? Exercise 10.5.1

Suppose the water pipes leading into your house are made of lead, while the rest of the plumbing in your house is iron. To eliminate the possibility of lead poisoning, you call a plumber to replace the lead pipes. He quotes you a very low price if he can use up his existing supply of copper pipe to do the job.

a. Do you accept his proposal?
b. What else should you have the plumber do while at your home?

Answer a

Not unless you plan to sell the house very soon because the **Cu/Fe** pipe joints will lead to rapid corrosion.

Answer b

Any existing **Pb/Fe** joints should be examined carefully for corrosion of the iron pipes due to the **Pb—Fe** junction; the less active **Pb** will have served as the cathode for the reduction of O_2, promoting oxidation of the more active **Fe** nearby.

Summary

Corrosion is a galvanic process that can be prevented using cathodic protection. The deterioration of metals through oxidation is a galvanic process called corrosion. Protective coatings consist of a second metal that is more difficult to oxidize than the metal being protected. Alternatively, a more easily oxidized metal can be applied to a metal surface, thus providing cathodic protection of the surface. A thin layer of zinc protects galvanized steel. Sacrificial electrodes can also be attached to an object to protect it.

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10.6: Electrolysis - A Deeper Look

Learning Objectives

- To understand electrolysis and describe it quantitatively.

In this chapter, we have described various galvanic cells in which a spontaneous chemical reaction is used to generate electrical energy. In an electrolytic cell, however, the opposite process, called **electrolysis**, occurs: an external voltage is applied to drive a nonspontaneous reaction. In this section, we look at how electrolytic cells are constructed and explore some of their many commercial applications.

Electrolytic Cells

If we construct an electrochemical cell in which one electrode is copper metal immersed in a 1 M Cu^{2+} solution and the other electrode is cadmium metal immersed in a $1\ M\ Cd^{2+}$ solution and then close the circuit, the potential difference between the two compartments will be 0.74 V. The cadmium electrode will begin to dissolve (Cd is oxidized to Cd^{2+}) and is the anode, while metallic copper will be deposited on the copper electrode (Cu^{2+} is reduced to Cu), which is the cathode (Figure **10.6.1***a*).

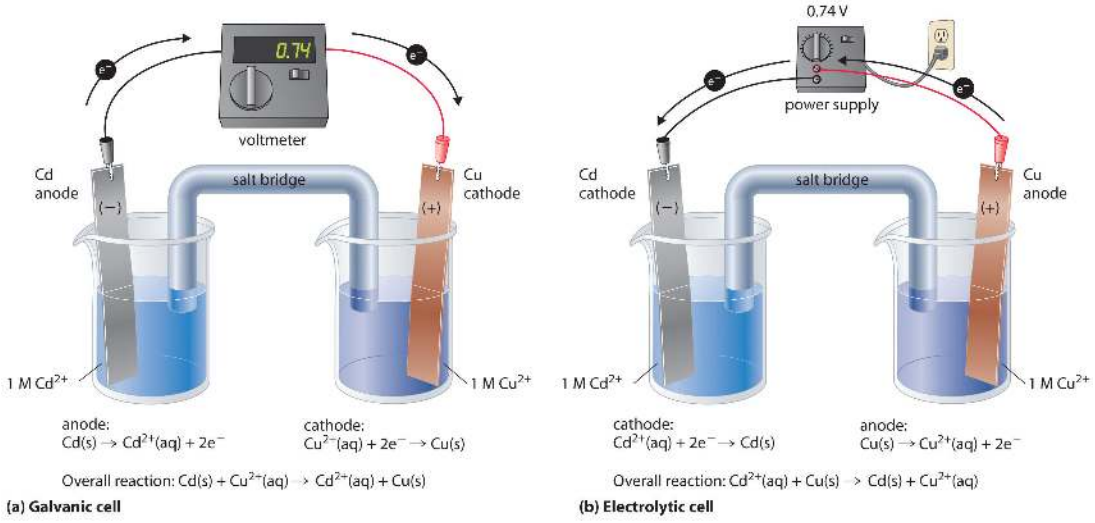


Figure **10.6.1**: An Applied Voltage Can Reverse the Flow of Electrons in a Galvanic Cd/Cu Cell. (a) When compartments that contain a Cd electrode immersed in 1 M Cd^{2+}(aq) and a Cu electrode immersed in 1 M Cu^{2+}(aq) are connected to create a galvanic cell, Cd(s) is spontaneously oxidized to Cd^{2+}(aq) at the anode, and Cu^{2+}(aq) is spontaneously reduced to Cu(s) at the cathode. The potential of the galvanic cell is 0.74 V. (b) Applying an external potential greater than 0.74 V in the reverse direction forces electrons to flow from the Cu electrode [which is now the anode, at which metallic Cu(s) is oxidized to Cu^{2+}(aq)] and into the Cd electrode [which is now the cathode, at which Cd^{2+}(aq) is reduced to Cd(s)]. The anode in an electrolytic cell is positive because electrons are flowing from it, whereas the cathode is negative because electrons are flowing into it. (CC BY-SA-NC; anonymous)

The overall reaction is as follows:

$$\mathrm{Cd\,(s) + Cu^{2+}\,(aq) \rightarrow Cd^{2+}\,(aq) + Cu\,(s)}$$

with $E°_{cell} = 0.74\ V$

This reaction is thermodynamically spontaneous as written ($\Delta G° < 0$):

$$\begin{aligned}\Delta G° &= -nFE°_{\text{cell}} \\ &= -(2\ \text{mol e}^-)[96,485\ \text{J/(V}\cdot\text{mol)}](0.74\ \text{V}) \\ &= -140\ \text{kJ (per mole Cd)}\end{aligned}$$

In this direction, the system is acting as a galvanic cell.

> *In an electrolytic cell, an external voltage is applied to drive a nonspontaneous reaction.*

The reverse reaction, the reduction of Cd^{2+} by Cu, is thermodynamically nonspontaneous and will occur only with an input of 140 kJ. We can force the reaction to proceed in the reverse direction by applying an electrical potential greater than 0.74 V from an external power supply. The applied voltage forces electrons through the circuit in the reverse direction, converting a galvanic cell to an electrolytic cell. Thus the copper electrode is now the anode (Cu is oxidized), and the cadmium electrode is now the cathode (Cd^{2+} is reduced) (Figure **10.6.1***b*). The signs of the cathode and the anode have switched to reflect the flow of electrons in the circuit. The half-reactions that occur at the cathode and the anode are as follows:

- half-reaction at the cathode:

$$\mathrm{Cd^{2+}(aq) + 2\,e^- \rightarrow Cd(s)} \tag{10.6.1}$$

with $E^\circ_{cathode} = -0.40\,V$

- half-reaction at the anode:

$$\mathrm{Cu(s) \rightarrow Cu^{2+}(aq) + 2\,e^-} \tag{10.6.2}$$

with $E^\circ_{anode} = 0.34\,V$

- Overall Reaction:

$$\mathrm{Cd^{2+}(aq) + Cu(s) \rightarrow Cd(s) + Cu^{2+}(aq)} \tag{10.6.3}$$

with $E^\circ_{cell} = -0.74\,V$

Because $E^\circ_{cell} < 0$, the overall reaction—the reduction of Cd^{2+} by Cu—clearly **cannot** occur spontaneously and proceeds only when sufficient electrical energy is applied. The differences between galvanic and electrolytic cells are summarized in Table **10.6.1**.

Table **10.6.1**: Comparison of Galvanic and Electrolytic Cells

Property	Galvanic Cell	Electrolytic Cell
ΔG	< 0	> 0
E_{cell}	> 0	< 0
Electrode Process		
anode	oxidation	oxidation
cathode	reduction	reduction
Sign of Electrode		
anode	−	+
cathode	+	−

Electrolytic Reactions

At sufficiently high temperatures, ionic solids melt to form liquids that conduct electricity extremely well due to the high concentrations of ions. If two inert electrodes are inserted into molten **NaCl**, for example, and an electrical potential is applied, Cl^- is oxidized at the anode, and Na^+ is reduced at the cathode. The overall reaction is as follows:

$$\mathrm{2\,NaCl(l) \rightarrow 2\,Na(l) + Cl_2(g)} \tag{10.6.4}$$

This is the reverse of the formation of **NaCl** from its elements. The product of the reduction reaction is liquid sodium because the melting point of sodium metal is 97.8°C, well below that of **NaCl** (801°C). Approximately 20,000 tons of sodium metal are produced commercially in the United States each year by the electrolysis of molten **NaCl** in a Downs cell (Figure **10.6.2**). In this specialized cell, $CaCl_2$ (melting point = 772°C) is first added to the **NaCl** to lower the melting point of the mixture to about 600°C, thereby lowering operating costs.

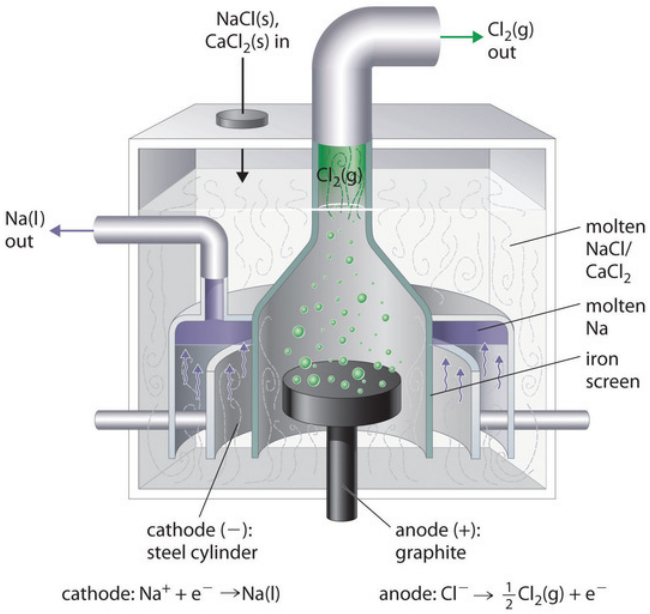


Figure 10.6.2: A Downs Cell for the Electrolysis of Molten NaCl. The electrolysis of a molten mixture of NaCl and $CaCl_2$ results in the formation of elemental sodium and chlorine gas. Because sodium is a liquid under these conditions and liquid sodium is less dense than molten sodium chloride, the sodium floats to the top of the melt and is collected in concentric capped iron cylinders surrounding the cathode. Gaseous chlorine collects in the inverted cone over the anode. An iron screen separating the cathode and anode compartments ensures that the molten sodium and gaseous chlorine do not come into contact. (CC BY-SA-NC; anonymous)

Similarly, in the Hall–Heroult process used to produce aluminum commercially, a molten mixture of about 5% aluminum oxide (Al_2O_3; melting point = 2054°C) and 95% cryolite (Na_3AlF_6; melting point = 1012°C) is electrolyzed at about 1000°C, producing molten aluminum at the cathode and CO_2 gas at the carbon anode. The overall reaction is as follows:

$$2\,Al_2O_3\,(l) + 3\,C\,(s) \longrightarrow 4\,Al\,(l) + 3\,CO_2\,(g) \tag{10.6.5}$$

Oxide ions react with oxidized carbon at the anode, producing CO_2(g).

There are two important points to make about these two commercial processes and about the electrolysis of molten salts in general.

1. The electrode potentials for molten salts are likely to be very different from the standard cell potentials listed in Table P2, which are compiled for the reduction of the hydrated ions in aqueous solutions under standard conditions.
2. Using a mixed salt system means there is a possibility of competition between different electrolytic reactions. When a mixture of NaCl and $CaCl_2$ is electrolyzed, Cl^- is oxidized because it is the only anion present, but either Na^+ or Ca^{2+} can be reduced. Conversely, in the Hall–Heroult process, only one cation is present that can be reduced (Al^{3+}), but there are three species that can be oxidized: C, O^{2-}, and F^-.

In the Hall–Heroult process, C is oxidized instead of O^{2-} or F^- because oxygen and fluorine are more electronegative than carbon, which means that C is a weaker oxidant than either O_2 or F_2. Similarly, in the Downs cell, we might expect electrolysis of a NaCl/$CaCl_2$ mixture to produce calcium rather than sodium because Na is slightly less electronegative than Ca (χ = 0.93 versus 1.00, respectively), making Na easier to oxidize and, conversely, Na^+ more difficult to reduce. In fact, the reduction of Na^+ to Na is the observed reaction. In cases where the electronegativities of two species are similar, other factors, such as the formation of complex ions, become important and may determine the outcome.

Example 10.6.1

If a molten mixture of $MgCl_2$ and KBr is electrolyzed, what products will form at the cathode and the anode, respectively?

Given: identity of salts

Asked for: electrolysis products

Strategy:

A. List all the possible reduction and oxidation products. Based on the electronegativity values shown in Figure 7.5, determine which species will be reduced and which species will be oxidized.

B. Identify the products that will form at each electrode.

Solution

A The possible reduction products are Mg and K, and the possible oxidation products are Cl_2 and Br_2. Because Mg is more electronegative than K (χ = 1.31 versus 0.82), it is likely that Mg will be reduced rather than K. Because Cl is more electronegative than Br (3.16 versus 2.96), Cl_2 is a stronger oxidant than Br_2.

B Electrolysis will therefore produce Br_2 at the anode and Mg at the cathode.

? Exercise 10.6.1

Predict the products if a molten mixture of $AlBr_3$ and LiF is electrolyzed.

Answer

Br_2 and Al

Electrolysis can also be used to drive the thermodynamically nonspontaneous decomposition of water into its constituent elements: H_2 and O_2. However, because pure water is a very poor electrical conductor, a small amount of an ionic solute (such as H_2SO_4 or Na_2SO_4) must first be added to increase its electrical conductivity. Inserting inert electrodes into the solution and applying a voltage between them will result in the rapid evolution of bubbles of H_2 and O_2 (Figure **10.6.3**).

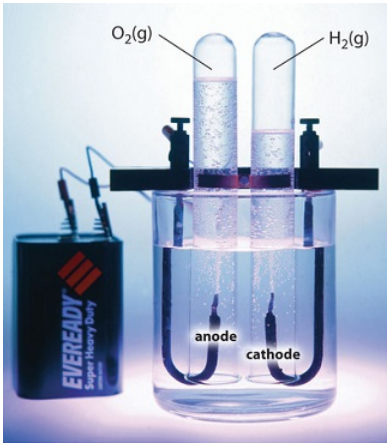


Figure **10.6.3**: The Electrolysis of Water. Applying an external potential of about 1.7–1.9 V to two inert electrodes immersed in an aqueous solution of an electrolyte such as H_2SO_4 or Na_2SO_4 drives the thermodynamically nonspontaneous decomposition of water into H_2 at the cathode and O_2 at the anode. (CC BY-SA-NC; anonymous)

The reactions that occur are as follows:

- cathode:

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} \qquad E^\circ_{cathode} = 0V \tag{10.6.6}$$

- anode:

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^- \qquad E^\circ_{anode} = 1.23\ V \tag{10.6.7}$$

- overall:

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 2H_{2(g)} \qquad E^\circ_{cell} = -1.23\ V \tag{10.6.8}$$

For a system that contains an electrolyte such as Na_2SO_4, which has a negligible effect on the ionization equilibrium of liquid water, the pH of the solution will be 7.00 and $[H^+] = [OH^-] = 1.0 \times 10^{-7}$. Assuming that $P_{O_2} = P_{H_2}$ = 1 atm, we can use the standard

potentials to calculate E for the overall reaction:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right)\log(P_{\text{O}_2}P^2_{\text{H}_2}) \tag{10.6.9}$$

$$= -1.23\ \text{V} - \left(\frac{0.0591\ \text{V}}{4}\right)\log(1) = -1.23\ \text{V} \tag{10.6.10}$$

Thus E_{cell} is −1.23 V, which is the value of $E°_{cell}$ if the reaction is carried out in the presence of 1 M H^+ rather than at pH 7.0.

In practice, a voltage about 0.4–0.6 V greater than the calculated value is needed to electrolyze water. This added voltage, called an **overvoltage**, represents the additional driving force required to overcome barriers such as the large activation energy for the formation of a gas at a metal surface. Overvoltages are needed in all electrolytic processes, which explain why, for example, approximately 14 V must be applied to recharge the 12 V battery in your car.

In general, any metal that does not react readily with water to produce hydrogen can be produced by the electrolytic reduction of an aqueous solution that contains the metal cation. The p-block metals and most of the transition metals are in this category, but metals in high oxidation states, which form oxoanions, cannot be reduced to the metal by simple electrolysis. Active metals, such as aluminum and those of groups 1 and 2, react so readily with water that they can be prepared only by the electrolysis of molten salts. Similarly, any nonmetallic element that does not readily oxidize water to O_2 can be prepared by the electrolytic oxidation of an aqueous solution that contains an appropriate anion. In practice, among the nonmetals, only F_2 cannot be prepared using this method. Oxoanions of nonmetals in their highest oxidation states, such as NO_3^-, SO_4^{2-}, PO_4^{3-}, are usually difficult to reduce electrochemically and usually behave like spectator ions that remain in solution during electrolysis.

> *In general, any metal that does not react readily with water to produce hydrogen can be produced by the electrolytic reduction of an aqueous solution that contains the metal cation.*

Electroplating

In a process called **electroplating**, a layer of a second metal is deposited on the metal electrode that acts as the cathode during electrolysis. Electroplating is used to enhance the appearance of metal objects and protect them from corrosion. Examples of electroplating include the chromium layer found on many bathroom fixtures or (in earlier days) on the bumpers and hubcaps of cars, as well as the thin layer of precious metal that coats silver-plated dinnerware or jewelry. In all cases, the basic concept is the same. A schematic view of an apparatus for electroplating silverware and a photograph of a commercial electroplating cell are shown in Figure 10.6.4.

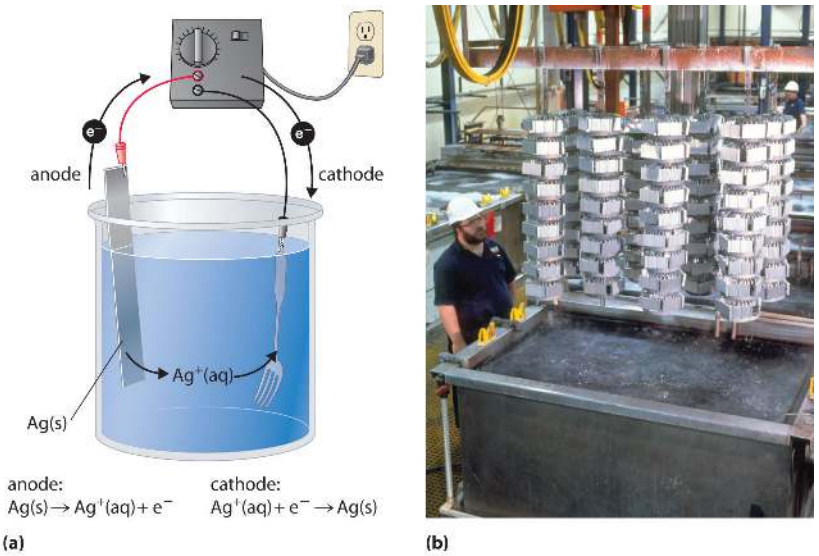


Figure 10.6.3: Electroplating. (a) Electroplating uses an electrolytic cell in which the object to be plated, such as a fork, is immersed in a solution of the metal to be deposited. The object being plated acts as the cathode, on which the desired metal is deposited in a thin layer, while the anode usually consists of the metal that is being deposited (in this case, silver) that maintains the solution concentration as it dissolves. (b) In this commercial electroplating apparatus, a large number of objects can be plated simultaneously by lowering the rack into the Ag^+ solution and applying the correct potential. (CC BY-SA-NC; anonymous)

The half-reactions in electroplating a fork, for example, with silver are as follows:

- cathode (fork):

$$Ag^+(aq) + e^- \longrightarrow Ag(s) \qquad E°_{cathode} = 0.80V$$

- anode (silver bar):

$$Ag(s) \longrightarrow Ag^+(aq) + e^- \qquad E°_{anode} = 0.80V$$

The overall reaction is the transfer of silver metal from one electrode (a silver bar acting as the anode) to another (a fork acting as the cathode). Because $E°_{cell} = 0\,V$, it takes only a small applied voltage to drive the electroplating process. In practice, various other substances may be added to the plating solution to control its electrical conductivity and regulate the concentration of free metal ions, thus ensuring a smooth, even coating.

Quantitative Considerations

If we know the stoichiometry of an electrolysis reaction, the amount of current passed, and the length of time, we can calculate the amount of material consumed or produced in a reaction. Conversely, we can use stoichiometry to determine the combination of current and time needed to produce a given amount of material.

The quantity of material that is oxidized or reduced at an electrode during an electrochemical reaction is determined by the stoichiometry of the reaction and the amount of charge that is transferred. For example, in the reaction

$$Ag^+(aq) + e^- \longrightarrow Ag(s)$$

1 mol of electrons reduces 1 mol of Ag^+ to Ag metal. In contrast, in the reaction

$$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$$

1 mol of electrons reduces only 0.5 mol of Cu^{2+} to Cu metal. Recall that the charge on 1 mol of electrons is 1 faraday (1 F), which is equal to 96,485 C. We can therefore calculate the number of moles of electrons transferred when a known current is passed through a cell for a given period of time. The total charge (q in coulombs) transferred is the product of the current (I in amperes) and the time (t, in seconds):

$$q = I \times t \tag{10.6.11}$$

The stoichiometry of the reaction and the total charge transferred enable us to calculate the amount of product formed during an electrolysis reaction or the amount of metal deposited in an electroplating process.

For example, if a current of 0.60 A passes through an aqueous solution of $CuSO_4$ for 6.0 min, the total number of coulombs of charge that passes through the cell is as follows:

$$\begin{aligned} q &= (0.60\ \text{A})(6.0\ \text{min})(60\ \text{s/min}) \\ &= 220\ \text{A} \cdot \text{s} \\ &= 220\ \text{C} \end{aligned}$$

The number of moles of electrons transferred to Cu^{2+} is therefore

$$\begin{aligned} \text{moles e}^- &= \frac{220\ \text{C}}{96{,}485\ \text{C/mol}} \\ &= 2.3 \times 10^{-3}\ \text{mol e}^- \end{aligned}$$

Because two electrons are required to reduce a single Cu^{2+} ion, the total number of moles of Cu produced is half the number of moles of electrons transferred, or 1.2×10^{-3} mol. This corresponds to 76 mg of Cu. In commercial electrorefining processes, much higher currents (greater than or equal to 50,000 A) are used, corresponding to approximately 0.5 F/s, and reaction times are on the order of 3–4 weeks.

Example 10.6.2

A silver-plated spoon typically contains about 2.00 g of Ag. If 12.0 h are required to achieve the desired thickness of the Ag coating, what is the average current per spoon that must flow during the electroplating process, assuming an efficiency of 100%?

Given: mass of metal, time, and efficiency

Asked for: current required

Strategy:

A. Calculate the number of moles of metal corresponding to the given mass transferred.

B. Write the reaction and determine the number of moles of electrons required for the electroplating process.

C. Use the definition of the faraday to calculate the number of coulombs required. Then convert coulombs to current in amperes.

Solution

A We must first determine the number of moles of Ag corresponding to 2.00 g of Ag:

$$\text{moles Ag} = \frac{2.00\ \text{g}}{107.868\ \text{g/mol}} = 1.85 \times 10^{-2}\ \text{mol Ag}$$

B The reduction reaction is $Ag^+(aq) + e^- \rightarrow Ag(s)$, so 1 mol of electrons produces 1 mol of silver.

C Using the definition of the faraday,

$$\text{coulombs} = (1.85 \times 10^{-2}\text{mol e}^-)(96{,}485\ \text{C/mol e}^-) = 1.78 \times 10^3\ \text{C / mole}$$

The current in amperes needed to deliver this amount of charge in 12.0 h is therefore

$$\begin{aligned} \text{amperes} &= \frac{1.78 \times 10^3\ \text{C}}{(12.0\ \text{h})(60\ \text{min/h})(60\ \text{s/min})} \\ &= 4.12 \times 10^{-2}\ \text{C/s} = 4.12 \times 10^{-2}\ \text{A} \end{aligned}$$

Because the electroplating process is usually much less than 100% efficient (typical values are closer to 30%), the actual current necessary is greater than 0.1 A.

? Exercise 10.6.2

A typical aluminum soft-drink can weighs about 29 g. How much time is needed to produce this amount of Al(s) in the Hall–Heroult process, using a current of 15 A to reduce a molten Al_2O_3/Na_3AlF_6 mixture?

Answer

5.8 h



Electroplating: Electroplating(opens in new window) [youtu.be]

Summary

In electrolysis, an external voltage is applied to drive a **nonspontaneous** reaction. The quantity of material oxidized or reduced can be calculated from the stoichiometry of the reaction and the amount of charge transferred. Relationship of charge, current and time:

$$q = I \times t$$

In electrolysis, an external voltage is applied to drive a nonspontaneous reaction. Electrolysis can also be used to produce H_2 and O_2 from water. In practice, an additional voltage, called an overvoltage, must be applied to overcome factors such as a large activation energy and a junction potential. Electroplating is the process by which a second metal is deposited on a metal surface, thereby enhancing an object's appearance or providing protection from corrosion. The amount of material consumed or produced in a reaction can be calculated from the stoichiometry of an electrolysis reaction, the amount of current passed, and the duration of the electrolytic reaction.

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10.E: Electrochemistry (Exercises)

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10.E.1 Electrochemical Cells

10.E.1.1 Review of Redox Chemistry

1. Identify the half-reaction $Fe^{3+} + 3e^- \rightarrow Fe$ as either oxidation, reduction, or not a redox half reaction.

◯	It is an oxidation half reaction.
◯	It is a reduction half reaction.
◯	It is not a redox half reaction.
	Check Answer

10.E.1.2 Galvanic Cells

10.E.2 The Gibbs Free Energy and Cell Voltage

10.E.3 oncentration Effects and the Nernst Equation

10.E.4 Batteries and Fuel Cells

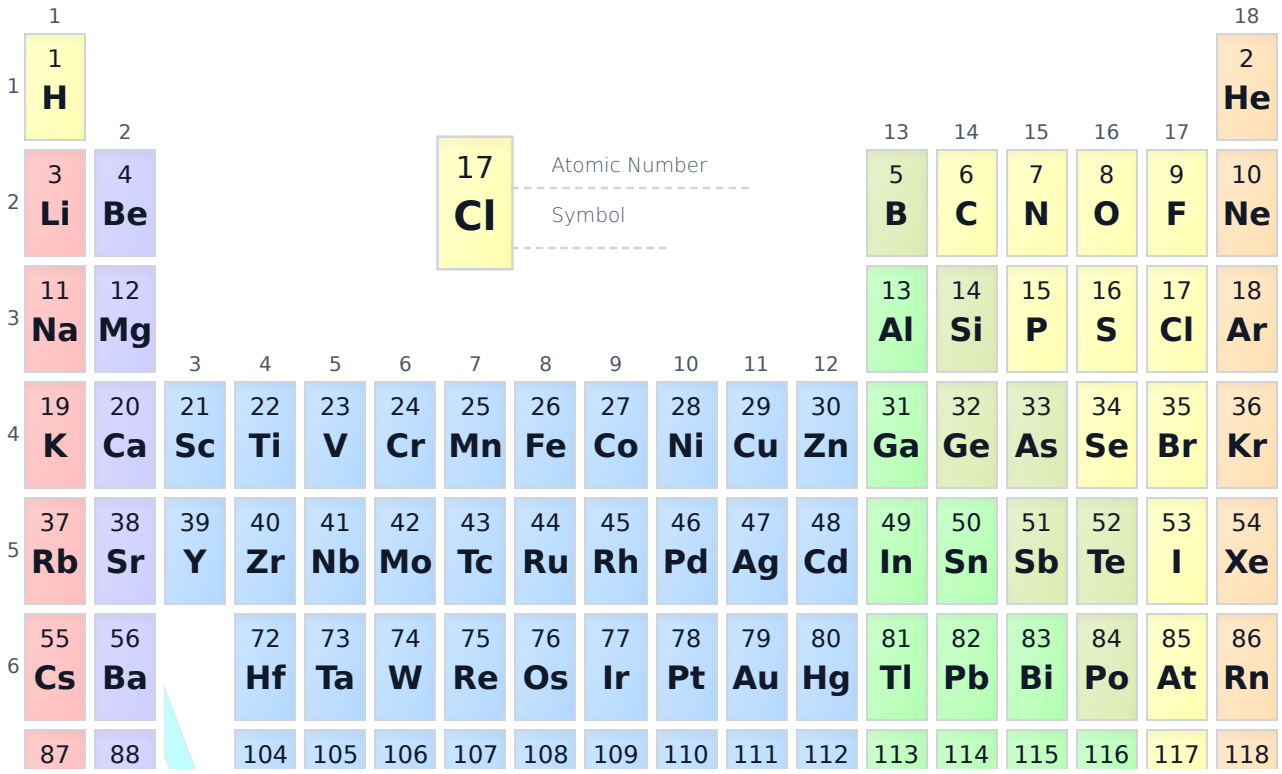
10.E.5 Corrosion and Its Prevention

10.E.6 Electrolysis - A Deeper Look

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PUBCHEM > PERIODIC TABLE

Periodic Table of Elements



A2: Standard Thermodynamic Quantities

Standard thermodynamic Quantities for Chemical Substances at 25°C. Source of data: CRC Handbook of Chemistry and Physics,84th Edition (2004).

Aluminum

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
Al(s)	0.0	0.0	28.3
Al(g)	330.0	289.4	164.6
$AlCl_3$(s)	−704.2	−628.8	109.3
Al_2O_3(s)	−1675.7	−1582.3	50.9

Barium

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
Ba(s)	0.0	0.0	62.5
Ba(g)	180.0	146.0	170.2
BaO(s)	−548.0	−520.3	72.1
$BaCO_3$(s)	−1213.0	−1134.4	112.1
$BaSO_4$(s)	−1473.2	−1362.2	132.2

Beryllium

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
Be(s)	0.0	0.0	9.5
Be(g)	324.0	286.6	136.3
$Be(OH)_2$(s)	−902.5	−815.0	45.5
BeO(s)	−609.4	−580.1	13.8

Bismuth

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
Bi(s)	0.0	0.0	56.7
Bi(g)	207.1	168.2	187.0

Bromine

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
Br(g)	111.9	82.4	175.0
$Br_2(l)$	0.0	0.0	152.2
$Br^-(aq)$	−121.6	−104.0	82.4
$Br_2(g)$	30.9	3.1	245.5
HBr(g)	−36.3	−53.4	198.7
HBr(aq)	−121.6	−104.0	82.4

Cadmium

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
Cd(s)	0.0	0.0	51.8
Cd(g)	111.8	—	167.7
$CdCl_2(s)$	−391.5	−343.9	115.3
CdS(s)	−161.9	−156.5	64.9

Calcium

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
Ca(s)	0.0	0.0	41.6
Ca(g)	177.8	144.0	154.9
$CaCl_2(s)$	−795.4	−748.8	108.4
$CaF_2(s)$	−1228.0	−1175.6	68.5
$Ca(OH)_2(s)$	−985.2	−897.5	83.4
CaO(s)	−634.9	−603.3	38.1
$CaSO_4(s)$	−1434.5	−1322.0	106.5
$CaCO_3$(s, calcite)	−1207.6	−1129.1	91.7
$CaCO_3$(s, aragonite)	−1207.8	−1128.2	88.0

Carbon

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
C(s, graphite)	0.0	0.0	5.7
C(s, diamond)	1.9	2.9	2.4
C(s, fullerene—C_{60})	2327.0	2302.0	426.0
C(s, fullerene—C_{70})	2555.0	2537.0	464.0
C(g)	716.7	671.3	158.1
C(g, fullerene—C_{60})	2502.0	2442.0	544.0
C(g, fullerene—C_{70})	2755.0	2692.0	614.0
CBr_4(s)	29.4	47.7	212.5
CBr_4(g)	83.9	67.0	358.1
CCl_2F_2(g)	−477.4	−439.4	300.8
CCl_2O(g)	−219.1	−204.9	283.5
CCl_4(l)	−128.2	−62.6	216.2
CCl_4(g)	−95.7	−53.6	309.9
CF_4(g)	−933.6	−888.3	261.6
$CHCl_3$(l)	−134.1	−73.7	201.7
$CHCl_3$(g)	−102.7	6.0	295.7
CH_2Cl_2(l)	−124.2	—	177.8
CH_2Cl_2(g)	−95.4	−68.9	270.2
CH_3Cl(g)	−81.9	−58.5	234.6
CH_4(g)	−74.6	−50.5	186.3
CH_3COOH(l)	−484.3	−389.9	159.8
CH_3OH(l)	−239.2	−166.6	126.8
CH_3OH(g)	−201.0	−162.3	239.9
CH_3NH_2(l)	−47.3	35.7	150.2
CH_3NH_2(g)	−22.5	32.7	242.9
CH_3CN(l)	40.6	86.5	149.6
CH_3CN(g)	74.0	91.9	243.4
CO(g)	−110.5	−137.2	197.7
CO_2(g)	−393.5	−394.4	213.8
CS_2(l)	89.0	64.6	151.3
CS_2(g)	116.7	67.1	237.8
C_2H_2(g)	227.4	209.9	200.9
C_2H_4(g)	52.4	68.4	219.3

$C_2H_6(g)$	−84.0	−32.0	229.2
$C_3H_8(g)$	−103.8	−23.4	270.3
$C_3H_6O_3(s)$ (lactic acid)	−694.1	−522.9	142.3
$C_6H_6(l)$	49.1	124.5	173.4
$C_6H_6(g)$	82.9	129.7	269.2
$C_6H_{12}(g)$	-167.2	-0.3	388.82
$C_6H_{12}O_6(s)$ (glucose)	−1273.3	−910.4	212.1
$C_2H_5OH(l)$	−277.6	−174.8	160.7
$C_2H_5OH(g)$	−234.8	−167.9	281.6
$(CH_3)_2O(l)$	−203.3	—	—
$(CH_3)_2O(g)$	−184.1	−112.6	266.4
$CH_3CO_2^-(aq)$	−486.0	−369.3	86.6
n-$C_{12}H_{26}(l)$ (dodecane)	−350.9	28.1	490.6

Cesium

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
Cs(s)	0.0	0.0	85.2
Cs(g)	76.5	49.6	175.6
CsCl(s)	−443.0	−414.5	101.2

Chlorine

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
Cl(g)	121.3	105.3	165.2
$Cl_2(g)$	0.0	0.0	223.1
$Cl^-(aq)$	−167.2	−131.2	56.5
HCl(g)	−92.3	−95.3	186.9
HCl(aq)	−167.2	−131.2	56.5
$ClF_3(g)$	−163.2	−123.0	281.6

Chromium

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
Cr(s)	0.0	0.0	23.8
Cr(g)	396.6	351.8	174.5
$CrCl_3(s)$	−556.5	−486.1	123.0
$CrO_3(g)$	−292.9	—	266.2
$Cr_2O_3(s)$	−1139.7	−1058.1	81.2

Cobalt

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
Co(s)	0.0	0.0	30.0
Co(g)	424.7	380.3	179.5
$CoCl_2$(s)	−312.5	−269.8	109.2

Copper

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
Cu(s)	0.0	0.0	33.2
Cu(g)	337.4	297.7	166.4
CuCl(s)	−137.2	−119.9	86.2
$CuCl_2$(s)	−220.1	−175.7	108.1
CuO(s)	−157.3	−129.7	42.6
Cu_2O(s)	−168.6	−146.0	93.1
CuS(s)	−53.1	−53.6	66.5
Cu_2S(s)	−79.5	−86.2	120.9
CuCN(s)	96.2	111.3	84.5

Fluorine

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
F(g)	79.4	62.3	158.8
F^-(aq)	−332.6	−278.8	−13.8
F_2(g)	0.0	0.0	202.8
HF(g)	−273.3	−275.4	173.8
HF(aq)	−332.6	−278.8	−13.8

Hydrogen

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
H(g)	218.0	203.3	114.7
H_2(g)	0.0	0.0	130.7
H^+(aq)	0.0	0.0	0.0

Iodine

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
I(g)	106.8	70.2	180.8
I^-(aq)	−55.2	−51.6	111.3
I_2(s)	0.0	0.0	116.1
I_2(g)	62.4	19.3	260.7
HI(g)	26.5	1.7	206.6
HI(aq)	−55.2	−51.6	111.3

Iron

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
Fe(s)	0.0	0.0	27.3
Fe(g)	416.3	370.7	180.5
Fe^{2+}(aq)	−89.1	−78.9	−137.7
Fe^{3+}(aq)	−48.5	−4.7	−315.9
$FeCl_2$(s)	−341.8	−302.3	118.0
$FeCl_3$(s)	−399.5	−334.0	142.3
FeO(s)	−272.0	−251.4	60.7
Fe_2O_3(s)	−824.2	−742.2	87.4
Fe_3O_4(s)	−1118.4	−1015.4	146.4
FeS_2(s)	−178.2	−166.9	52.9
$FeCO_3$(s)	−740.6	−666.7	92.9

Lead

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
Pb(s)	0.0	0.0	64.8
Pb(g)	195.2	162.2	175.4
PbO(s, red or litdarge)	−219.0	−188.9	66.5
PbO(s, yellow or massicot)	−217.3	−187.9	68.7
PbO_2(s)	−277.4	−217.3	68.6
$PbCl_2$(s)	−359.4	−314.1	136.0
PbS(s)	−100.4	−98.7	91.2
$PbSO_4$(s)	−920.0	−813.0	148.5
$PbCO_3$(s)	−699.1	−625.5	131.0
$Pb(NO_3)_2$(s)	−451.9	—	—
$Pb(NO_3)_2$(aq)	−416.3	−246.9	303.3

Lithium

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
Li(s)	0.0	0.0	29.1
Li(g)	159.3	126.6	138.8
$Li^+(aq)$	−278.5	−293.3	13.4
LiCl(s)	−408.6	−384.4	59.3
$Li_2O(s)$	−597.9	−561.2	37.6

Magnesium

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
Mg(s)	0.0	0.0	32.7
Mg(g)	147.1	112.5	148.6
$Mg^{2+}(aq)$	-466.85	-454.8	-138.1
$MgCl_2(s)$	−641.3	−591.8	89.6
MgO(s)	−601.6	−569.3	27.0
$Mg(OH)_2(s)$	−924.5	−833.5	63.2
$MgSO_4(s)$	−1284.9	−1170.6	91.6
MgS(s)	−346.0	−341.8	50.3

Manganese

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
Mn(s)	0.0	0.0	32.0
Mn(g)	280.7	238.5	173.7
$MnCl_2(s)$	−481.3	−440.5	118.2
MnO(s)	−385.2	−362.9	59.7
$MnO_2(s)$	−520.0	−465.1	53.1
$KMnO_4(s)$	−837.2	−737.6	171.7
$MnO_4^-(aq)$	−541.4	−447.2	191.2

Mercury

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
Hg(l)	0.0	0.0	75.9
Hg(g)	61.4	31.8	175.0
$HgCl_2$(s)	−224.3	−178.6	146.0
Hg_2Cl_2(s)	−265.4	−210.7	191.6
HgO(s)	−90.8	−58.5	70.3
HgS(s, red)	−58.2	−50.6	82.4
Hg_2(g)	108.8	68.2	288.1

Molybdenum

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
Mo(s)	0.0	0.0	28.7
Mo(g)	658.1	612.5	182.0
MoO_2(s)	−588.9	−533.0	46.3
MoO_3(s)	−745.1	−668.0	77.7

Nickel

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
Ni(s)	0.0	0.0	29.9
Ni(g)	429.7	384.5	182.2
$NiCl_2$(s)	−305.3	−259.0	97.7
$Ni(OH)_2$(s)	−529.7	−447.2	88.0

Nitrogen

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
N(g)	472.7	455.5	153.3
N_2(g)	0.0	0.0	191.6
NH_3(g)	−45.9	−16.4	192.8
NH_4^+(aq)	−132.5	−79.3	113.4
N_2H_4(l)	50.6	149.3	121.2
N_2H_4(g)	95.4	159.4	238.5
NH_4Cl(s)	−314.4	−202.9	94.6
NH_4OH(l)	−361.2	−254.0	165.6
NH_4NO_3(s)	−365.6	−183.9	151.1
$(NH_4)_2SO_4$(s)	−1180.9	−901.7	220.1
NO(g)	91.3	87.6	210.8
NO_2(g)	33.2	51.3	240.1
N_2O(g)	81.6	103.7	220.0
N_2O_4(l)	−19.5	97.5	209.2
N_2O_4(g)	11.1	99.8	304.4
HNO_2(g)	−79.5	−46.0	254.1
HNO_3(l)	−174.1	−80.7	155.6
HNO_3(g)	−133.9	−73.5	266.9
HNO_3(aq)	−207.4	−111.3	146.4
NF_3(g)	−132.1	−90.6	260.8
HCN(l)	108.9	125.0	112.8
HCN(g)	135.1	124.7	201.8

Osmium

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
Os(s)	0.0	0.0	32.6
Os(g)	791.0	745.0	192.6
OsO_4(s)	−394.1	−304.9	143.9
OsO_4(g)	−337.2	−292.8	293.8

Oxygen

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
O(g)	249.2	231.7	161.1
O_2(g)	0.0	0.0	205.2
O_3(g)	142.7	163.2	238.9
OH^-(aq)	−230.0	−157.2	−10.8
H_2O(l)	−285.8	−237.1	70.0
H_2O(g)	−241.8	−228.6	188.8
H_2O_2(l)	−187.8	−120.4	109.6
H_2O_2(g)	−136.3	−105.6	232.7

Phosphorus

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
P(s, white)	0.0	0.0	41.1
P(s, red) −17.6	−17.6	−12.5	22.8
P(s, black)	−39.3	—	—
P(g, white)	316.5	280.1	163.2
P_2(g)	144.0	103.5	218.1
P_4(g)	58.9	24.4	280.0
PCl_3(l)	−319.7	−272.3	217.1
PCl_3(g)	−287.0	−267.8	311.8
$POCl_3$(l)	−597.1	−520.8	222.5
$POCl_3$(g)	−558.5	−512.9	325.5
PCl_5(g)	−374.9	−305.0	364.6
PH_3(g)	5.4	13.5	210.2
H_3PO_4(s)	−1284.4	−1124.3	110.5
H_3PO_4(l)	−1271.7	−1123.6	150.8

Potassium

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
K(s)	0.0	0.0	64.7
K(g)	89.0	60.5	160.3
KBr(s)	−393.8	−380.7	95.9
KCl(s)	−436.5	−408.5	82.6
$KClO_3$(s)	−397.7	−296.3	143.1
K_2O(s)	−361.5	−322.1	94.1
K_2O_2(s)	−494.1	−425.1	102.1
KNO_2(s)	−369.8	−306.6	152.1
KNO_3(s)	−494.6	−394.9	133.1
KSCN(s)	−200.2	−178.3	124.3
K_2CO_3(s)	−1151.0	−1063.5	155.5
K_2SO_4(s)	−1437.8	−1321.4	175.6

Rubidium

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
Rb(s)	0.0	0.0	76.8
Rb(g)	80.9	53.1	170.1
RbCl(s)	−435.4	−407.8	95.9

Selenium

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
Se(s, gray)	0.0	0.0	42.4
Se(g, gray)	227.1	187.0	176.7
H_2Se(g)	29.7	15.9	219.0

Silicon

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
Si(s)	0.0	0.0	18.8
Si(g)	450.0	405.5	168.0
$SiCl_4$(l)	−687.0	−619.8	239.7
$SiCl_4$(g)	−657.0	−617.0	330.7
SiH_4(g)	34.3	56.9	204.6
SiC(s, cubic)	−65.3	−62.8	16.6
SiC(s, hexagonal)	−62.8	−60.2	16.5

Silver

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
Ag(s)	0.0	0.0	42.6
Ag(g)	284.9	246.0	173.0
Ag^+(aq)	105.6	77.1	72.7
AgBr(s)	−100.4	−96.9	107.1
AgCl(s)	−127.0	−109.8	96.3
$AgNO_3$(s)	−124.4	−33.4	140.9
Ag_2O(s)	−31.1	−11.2	121.3
Ag_2S(s)	−32.6	−40.7	144.0

Sodium

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
Na(s)	0.0	0.0	51.3
Na(g)	107.5	77.0	153.7
Na^+(aq)	−240.1	−261.9	59.0
NaF(s)	−576.6	−546.3	51.1
NaF(aq)	−572.8	−540.7	45.2
NaCl(s)	−411.2	−384.1	72.1
NaCl(aq)	−407.3	−393.1	115.5
NaBr(s)	−361.1	−349.0	86.8
NaBr(g)	−143.1	−177.1	241.2
NaBr(aq)	−361.7	−365.8	141.4
NaO_2(s)	−260.2	−218.4	115.9
Na_2O(s)	−414.2	−375.5	75.1
Na_2O_2(s)	−510.9	−447.7	95.0
NaCN(s)	−87.5	−76.4	115.6
$NaNO_3$(aq)	−447.5	−373.2	205.4
$NaNO_3$(s)	−467.9	−367.0	116.5
NaN_3(s)	21.7	93.8	96.9
Na_2CO_3(s)	−1130.7	−1044.4	135.0
Na_2SO_4(s)	−1387.1	−1270.2	149.6

Sulfur

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
S(s, rhombic)	0.0	0.0	32.1
S(g, rhombic)	277.2	236.7	167.8
$SO_2(g)$	−296.8	−300.1	248.2
$SO_3(g)$	−395.7	−371.1	256.8
$SO_4^{2-}(aq)$	−909.3	−744.5	20.1
$SOCl_2(g)$	−212.5	−198.3	309.8
$H_2S(g)$	−20.6	−33.4	205.8
$H_2SO_4(aq)$	−909.3	−744.5	20.1

Tin

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
Sn(s, white)	0.0	0.0	51.2
Sn(s, gray)	−2.1	0.1	44.1
Sn(g, white)	301.2	266.2	168.5
$SnCl_4(l)$	−511.3	−440.1	258.6
$SnCl_4(g)$	−471.5	−432.2	365.8
$SnO_2(s)$	−557.6	−515.8	49.0

Titanium

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
Ti(s)	0.0	0.0	30.7
Ti(g)	473.0	428.4	180.3
$TiCl_2(s)$	−513.8	−464.4	87.4
$TiCl_3(s)$	−720.9	−653.5	139.7
$TiCl_4(l)$	−804.2	−737.2	252.3
$TiCl_4(g)$	−763.2	−726.3	353.2
$TiO_2(s)$	−944.0	−888.8	50.6

Uranium

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
U(s)	0.0	0.0	50.2
U(g)	533.0	488.4	199.8
UO_2(s)	−1085.0	−1031.8	77.0
UO_2(g)	−465.7	−471.5	274.6
UF_4(s)	−1914.2	−1823.3	151.7
UF_4(g)	−1598.7	−1572.7	368.0
UF_6(s)	−2197.0	−2068.5	227.6
UF_6(g)	−2147.4	−2063.7	377.9

Vanadium

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
V(s)	0.0	0.0	28.9
V(g)	514.2	754.4	182.3
VCl_3(s)	−580.7	−511.2	131.0
VCl_4(l)	−569.4	−503.7	255.0
VCl_4(g)	−525.5	−492.0	362.4
V_2O_5(s)	−1550.6	−1419.5	131.0

Zinc

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
Zn(s)	0.0	0.0	41.6
Zn(g)	130.4	94.8	161.0
$ZnCl_2$(s)	−415.1	−369.4	111.5
$Zn(NO_3)_2$(s)	−483.7	—	—
ZnS(s, sphalerite)	−206.0	−201.3	57.7
$ZnSO_4$(s)	−982.8	−871.5	110.5

Zirconium

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	$S°$ (J/mol K)
Zr(s)	0.0	0.0	39.0
Zr(g)	608.8	566.5	181.4
$ZrCl_2$(s)	−502.0	−386	110
$ZrCl_4$(s)	−980.5	−889.9	181.6

A3: Standard Reduction Potentials by Value

The following table provides E^o for selected reduction reactions. Values are from the following sources: Bard, A. J.; Parsons, B.; Jordon, J., eds. *Standard Potentials in Aqueous Solutions*, Dekker: New York, 1985; Milazzo, G.; Caroli, S.; Sharma, V. K. *Tables of Standard Electrode Potentials*, Wiley: London, 1978; Swift, E. H.; Butler, E. A. *Quantitative Measurements and Chemical Equilibria*, Freeman: New York, 1972.

The table is ordered such that the stronger (more reactive) reductants are at the top and the stronger oxidants are at the bottom.

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Standard Cathode (Reduction) Half-Reaction	Standard Reduction Potential E° (volts)
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	-3.040
$Rb^+ + e^- \rightleftharpoons Rb\ (s)$	-2.98
$K^+(aq) + e^- \rightleftharpoons K(s)$	-2.93
$Ba^{2+} + 2e^- \rightleftharpoons Ba(s)$	-2.92
$Cs^+(aq) + e^- \rightleftharpoons Cs(s)$	-2.92
$Ba^{2+}(aq) + 2e^- \rightleftharpoons Ba(s)$	-2.91
$Sr^{2+}(aq) + 2e^- \rightleftharpoons Sr(s)$	-2.89
$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$	-2.84
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	-2.713
$Mg(OH)_2(s) + 2e^- \rightleftharpoons Mg(s) + 2OH^-$	-2.687
$La^{3+} + 3e^- \rightleftharpoons La(s)$	-2.38
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	-2.356
$Ce^{3+} + 3e^- \rightleftharpoons Ce(s)$	-2.336
$Al(OH)_4^- + 3e^- \rightleftharpoons Al(s) + 4OH^-$	-2.310
$BaO(s) + 2H^+ + 2e^- \rightleftharpoons Ba(s) + H_2O(l)$	-2.166
$AlF_6^{3-} + 3e^- \rightleftharpoons Al(s) + 6F^-$	-2.07
$Be^{2+} + 2e^- \rightleftharpoons Be(s)$	-1.99
$B(OH)_4^- + 3e^- \rightleftharpoons B(s) + 4OH^-$	-1.811
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	-1.676
$U^{3+} + 3e^- \rightleftharpoons U(s)$	-1.66
$ZnO_2 + 4H^+ + 4e^- \rightleftharpoons Zn(s) + 2H_2O$	-1.473
$SiF_6^{2-} + 4e^- \rightleftharpoons Si(s) + 6F^-$	-1.37
$Zn(CN)_4^{2-} + 2e^- \rightleftharpoons Zn(s) + 4CN$	-1.34
$Zn(OH)_4^{2-} + 2e^- \rightleftharpoons Zn(s) + 4OH^-$	-1.285
$Mn^{2+} + 2e^- \rightleftharpoons Mn(s)$	-1.17
$CdS(s) + 2e^- \rightleftharpoons Cd(s) + S^{2-}$	-1.17
$V^{2+} + 2e^- \rightleftharpoons V(s)$	-1.13
$2SO_3^{2-} + 2H_2O(l) + 2e^- \rightleftharpoons S_2O_4^{2-} + 4OH^-$	-1.13
$Zn(NH_3)_4^{2+} + 2e^- \rightleftharpoons Zn(s) + 4NH_3$	-1.04
$O_2\ (aq) + e^- \rightleftharpoons O_2^-(aq)$	-1.0
$Cd(CN)_4^{2-} + 2e^- \rightleftharpoons Cd(s) + 4CN^-$	-0.943
$MoO_4^{2-} + 4H_2O(l) + 6e^- \rightleftharpoons Mo(s) + 8OH^-$	-0.913
$SO_4^{2-} + H_2O(l) + 2e^- \rightleftharpoons SO_3^{2-} + 2OH^-$	-0.936

Standard Cathode (Reduction) Half-Reaction	Standard Reduction Potential E° (volts)
$SiO_2(s) + 4H^+ + 4e^- \rightleftharpoons Si(s) + 2H_2O(l)$	-0.909
$Cr^{2+} + 2e^- \rightleftharpoons Cr(s)$	-0.90
$B(OH)_3 + 3H^+ + 3e^- \rightleftharpoons B(s) + 3H_2O(l)$	-0.890
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	-0.828
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	-0.7618
$Co(OH)_2(s) + 2e^- \rightleftharpoons Co(s) + 2OH^-$	-0.746
$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$	-0.74
$Ni(OH)_2 + 2e^- \rightleftharpoons Ni(s) + 2OH^-$	-0.72
$Ag_2S(s) + 2e^- \rightleftharpoons 2Ag(s) + S^{2-}$	-0.71
$Se(s) + 2e^- \rightleftharpoons Se^{2-}$	-0.67 in 1 M NaOH
$Cd(NH_3)_4^{2+} + 2e^- \rightleftharpoons Cd(s) + 4NH_3$	-0.622
$2SO_3^{2-} + 3H_2O(l) + 4e^- \rightleftharpoons S_2O_3^{2-} + 6OH^-$	-0.576 in 1 M NaOH
$Ga^{3+} + 3e^- \rightleftharpoons Ga(s)$	-0.56
$U^{4+} + e^- \rightleftharpoons U^{3+}$	-0.52
$SiO_2(s) + 8H^+ + 8e^- \rightleftharpoons SiH_4(g) + 2H_2O(l)$	-0.516
$Sb + 3H^+ + 3e^- \rightleftharpoons SbH_3(g)$	-0.510
$H_3PO_3 + 2H^+ + 2e^- \rightleftharpoons H_3PO_2 + H_2O(l)$	-0.50
$Ni(NH_3)_6^{2+} + 2e^- \rightleftharpoons Ni(s) + 6NH_3$	-0.49
$2CO_2(g) + 2H^+ + 2e^- \rightleftharpoons H_2C_2O_4$	-0.481
$Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$	-0.424
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	-0.44
$S(s) + 2e^- \rightleftharpoons S^{2-}$	-0.407
$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s)$	-0.4030
$Ag(NH_3)_2^+ + e^- \rightleftharpoons Ag(s) + 2NH_3$	-0.373
$Ti^{3+} + e^- \rightleftharpoons Ti^{2+}$	-0.37
$PbSO_4(s) + 2e^- \rightleftharpoons Pb(s) + SO_4^{2-}$	-0.356
$Co^{2+}(aq) + 2e^- \rightleftharpoons Co(s)$	-0.277
$2SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons S_2O_6^{2-} + 2H_2O(l)$	-0.25
$N_2(g) + 5H^+ + 4e^- \rightleftharpoons N_2H_5^+$	-0.23
$H_3PO_4 + 2H^+ + 2e^- \rightleftharpoons H_3PO_3 + H_2O(l)$	-0.28
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	-0.257
$V^{3+} + e^- \rightleftharpoons V^{2+}$	-0.255
$As + 3H^+ + 3e^- \rightleftharpoons AsH_3(g)$	-0.225

Standard Cathode (Reduction) Half-Reaction	Standard Reduction Potential E° (volts)
$CO_2(g) + 2H^+ + 2e^- \rightleftharpoons HCO_2H$	-0.20
$Mo^{3+} + 3e^- \rightleftharpoons Mo(s)$	-0.2
$Ti^{2+} + 2e^- \rightleftharpoons Ti(s)$	-0.163
$MoO_2(s) + 4H^+ + 4e^- \rightleftharpoons Mo(s) + 2H_2O(l)$	-0.152
$AgI(s) + e^- \rightleftharpoons Ag(s) + I^-$	-0.152
$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$	-0.136
$CrO_4^{2-} + 4H_2O(l) + 3e^- \rightleftharpoons 2Cr(OH)_4^- + 4OH^-$	-0.13 in 1 M NaOH
$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$	-0.126
$WO_2(s) + 4H^+ + 4e^- \rightleftharpoons W(s) + 2H_2O(l)$	-0.119
$Se(s) + 2H^+ + 2e^- \rightleftharpoons H_2Se(g)$	-0.115
$CO_2(g) + 2H^+ + 2e^- \rightleftharpoons CO(g) + H_2O(l)$	-0.106
$WO_3(s) + 6H^+ + 6e^- \rightleftharpoons W(s) + 3H_2O(l)$	-0.090
$Hg_2I_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2I^-$	-0.0405
$Fe^{3+}(aq) + 3e^- \rightleftharpoons Fe(s)$	-0.037
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00
$P(s,white) + 3H^+ + 3e^- \rightleftharpoons PH_3(g)$	0.06
$AgBr(s) + e^- \rightleftharpoons Ag(s) + Br^-$	0.071
$S_4O_6^{2-} + 2e^- \rightleftharpoons 2S_2O_3^{2-}$	0.080
$Co(NH_3)_6^{3+} + e^- \rightleftharpoons Co(NH_3)_6^{2+}$	0.1
$Ru(NH_3)_6^{3+} + e^- \rightleftharpoons Ru(s) + Ru(NH_3)_6^{2+}$	0.10
$S(s) + 2H^+ + 2e^- \rightleftharpoons H_2S$	0.144
$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq)$	0.154
$Cu^{2+}(aq) + e^- \rightleftharpoons Cu^+(aq)$	0.159
$UO_2^{2+} + e^- \rightleftharpoons UO_2^+$	0.16
$Co(OH)_3(s) + e^- \rightleftharpoons Co(OH)_2(s) + OH^-$	0.17
$ClO_4^-(aq) + H_2O(l) + 2e^- \rightleftharpoons ClO_3^-(aq) + 2OH^-(aq)$	0.17
$SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons H_2SO_3(aq) + H_2O(l)$	0.172
$BiCl_4^- + 3e^- \rightleftharpoons Bi(s) + 4Cl^-$	0.199
$SbO^+ + 2H^+ + 3e^- \rightleftharpoons Sb(s) + H_2O(l)$	0.212
$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-(aq)$	0.2223
$HCHO + 2H^+ + 2e^- \rightleftharpoons CH_3OH$	0.2323
$HAsO_2 + 3H^+ + 3e^- \rightleftharpoons As(s) + 2H_2O(l)$	0.240
$Ru^{3+} + e^- \rightleftharpoons Ru^{2+}$	0.249

Standard Cathode (Reduction) Half-Reaction	Standard Reduction Potential E° (volts)
$IO_3^- + 3H_2O(l) + 6e^- \rightleftharpoons I^- + 6OH^-$	0.257
$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-$	0.2682
$UO_2^+ + 4H^+ + e^- \rightleftharpoons U^{4+} + 2H_2O(l)$	0.27
$Bi^{3+} + 3e^- \rightleftharpoons Bi(s)$	0.317
$UO_2^{2+} + 4H^+ + 2e^- \rightleftharpoons U^{4+} + 2H_2O(l)$	0.327
$VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O(l)$	0.337
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	0.3419
$ClO_3^-(aq) + H_2O(l) + 2e^- \rightleftharpoons ClO_2^-(aq) + 2OH^-(aq)$	0.35
$Fe(CN)_6^{3-} + e^- \rightleftharpoons Fe(CN)_6^{4-}$	0.356
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-$	0.401
$ClO^- + H_2O(l) + e^- \rightleftharpoons \frac{1}{2}Cl_2(g) + 2OH^-$	0.421 in 1 M NaOH
$Ag_2C_2O_4(s) + 2e^- \rightleftharpoons 2Ag(s) + C_2O_4^{2-}$	0.47
$Cu^+(aq) + e^- \rightleftharpoons Cu(s)$	0.52
$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	0.5355
$I_3^- + 2e^- \rightleftharpoons 3I^-$	0.536
$Cu^{2+} + Cl^- + e^- \rightleftharpoons CuCl(s)$	0.559
$H_3AsO_4 + 2H^+ + 2e^- \rightleftharpoons HAsO_2 + 2H_2O(l)$	0.560
$S_2O_6^{2-} + 4H^+ + 2e^- \rightleftharpoons 2H_2SO_3$	0.569
$ClO_2^-(aq) + H_2O(l) + 2e^- \rightleftharpoons ClO^-(aq) + 2OH^-(aq)$	0.59
$MnO_4^- + 2H_2O(l) + 3e^- \rightleftharpoons MnO_2(s) + 4OH^-$	0.60
$Sb_2O_5(s) + 6H^+ + 4e^- \rightleftharpoons 2SbO^+ + 3H_2O(l)$	0.605
$PtCl_6^{2-} + 2e^- \rightleftharpoons PtCl_4^{2-} + 2Cl^-$	0.68
$RuO_2(s) + 4H^+ + 4e^- \rightleftharpoons Ru(s) + 2H_2O(l)$	0.68
$O_2(g) + 2H^+ + 2e^- \rightleftharpoons H_2O_2$	0.695
$PtCl_4^{2-} + 2e^- \rightleftharpoons Pt(s) + 4Cl^-$	0.73
$H_2SeO_3 + 4H^+ + 4e^- \rightleftharpoons Se(s) + 3H_2O(l)$	0.74
$Tl^{3+} + 3e^- \rightleftharpoons Tl(s)$	0.742
$Tl^{3+} + 2e^- \rightleftharpoons Tl^+$	0.77 in 1 M HCl
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+(aq)}$	0.771
$Hg_2^{2+}(aq) + 2e^- \rightleftharpoons 2Hg(l)$	0.7960
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	0.7996
$Hg^{2+}(aq) + 2e^- \rightleftharpoons Hg(l)$	0.8535
$Cu^{2+} + I^- + e^- \rightleftharpoons CuI(s)$	0.86

Standard Cathode (Reduction) Half-Reaction	Standard Reduction Potential E° (volts)
$Ru(CN)_6^{3-} + e^- \rightleftharpoons Ru(s) + Ru(CN)_6^{4-}$	0.86
$ClO^- + H_2O(l) + 2e^- \rightleftharpoons Cl^- + 2OH^-$	0.890 in 1 M NaOH
$2Hg^{2+}(aq) + 2e^- \rightleftharpoons Hg_2^{2+}(aq)$	0.911
$HgO(s) + 2H^+ + 2e^- \rightleftharpoons Hg(l) + H_2O(l)$	0.926
$NO_3^- + 3H^+ + 2e^- \rightleftharpoons HNO_2 + H_2O(l)$	0.94
$MnO_2(s) + 4H^+ + e^- \rightleftharpoons Mn^{3+}(aq) + 2H_2O(l)$	0.95
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$	0.96
$HIO + H^+ + 2e^- \rightleftharpoons I^- + H_2O(l)$	0.985
$HNO_2 + H^+ + e^- \rightleftharpoons NO(g) + H_2O(l)$	0.996
$VO_2^{2+} + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O(l)$	1.000
$AuCl_4^- + 3e^- \rightleftharpoons Au(s) + 4Cl^-$	1.002
$NO_2(g) + H^+(aq) + e^- \rightleftharpoons HNO_2(aq)$	1.07
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq)$	1.087
$Fe(phen)_6^{3+} + e^- \rightleftharpoons Fe(phen)_6^{2+}$	1.147
$SeO_4^{3-} + 4H^+ + e^- \rightleftharpoons H_2SeO_3 + H_2O(l)$	1.151
$ClO_3^- + 2H^+ + e^- \rightleftharpoons ClO_2(g) + H_2O$	1.175
$ClO_3^- + 3H^+ + 2e^- \rightleftharpoons HClO_2 + H_2O$	1.181
$IO_3^- + 6H^+ + 5e^- \rightleftharpoons \frac{1}{2}I_2(s) + 3H_2O(l)$	1.195
$Pt^{2+} + 2e^- \rightleftharpoons Pt(s)$	1.2
$ClO_4^- + 2H^+ + 2e^- \rightleftharpoons ClO_3^- + H_2O$	1.201
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	1.229
$MnO_2(s) + 4H^+ + 2e^- \rightleftharpoons Mn^{2+} + 2H_2O(l)$	1.23
$2HNO_2 + 4H^+ + 4e^- \rightleftharpoons N_2O(g) + 3H_2O(l)$	1.297
$HOBr + H^+ + 2e^- \rightleftharpoons Br^- + H_2O(l)$	1.341
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$	1.36
$Au^{3+} + 2e^- \rightleftharpoons Au^+$	1.36
$Hg_2Br_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Br^-$	1.392
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	1.396
$Hg_2Br_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Br^-$	1.392
$Ce^{4+}(aq) + e^- \rightleftharpoons Ce^{3+}(aq)$	1.44
$PbO_2(s) + 4H^+ + 2e^- \rightleftharpoons Pb^{2+}(aq) + 2H_2O(l)$	1.46
$BrO_3^- + 6H^+ + 6e^- \rightleftharpoons Br^- + 3H_2O$	1.478
$Mn^{3+} + e^- \rightleftharpoons Mn^{2+}$	1.5

Standard Cathode (Reduction) Half-Reaction	Standard Reduction Potential E° (volts)
$BrO_3^- + 6H^+ + 5e^- \rightleftharpoons \frac{1}{2}Br_2(l) + 3H_2O$	1.5
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$	1.51
$Au^{3+} + 3e^- \rightleftharpoons Au(s)$	1.52
$2NO(g) + 2H^+ + 2e^- \rightleftharpoons N_2O(g) + H_2O(l)$	1.59
$HOBr + H^+ + e^- \rightleftharpoons \frac{1}{2}Br^- + H_2O(l)$	1.604
$HClO_2 + 2H^+ + 2e^- \rightleftharpoons HOCl + H_2O$	1.64
$PbO_2(s) + SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons PbSO_4(s) + 2H_2O(l)$	1.690
$MnO_4^- + 4H^+ + 3e^- \rightleftharpoons MnO_2(s) + 2H_2O(l)$	1.70
$Ce^{4+} + e^- \rightleftharpoons Ce^{3+}$	1.72
$N_2O(g) + 2H^+ + 2e^- \rightleftharpoons N_2(g) + H_2O(l)$	1.77
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$	1.763
$Au^+ + e^- \rightleftharpoons Au(s)$	1.83
$Co^{3+}(aq) + e^- \rightleftharpoons Co^{2+}(aq)$	1.92
$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$	1.96
$O_3(g) + 2H^+(aq) + 2e^- \rightleftharpoons O_2(g) + H_2O(l)$	2.07
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	2.87
$F_2(g) + 2H^+ + 2e^- \rightleftharpoons 2HF$	3.053

Contributors and Attributions

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A4: Standard Reduction Potentials by Element

The following table provides E^o and $E^{o\prime}$ values for selected reduction reactions. Values are from the following sources: Bard, A. J.; Parsons, B.; Jordon, J., eds. *Standard Potentials in Aqueous Solutions*, Dekker: New York, 1985; Milazzo, G.; Caroli, S.; Sharma, V. K. *Tables of Standard Electrode Potentials*, Wiley: London, 1978; Swift, E. H.; Butler, E. A. *Quantitative Measurements and Chemical Equilibria*, Freeman: New York, 1972.

Solids, gases, and liquids are identified; all other species are aqueous. Reduction reactions in acidic solution are written using H^+ in place of H_3O^+. You may rewrite a reaction by replacing H^+ with H_3O^+ and adding to the opposite side of the reaction one molecule of H_2O per H^+; thus

$$\mathbf{H_3AsO_4 + 2\,H^+ + 2\,e^- \rightleftharpoons HAsO_2 + 2\,H_2O}$$

becomes

$$\mathbf{H_3AsO_4 + 2\,H_3O^+ + 2\,e^- \rightleftharpoons HAsO_2 + 4\,H_2O}$$

Conditions for formal potentials ($E^{o\prime}$) are listed next to the potential.

Aluminum	$E°$ (V)
$Al^{3+} + 3e^- \rightleftharpoons Al(s)$	–1.676
$Al(OH)_4^- + 3e^- \rightleftharpoons Al(s) + 4OH^-$	–2.310
$AlF_6^{3-} + 3e^- \rightleftharpoons Al(s) + 6F^-$	–2.07

Antimony	$E°$ (V)
$Sb + 3H^+ + 3e^- \rightleftharpoons SbH_3(g)$	–0.510
$Sb_2O_5(s) + 6H^+ + 4e^- \rightleftharpoons 2SbO^+ + 3H_2O(l)$	0.605
$SbO^+ + 2H^+ + 3e^- \rightleftharpoons Sb(s) + H_2O(l)$	0.212

Arsenic	$E°$ (V)
$As + 3H^+ + 3e^- \rightleftharpoons AsH_3(g)$	–0.225
$H_3AsO_4 + 2H^+ + 2e^- \rightleftharpoons HAsO_2 + 2H_2O(l)$	0.560
$HAsO_2 + 3H^+ + 3e^- \rightleftharpoons As(s) + 2H_2O(l)$	0.240

Barium	$E°$ (V)
$Ba^{2+} + 2e^- \rightleftharpoons Ba(s)$	–2.91
$BaO(s) + 2H^+ + 2e^- \rightleftharpoons Ba(s) + H_2O(l)$	2.365

Beryllium	$E°$ (V)
$Be^{2+} + 2e^- \rightleftharpoons Be(s)$	–1.99

Bismuth	$E°$ (V)
$Bi^{3+} + 3e^- \rightleftharpoons Bi(s)$	0.317
$BiCl_4^- + 3e^- \rightleftharpoons Bi(s) + 4Cl^-$	0.199

Boron	$E°$ (V)
$B(OH)_3 + 3H^+ + 3e^- \rightleftharpoons B(s) + 3H_2O(l)$	–0.890
$B(OH)_4^- + 3e^- \rightleftharpoons B(s) + 4OH^-$	–1.811

Bromine	$E°$ (V)
$Br_2 + 2e^- \rightleftharpoons 2Br^-$	1.087
$HOBr + H^+ + 2e^- \rightleftharpoons Br^- + H_2O(l)$	1.341
$HOBr + H^+ + e^- \rightleftharpoons ½Br^- + H_2O(l)$	1.604
$BrO^- + H_2O(l) + 2e^- \rightleftharpoons Br^- + 2OH^-$	0.76 in 1 M NaOH
$BrO_3^- + 6H^+ + 5e^- \rightleftharpoons ½Br_2(l) + 3H_2O$	1.5
$BrO_3^- + 6H^+ + 6e^- \rightleftharpoons Br^- + 3H_2O$	1.478

Cadmium	$E°$ (V)
$Cd^{2+} + 2e^- \rightleftharpoons Cd(s)$	–0.4030
$Cd(CN)_4^{2-} + 2e^- \rightleftharpoons Cd(s) + 4CN^-$	–0.943
$Cd(NH_3)_4^{2+} + 2e^- \rightleftharpoons Cd(s) + 4NH_3$	–0.622

Calcium	$E°$ (V)
$Ca^{2+} + 2e^- \rightleftharpoons Ca(s)$	–2.84

Carbon	$E°$ (V)
$CO_2(g) + 2H^+ + 2e^- \rightleftharpoons CO(g) + H_2O(l)$	–0.106
$CO_2(g) + 2H^+ + 2e^- \rightleftharpoons HCO_2H$	–0.20
$2CO_2(g) + 2H^+ + 2e^- \rightleftharpoons H_2C_2O_4$	–0.481
$HCHO + 2H^+ + 2e^- \rightleftharpoons CH_3OH$	0.2323

Cerium	$E°$ (V)
$Ce^{3+} + 3e^- \rightleftharpoons Ce(s)$	–2.336
$Ce^{4+} + e^- \rightleftharpoons Ce^{3+}$	1.61

Cesium	$E°$ (V)
$Cs^+(aq) + e^- \rightleftharpoons Cs(s)$	-2.92

Chlorine	$E°$ (V)
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-$	1.396
$ClO^- + H_2O(l) + e^- \rightleftharpoons ½Cl_2(g) + 2OH^-$	0.421 in 1 M NaOH
$ClO^- + H_2O(l) + 2e^- \rightleftharpoons Cl^- + 2OH^-$	0.890 in 1 M NaOH
$HClO_2 + 2H^+ + 2e^- \rightleftharpoons HOCl + H_2O$	1.64
$ClO_3^- + 2H^+ + e^- \rightleftharpoons ClO_2(g) + H_2O$	1.175
$ClO_3^- + 3H^+ + 2e^- \rightleftharpoons HClO_2 + H_2O$	1.181
$ClO_4^- + 2H^+ + 2e^- \rightleftharpoons ClO_3^- + H_2O$	1.201
$ClO_4^-(aq) + H_2O(l) + 2e^- \rightleftharpoons ClO_3^-(aq) + 2OH^-(aq)$	0.17
$ClO_3^-(aq) + H_2O(l) + 2e^- \rightleftharpoons ClO_2^-(aq) + 2OH^-(aq)$	0.35
$ClO_2^-(aq) + H_2O(l) + 2e^- \rightleftharpoons ClO^-(aq) + 2OH^-(aq)$	0.59

Chromium	$E°$ (V)
$Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$	–0.424
$Cr^{2+} + 2e^- \rightleftharpoons Cr(s)$	–0.90
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O(l)$	1.36
$CrO_4^{2-} + 4H_2O(l) + 3e^- \rightleftharpoons 2Cr(OH)_4^- + 4OH^-$	–0.13 in 1 M NaOH

Cobalt	$E°$ (V)
$Co^{2+} + 2e^- \rightleftharpoons Co(s)$	–0.277
$Co^{3+} + e^- \rightleftharpoons Co^{2+}$	1.92
$Co(NH_3)_6^{3+} + e^- \rightleftharpoons Co(NH_3)_6^{2+}$	0.1
$Co(OH)_3(s) + e^- \rightleftharpoons Co(OH)_2(s) + OH^-$	0.17
$Co(OH)_2(s) + 2e^- \rightleftharpoons Co(s) + 2OH^-$	–0.746

Copper	$E°$ (V)
$Cu^+ + e^- \rightleftharpoons Cu(s)$	0.520
$Cu^{2+} + e^- \rightleftharpoons Cu^+$	0.159
$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$	0.3419
$Cu^{2+} + I^- + e^- \rightleftharpoons CuI(s)$	0.86
$Cu^{2+} + Cl^- + e^- \rightleftharpoons CuCl(s)$	0.559

Fluorine	$E°$ (V)
$F_2(g) + 2H^+ + 2e^- \rightleftharpoons 2HF$	3.053
$F_2(g) + 2e^- \rightleftharpoons 2F^-$	2.87

Gallium	$E°$ (V)
$Ga^{3+} + 3e^- \rightleftharpoons Ga(s)$	-0.56

Gold	$E°$ (V)
$Au^+ + e^- \rightleftharpoons Au(s)$	1.83
$Au^{3+} + 2e^- \rightleftharpoons Au^+$	1.36
$Au^{3+} + 3e^- \rightleftharpoons Au(s)$	1.52
$AuCl_4^- + 3e^- \rightleftharpoons Au(s) + 4Cl^-$	1.002

Hydrogen	$E°$ (V)
$2H^+ + 2e^- \rightleftharpoons H_2(g)$	0.00000
$H_2O + e^- \rightleftharpoons ½H_2(g) + OH^-$	–0.828

Iodine	$E°$ (V)
$I_2(s) + 2e^- \rightleftharpoons 2I^-$	0.5355
$I_3^- + 2e^- \rightleftharpoons 3I^-$	0.536
$HIO + H^+ + 2e^- \rightleftharpoons I^- + H_2O(l)$	0.985
$IO_3^- + 6H^+ + 5e^- \rightleftharpoons ½I_2(s) + 3H_2O(l)$	1.195
$IO_3^- + 3H_2O(l) + 6e^- \rightleftharpoons I^- + 6OH^-$	0.257

Iron	$E°$ (V)
$Fe^{2+} + 2e^- \rightleftharpoons Fe(s)$	–0.44
$Fe^{3+} + 3e^- \rightleftharpoons Fe(s)$	–0.037
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	0.771
$Fe(CN)_6^{3-} + e^- \rightleftharpoons Fe(CN)_6^{4-}$	0.356
$Fe(phen)_6^{3+} + e^- \rightleftharpoons Fe(phen)_6^{2+}$	1.147

Lanthanum	$E°$ (V)
$La^{3+} + 3e^- \rightleftharpoons La(s)$	–2.38

Lead	$E°$ (V)
$Pb^{2+} + 2e^- \rightleftharpoons Pb(s)$	–0.126
$PbO_2(s) + 4H^+ + 2e^- \rightleftharpoons Pb^{2+}(aq) + 2H_2O(l)$	1.46
$PbO_2(s) + SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons PbSO_4(s) + 2H_2O(l)$	1.690
$PbSO_4(s) + 2e^- \rightleftharpoons Pb(s) + SO_4^{2-}$	–0.356

Lithium	$E°$ (V)
$Li^+ + e^- \rightleftharpoons Li(s)$	–3.040

Magnesium	$E°$ (V)
$Mg^{2+} + 2e^- \rightleftharpoons Mg(s)$	–2.356
$Mg(OH)_2(s) + 2e^- \rightleftharpoons Mg(s) + 2OH^-$	–2.687

Manganese	$E°$ (V)
$Mn^{2+} + 2e^- \rightleftharpoons Mn(s)$	–1.17
$Mn^{3+} + e^- \rightleftharpoons Mn^{2+}$	1.5
$MnO_2(s) + 4H^+ + 2e^- \rightleftharpoons Mn^{2+} + 2H_2O(l)$	1.23
$MnO_2(s) + 4H^+ + e^- \rightleftharpoons Mn^{3+}(aq) + 2H_2O(I)$	0.95
$MnO_4^- + 4H^+ + 3e^- \rightleftharpoons MnO_2(s) + 2H_2O(l)$	1.70
$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O(l)$	1.51
$MnO_4^- + 2H_2O(l) + 3e^- \rightleftharpoons MnO_2(s) + 4OH^-$	0.60

Mercury	$E°$ (V)
$Hg^{2+} + 2e^- \rightleftharpoons Hg(l)$	0.8535
$2Hg^{2+} + 2e^- \rightleftharpoons Hg_2^{2+}$	0.911
$Hg_2^{2+} + 2e^- \rightleftharpoons 2Hg(l)$	0.7960
$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-$	0.2682
$HgO(s) + 2H^+ + 2e^- \rightleftharpoons Hg(l) + H_2O(l)$	0.926
$Hg_2Br_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Br^-$	1.392
$Hg_2I_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2I^-$	–0.0405

Molybdenum	$E°$ (V)
$Mo^{3+} + 3e^- \rightleftharpoons Mo(s)$	–0.2
$MoO_2(s) + 4H^+ + 4e^- \rightleftharpoons Mo(s) + 2H_2O(l)$	–0.152
$MoO_4^{2-} + 4H_2O(l) + 6e^- \rightleftharpoons Mo(s) + 8OH^-$	–0.913

Nickel	$E°$ (V)
$Ni^{2+} + 2e^- \rightleftharpoons Ni(s)$	–0.257
$Ni(OH)_2 + 2e^- \rightleftharpoons Ni(s) + 2OH^-$	–0.72
$Ni(NH_3)_6^{2+} + 2e^- \rightleftharpoons Ni(s) + 6NH_3$	–0.49

Nitrogen	$E°$ (V)
$N_2(g) + 5H^+ + 4e^- \rightleftharpoons N_2H_5^+$	–0.23
$N_2O(g) + 2H^+ + 2e^- \rightleftharpoons N_2(g) + H_2O(l)$	1.77
$2NO(g) + 2H^+ + 2e^- \rightleftharpoons N_2O(g) + H_2O(l)$	1.59
$HNO_2 + H^+ + e^- \rightleftharpoons NO(g) + H_2O(l)$	0.996
$2HNO_2 + 4H^+ + 4e^- \rightleftharpoons N_2O(g) + 3H_2O(l)$	1.297
$NO_3^- + 3H^+ + 2e^- \rightleftharpoons HNO_2 + H_2O(l)$	0.94
$NO_2(g) + H^+(aq) + e^- \rightleftharpoons HNO_2(aq)$	1.07
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$	0.96

Oxygen	$E°$ (V)
$O_2(g) + 2H^+ + 2e^- \rightleftharpoons H_2O_2$	0.695
$O_2(g) + 4H^+ + 4e^- \rightleftharpoons 2H_2O(l)$	1.229
$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O(l)$	1.763
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-$	0.401
$O_3(g) + 2H^+ + 2e^- \rightleftharpoons O_2(g) + H_2O(l)$	2.07
$O_2(g) + e^- \rightleftharpoons O_2^-(aq)$	-0.33
$O_2(aq) + e^- \rightleftharpoons O_2^-(aq)$	-0.16

Phosphorous	$E°$ (V)
$P(s, white) + 3H^+ + 3e^- \rightleftharpoons PH_3(g)$	0.06
$H_3PO_3 + 2H^+ + 2e^- \rightleftharpoons H_3PO_2 + H_2O(l)$	-0.50
$H_3PO_4 + 2H^+ + 2e^- \rightleftharpoons H_3PO_3 + H_2O(l)$	-0.28

Platinum	$E°$ (V)
$Pt^{2+} + 2e^- \rightleftharpoons Pt(s)$	1.2
$PtCl_4^{2-} + 2e^- \rightleftharpoons Pt(s) + 4Cl^-$	0.73
$PtCl_6^{2-} + 2e^- \rightleftharpoons PtCl_4^{2-} + 2Cl^-$	0.68

Potassium	$E°$ (V)
$K^+ + e^- \rightleftharpoons K(s)$	-2.93

Rubidium	$E°$ (V)
$Rb^+ + e^- \rightleftharpoons Rb\ (s)$	-2.98

Ruthenium	$E°$ (V)
$Ru^{3+} + e^- \rightleftharpoons Ru^{2+}$	0.249
$RuO_2(s) + 4H^+ + 4e^- \rightleftharpoons Ru(s) + 2H_2O(l)$	0.68
$Ru(NH_3)_6^{3+} + e^- \rightleftharpoons Ru(s) + Ru(NH_3)_6^{2+}$	0.10
$Ru(CN)_6^{3-} + e^- \rightleftharpoons Ru(s) + Ru(CN)_6^{4-}$	0.86

Selenium	$E°$ (V)
$Se(s) + 2e^- \rightleftharpoons Se^{2-}$	–0.67 in 1 M NaOH
$Se(s) + 2H^+ + 2e^- \rightleftharpoons H_2Se(g)$	–0.115
$H_2SeO_3 + 4H^+ + 4e^- \rightleftharpoons Se(s) + 3H_2O(l)$	0.74
$SeO_4^{3-} + 4H^+ + e^- \rightleftharpoons H_2SeO_3 + H_2O(l)$	1.151

Silicon	$E°$ (V)
$SiF_6^{2-} + 4e^- \rightleftharpoons Si(s) + 6F^-$	–1.37
$SiO_2(s) + 4H^+ + 4e^- \rightleftharpoons Si(s) + 2H_2O(l)$	–0.909
$SiO_2(s) + 8H^+ + 8e^- \rightleftharpoons SiH_4(g) + 2H_2O(l)$	–0.516

Silver	$E°$ (V)
$Ag^+ + e^- \rightleftharpoons Ag(s)$	0.7996
$AgBr(s) + e^- \rightleftharpoons Ag(s) + Br^-$	0.071
$Ag_2C_2O_4(s) + 2e^- \rightleftharpoons 2Ag(s) + C_2O_4^{2-}$	0.47
$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-$	0.2223
$AgI(s) + e^- \rightleftharpoons Ag(s) + I^-$	–0.152
$Ag_2S(s) + 2e^- \rightleftharpoons 2Ag(s) + S^{2-}$	–0.71
$Ag(NH_3)_2^+ + e^- \rightleftharpoons Ag(s) + 2NH_3$	–0.373

Sodium	$E°$ (V)
$Na^+ + e^- \rightleftharpoons Na(s)$	–2.713

Strontium	$E°$ (V)
$Sr^{2+} + 2e^- \rightleftharpoons Sr(s)$	–2.89

Sulfur	$E°$ (V)
$\boldsymbol{S(s) + 2e^- \rightleftharpoons S^{2-}}$	–0.407
$S(s) + 2H^+ + 2e^- \rightleftharpoons H_2S$	0.144
$S_2O_6^{2-} + 4H^+ + 2e^- \rightleftharpoons 2H_2SO_3$	0.569
$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$	1.96
$S_4O_6^{2-} + 2e^- \rightleftharpoons 2S_2O_3^{2-}$	0.080
$2SO_3^{2-} + 2H_2O(l) + 2e^- \rightleftharpoons S_2O_4^{2-} + 4OH^-$	–1.13
$2SO_3^{2-} + 3H_2O(l) + 4e^- \rightleftharpoons S_2O_3^{2-} + 6OH^-$	
$2SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons S_2O_6^{2-} + 2H_2O(l)$	–0.25
$SO_4^{2-} + H_2O(l) + 2e^- \rightleftharpoons SO_3^{2-} + 2OH^-$	–0.936
$SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons H_2SO_3^{2-} + H_2O(l)$	0.172

Thallium	$E°$ (V)
$\boldsymbol{Tl^{3+} + 2e^- \rightleftharpoons Tl^+}$	0.77 in 1 M HCl
$Tl^{3+} + 3e^- \rightleftharpoons Tl(s)$	0.742

Tin	$E°$ (V)
$Sn^{2+} + 2e^- \rightleftharpoons Sn(s)$	-0.14
$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$	0.154

Titanium	$E°$ (V)
$\boldsymbol{Ti^{2+} + 2e^- \rightleftharpoons Ti(s)}$	–0.163
$Ti^{3+} + e^- \rightleftharpoons Ti^{2+}$	–0.37

Tungsten	$E°$ (V)
$\boldsymbol{WO_2(s) + 4H^+ + 4e^- \rightleftharpoons W(s) + 2H_2O(l)}$	–0.119
$WO_3(s) + 6H^+ + 6e^- \rightleftharpoons W(s) + 3H_2O(l)$	–0.090

Uranium	$E°$ (V)
$U^{3+} + 3e^- \rightleftharpoons U(s)$	–1.66
$U^{4+} + e^- \rightleftharpoons U^{3+}$	–0.52
$UO_2^+ + 4H^+ + e^- \rightleftharpoons U^{4+} + 2H_2O(l)$	0.27
$UO_2^{2+} + e^- \rightleftharpoons UO_2^+$	0.16
$UO_2^{2+} + 4H^+ + 2e^- \rightleftharpoons U^{4+} + 2H_2O(l)$	0.327

Vanadium	$E°$ (V)
$V^{2+} + 2e^- \rightleftharpoons V(s)$	–1.13
$V^{3+} + e^- \rightleftharpoons V^{2+}$	–0.255
$VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O(l)$	0.337
$VO_2^{2+} + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O(l)$	1.000

Zinc	$E°$ (V)
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	–0.7618
$Zn(OH)_4^{2-} + 2e^- \rightleftharpoons Zn(s) + 4OH^-$	–1.285
$Zn(NH_3)_4^{2+} + 2e^- \rightleftharpoons Zn(s) + 4NH_3$	–1.04
$Zn(CN)_4^{2-} + 2e^- \rightleftharpoons Zn(s) + 4CN$	–1.34
$ZnO_2 + 4H^+ + 4e^- \rightleftharpoons Zn(s) + 2H_2O$	-1.473

Contributors and Attributions

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GLOSSARY

Accuracy | how closely a measurement aligns with a correct value

Acid anhydride | compound that reacts with water to form an acid or acidic solution

Acid ionization | reaction involving the transfer of a proton from an acid to water, yielding hydronium ions and the conjugate base of the acid

Acid ionization constant (K_a) | equilibrium constant for the ionization of a weak acid

Acid-base indicator | organic acid or base whose color changes depending on the pH of the solution it is in

Acidic | describes a solution in which $[H_3O^+] > [OH^-]$

Actinide | inner transition metal in the bottom of the bottom two rows of the periodic table

Actinide series | (also, actinoid series) actinium and the elements in the second row or the *f*-block, atomic numbers 89–103

Activated complex | (also, transition state) unstable combination of reactant species representing the highest energy state of a reaction system

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

Active electrode | electrode that participates in the oxidation-reduction reaction of an electrochemical cell; the mass of an active electrode changes during the oxidation-reduction reaction

Actual yield | amount of product formed in a reaction

Addition reaction | reaction in which a double carbon-carbon bond forms a single carbon-carbon bond by the addition of a reactant. Typical reaction for an alkene.

Adhesive force | force of attraction between molecules of different chemical identities

Alcohol | organic compound with a hydroxyl group (–OH) bonded to a carbon atom

Alkali metal | element in group 1

Alkaline earth metal | element in group 2

Alkaline earth metal | any of the metals (beryllium, magnesium, calcium, strontium, barium, and radium) occupying group 2 of the periodic table; they are reactive, divalent metals that form basic oxides

Alkane | molecule consisting of only carbon and hydrogen atoms connected by single (σ) bonds

Alkene | molecule consisting of carbon and hydrogen containing at least one carbon-carbon double bond

Alkyl group | substituent, consisting of an alkane missing one hydrogen atom, attached to a larger structure

Alkyne | molecule consisting of carbon and hydrogen containing at least one carbon-carbon triple bond

Allotropes | two or more forms of the same element, in the same physical state, with different chemical structures

Alloy | solid mixture of a metallic element and one or more additional elements

Alpha (α) decay | loss of an alpha particle during radioactive decay

Alpha particle | (α or ^4_2He or $^4_2\alpha$) high-energy helium nucleus; a helium atom that has lost two electrons and contains two protons and two neutrons

Alpha particle (α particle) | positively charged particle consisting of two protons and two neutrons

Amide | organic molecule that features a nitrogen atom connected to the carbon atom in a carbonyl group

Amine | organic molecule in which a nitrogen atom is bonded to one or more alkyl group

Amorphous | solid material such as a glass that does not have a regular repeating component to its three-dimensional structure; a solid but not a crystal

Amorphous solid | (also, noncrystalline solid) solid in which the particles lack an ordered internal structure

Amphiphilic | molecules possessing both hydrophobic (nonpolar) and a hydrophilic (polar) parts

Amphiprotic | species that may either gain or lose a proton in a reaction

Amphoteric | species that can act as either an acid or a base

Amplitude | extent of the displacement caused by a wave (for sinusoidal waves, it is one-half the difference from the peak height to the trough depth, and the intensity is proportional to the square of the amplitude)

Analyte | chemical species of interest

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

Anion | negatively charged atom or molecule (contains more electrons than protons)

Anode | electrode in an electrochemical cell at which oxidation occurs; information about the anode is recorded on the left side of the salt bridge in cell notation

Antimatter | particles with the same mass but opposite properties (such as charge) of ordinary particles

Aqueous solution | solution for which water is the solvent

Aromatic hydrocarbon | cyclic molecule consisting of carbon and hydrogen with delocalized alternating carbon-carbon single and double bonds, resulting in enhanced stability

Arrhenius equation | mathematical relationship between the rate constant and the activation energy of a reaction

Atmosphere (atm) | unit of pressure; 1 atm = 101,325 Pa

Atom | smallest particle of an element that can enter into a chemical combination

Atomic mass | average mass of atoms of an element, expressed in amu

Atomic mass unit (amu) | (also, unified atomic mass unit, u, or Dalton, Da) unit of mass equal to $\frac{1}{12}$ of the mass of a ^{12}C atom

Atomic number (Z) | number of protons in the nucleus of an atom

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

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

Autoionization | reaction between identical species yielding ionic products; for water, this reaction involves transfer of protons to yield hydronium and hydroxide ions

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

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

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

Balanced equation | chemical equation with equal numbers of atoms for each element in the reactant and product

Band of stability | (also, belt of stability, zone of stability, or valley of stability) region of graph of number of protons versus number of neutrons containing stable (nonradioactive) nuclides

Bar | (bar or b) unit of pressure; 1 bar = 100,000 Pa

Barometer | device used to measure atmospheric pressure

Base anhydride | metal oxide that behaves as a base towards acids

Base ionization | reaction involving the transfer of a proton from water to a base, yielding hydroxide ions and the conjugate acid of the base

Base ionization constant (K_b) | equilibrium constant for the ionization of a weak base

Basic | describes a solution in which $[H_3O^+] < [OH^-]$

Becquerel (Bq) | SI unit for rate of radioactive decay; 1 Bq = 1 disintegration/s

Beta (β) decay | breakdown of a neutron into a proton, which remains in the nucleus, and an electron, which is emitted as a beta particle

Beta particle | (β or ${}^{0}_{-1}e$ or ${}^{0}_{-1}\beta$) high-energy electron

Bicarbonate anion | salt of the hydrogen carbonate ion, HCO_3^-

Bidentate ligand | ligand that coordinates to one central metal through coordinate bonds from two different atoms

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

Binary compound | compound containing two different elements.

Binding energy per nucleon | total binding energy for the nucleus divided by the number of nucleons in the nucleus

Bismuth | heaviest member of group 15; a less reactive metal than other representative metals

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

Body-centered cubic (BCC) solid | crystalline structure that has a cubic unit cell with lattice points at the corners and in the center of the cell

Body-centered cubic unit cell | simplest repeating unit of a body-centered cubic crystal; it is a cube containing lattice points at each corner and in the center of the cube

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

Boiling point | temperature at which the vapor pressure of a liquid equals the pressure of the gas above it

Boiling point elevation | elevation of the boiling point of a liquid by addition of a solute

Boiling point elevation constant | the proportionality constant in the equation relating boiling point elevation to solute molality; also known as the ebullioscopic constant

Bomb calorimeter | device designed to measure the energy change for processes occurring under conditions of constant volume; commonly used for reactions involving solid and gaseous reactants or products

Bond angle | angle between any two covalent bonds that share a common atom

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

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

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

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

Borate | compound containing boron-oxygen bonds, typically with clusters or chains as a part of the chemical structure

Born-Haber cycle | thermochemical cycle relating the various energetic steps involved in the formation of an ionic solid from the relevant elements

Bragg equation | equation that relates the angles at which X-rays are diffracted by the atoms within a crystal

Brønsted-Lowry acid | proton donor

Brønsted-Lowry base | proton acceptor

Buffer | mixture of a weak acid or a weak base and the salt of its conjugate; the pH of a buffer resists change when small amounts of acid or base are added

Buffer capacity | amount of an acid or base that can be added to a volume of a buffer solution before its pH changes significantly (usually by one pH unit)

Buret | device used for the precise delivery of variable liquid volumes, such as in a titration analysis

Calorie (cal) | unit of heat or other energy; the amount of energy required to raise 1 gram of water by 1 degree Celsius; 1 cal is defined as 4.184 J

Calorimeter | device used to measure the amount of heat absorbed or released in a chemical or physical process

Calorimetry | process of measuring the amount of heat involved in a chemical or physical process

Capillary action | flow of liquid within a porous material due to the attraction of the liquid molecules to the surface of the material and to other liquid molecules

Carbonate | salt of the anion CO_3^{2-}; often formed by the reaction of carbon dioxide with bases

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

Cathode | electrode in an electrochemical cell at which reduction occurs; information about the cathode is recorded on the right side of the salt bridge in cell notation

Cathodic protection | method of protecting metal by using a sacrificial anode and effectively making the metal that needs protecting the cathode, thus preventing its oxidation

Cation | positively charged atom or molecule (contains fewer electrons than protons)

Cell notation | shorthand way to represent the reactions in an electrochemical cell

Cell potential | difference in electrical potential that arises when dissimilar metals are connected; the driving force for the flow of charge (current) in oxidation-reduction reactions

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

Central metal | ion or atom to which one or more ligands is attached through coordinate covalent bonds

Chain reaction | repeated fission caused when the neutrons released in fission bombard other atoms

Chalcogen | element in group 16

Chelate | complex formed from a polydentate ligand attached to a central metal

Chelating ligand | ligand that attaches to a central metal ion by bonds from two or more donor atoms

Chemical change | change producing a different kind of matter from the original kind of matter

Chemical equation | symbolic representation of a chemical reaction

Chemical property | behavior that is related to the change of one kind of matter into another kind of matter

Chemical reduction | method of preparing a representative metal using a reducing agent

Chemical symbol | one-, two-, or three-letter abbreviation used to represent an element or its atoms

Chemical thermodynamics | area of science that deals with the relationships between heat, work, and all forms of energy associated with chemical and physical processes

Chemistry | study of the composition, properties, and interactions of matter

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

Chlor-alkali process | electrolysis process for the synthesis of chlorine and sodium hydroxide

Circuit | path taken by a current as it flows because of an electrical potential difference

***cis* configuration** | configuration of a geometrical isomer in which two similar groups are on the same side of an imaginary reference line on the molecule

Clausius-Clapeyron equation | mathematical relationship between the temperature, vapor pressure, and enthalpy of vaporization for a substance

Coefficient | number placed in front of symbols or formulas in a chemical equation to indicate their relative amount

Cohesive force | force of attraction between identical molecules

Colligative property | property of a solution that depends only on the concentration of a solute species

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

Colloid | (also, colloidal dispersion) mixture in which relatively large solid or liquid particles are dispersed uniformly throughout a gas, liquid, or solid

Color-change interval | range in pH over which the color change of an indicator takes place

Combustion analysis | gravimetric technique used to determine the elemental composition of a compound via the collection and weighing of its gaseous combustion products

Common ion effect | effect on equilibrium when a substance with an ion in common with the dissolved species is added to the solution; causes a decrease in the solubility of an ionic species, or a decrease in the ionization of a weak acid or base

Complete ionic equation | chemical equation in which all dissolved ionic reactants and products, including spectator ions, are explicitly represented by formulas for their dissociated ions

Compound | pure substance that can be decomposed into two or more elements

Compressibility factor (Z) | ratio of the experimentally measured molar volume for a gas to its molar volume as computed from the ideal gas equation

Concentrated | qualitative term for a solution containing solute at a relatively high concentration

Concentration | quantitative measure of the relative amounts of solute and solvent present in a solution

Concentration cell | galvanic cell in which the two half-cells are the same except for the concentration of the solutes; spontaneous when the overall reaction is the dilution of the solute

Condensation | change from a gaseous to a liquid state

Conjugate acid | substance formed when a base gains a proton

Conjugate base | substance formed when an acid loses a proton

Containment system | (also, shield) a three-part structure of materials that protects the exterior of a nuclear fission reactor and operating personnel from the high temperatures, pressures, and radiation levels inside the reactor

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

Control rod | material inserted into the fuel assembly that absorbs neutrons and can be raised or lowered to adjust the rate of a fission reaction

Coordination compound | stable compound in which the central metal atom or ion acts as a Lewis acid and accepts one or more pairs of electrons

Coordination compound | substance consisting of atoms, molecules, or ions attached to a central atom through Lewis acid-base interactions

Coordination number | number of atoms closest to any given atom in a crystal or to the central metal atom in a complex

Coordination number | number of coordinate covalent bonds to the central metal atom in a complex or the number of closest contacts to an atom in a crystalline form

Coordination sphere | central metal atom or ion plus the attached ligands of a complex

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

Corrosion | degradation of metal through an electrochemical process

Covalent bond | attractive force between the nuclei of a molecule's atoms and pairs of electrons between the atoms

Covalent bond | bond formed when electrons are shared between atoms

Covalent compound | (also, molecular compound) composed of molecules formed by atoms of two or more different elements

Covalent network solid | solid whose particles are held together by covalent bonds

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

Crenation | process whereby biological cells become shriveled due to loss of water by osmosis

Critical mass | amount of fissionable material that will support a self-sustaining (nuclear fission) chain reaction

Critical point | temperature and pressure above which a gas cannot be condensed into a liquid

Crystal field splitting (Δ_{oct}) | difference in energy between the t_{2g} and e_g sets or t and e sets of orbitals

Crystal field theory | model that explains the energies of the orbitals in transition metals in terms of electrostatic interactions with the ligands but does not include metal ligand bonding

Crystalline solid | solid in which the particles are arranged in a definite repeating pattern

Cubic centimeter (cm^3 or cc) | volume of a cube with an edge length of exactly 1 cm

Cubic closest packing (CCP) | crystalline structure in which planes of closely packed atoms or ions are stacked as a series of three alternating layers of different relative orientations (ABC)

Cubic meter (m^3) | SI unit of volume

Curie (Ci) | larger unit for rate of radioactive decay frequently used in medicine; 1 Ci = 3.7×10^{10} disintegrations/s

Current | flow of electrical charge; the SI unit of charge is the coulomb (C) and current is measured in amperes $\left(\mathbf{1\ A = 1\ \frac{C}{s}}\right)$

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

***d*-block element** | one of the elements in groups 3–11 with valence electrons in *d* orbitals

Dalton (Da) | alternative unit equivalent to the atomic mass unit

Dalton's atomic theory | set of postulates that established the fundamental properties of atoms

Daughter nuclide | nuclide produced by the radioactive decay of another nuclide; may be stable or may decay further

Density | ratio of mass to volume for a substance or object

Deposition | change from a gaseous state directly to a solid state

Diffraction | redirection of electromagnetic radiation that occurs when it encounters a physical barrier of appropriate dimensions

Dilute | qualitative term for a solution containing solute at a relatively low concentration

Dilution | process of adding solvent to a solution in order to lower the concentration of solutes

Dimensional analysis | (also, factor-label method) versatile mathematical approach that can be applied to computations ranging from simple unit conversions to more complex, multi-step calculations involving several different quantities

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

Dipole-dipole attraction | intermolecular attraction between two permanent dipoles

Diprotic acid | acid containing two ionizable hydrogen atoms per molecule. A diprotic acid ionizes in two steps

Diprotic base | base capable of accepting two protons. The protons are accepted in two steps

Dispersed phase | substance present as relatively large solid or liquid particles in a colloid

Dispersion force | (also, London dispersion force) attraction between two rapidly fluctuating, temporary dipoles; significant only when particles are very close together

Dispersion medium | solid, liquid, or gas in which colloidal particles are dispersed

Disproportionation reaction | chemical reaction where a single reactant is simultaneously reduced and oxidized; it is both the reducing agent and the oxidizing agent

Dissociation | physical process accompanying the dissolution of an ionic compound in which the compound's constituent ions are solvated and dispersed throughout the solution

Dissolved | describes the process by which solute components are dispersed in a solvent

Donor atom | atom in a ligand with a lone pair of electrons that forms a coordinate covalent bond to a central metal

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

Downs cell | electrochemical cell used for the commercial preparation of metallic sodium (and chlorine) from molten sodium chloride

Dynamic equilibrium | state of a system in which reciprocal processes are occurring at equal rates

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

e_g orbitals | set of two *d* orbitals that are oriented on the Cartesian axes for coordination complexes; in octahedral complexes, they are higher in energy than the t_{2g} orbitals

Electrical potential | energy per charge; in electrochemical systems, it depends on the way the charges are distributed within the system; the SI unit of electrical potential is the volt $\left(1\,\mathrm{V} = 1\,\frac{\mathrm{J}}{\mathrm{C}}\right)$

Electrical work (w_{ele}) | negative of total charge times the cell potential; equal to w_{max} for the system, and so equals the free energy change (ΔG)

Electrolyte | substance that produces ions when dissolved in water

Electromagnetic radiation | energy transmitted by waves that have an electric-field component and a magnetic-field component

Electromagnetic spectrum | range of energies that electromagnetic radiation can comprise, including radio, microwaves, infrared, visible, ultraviolet, X-rays, and gamma rays; since electromagnetic radiation energy is proportional to the frequency and inversely proportional to the wavelength, the spectrum can also be specified by ranges of frequencies or wavelengths

Electron | negatively charged, subatomic particle of relatively low mass located outside the nucleus

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

Electron capture | combination of a core electron with a proton to yield a neutron within the nucleus

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

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

Electron volt (eV) | measurement unit of nuclear binding energies, with 1 eV equaling the amount energy due to the moving an electron across an electric potential difference of 1 volt

Electron-pair geometry | arrangement around a central atom of all regions of electron density (bonds, lone pairs, or unpaired electrons)

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

Element | substance that is composed of a single type of atom; a substance that cannot be decomposed by a chemical change

Empirical formula | formula showing the composition of a compound given as the simplest whole-number ratio of atoms

Empirical formula mass | sum of average atomic masses for all atoms represented in an empirical formula

Emulsifying agent | amphiphilic substance used to stabilize the particles of some emulsions

Emulsion | colloid formed from immiscible liquids

End point | measured volume of titrant solution that yields the change in sample solution appearance or other property expected for stoichiometric equivalence (see *equivalence point*)

Endothermic process | chemical reaction or physical change that absorbs heat

Energy | capacity to supply heat or do work

Enthalpy (*H*) | sum of a system's internal energy and the mathematical product of its pressure and volume

Enthalpy change (ΔH) | heat released or absorbed by a system under constant pressure during a chemical or physical process

Entropy (*S*) | state function that is a measure of the matter and/or energy dispersal within a system, determined by the number of system microstates often described as a measure of the disorder of the system

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

Equilibrium | in chemical reactions, the state in which the conversion of reactants into products and the conversion of products back into reactants occur simultaneously at the same rate; state of balance

Equilibrium constant (*K*) | value of the reaction quotient for a system at equilibrium

Equivalence point | volume of titrant solution required to react completely with the analyte in a titration analysis; provides a stoichiometric amount of titrant for the sample's analyte according to the titration reaction

Ether | organic compound with an oxygen atom that is bonded to two carbon atoms

Exact number | number derived by counting or by definition

Excess reactant | reactant present in an amount greater than required by the reaction stoichiometry

Excited state | state having an energy greater than the ground-state energy

Exothermic process | chemical reaction or physical change that releases heat

Expansion work (pressure-volume work) | work done as a system expands or contracts against external pressure

Extensive property | property of a substance that depends on the amount of the substance

External beam radiation therapy | radiation delivered by a machine outside the body

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

***f*-block element** | (also, inner transition element) one of the elements with atomic numbers 58–71 or 90–103 that have valence electrons in *f* orbitals; they are frequently shown offset below the periodic table

Face-centered cubic (FCC) solid | crystalline structure consisting of a cubic unit cell with lattice points on the corners and in the center of each face

Face-centered cubic unit cell | simplest repeating unit of a face-centered cubic crystal; it is a cube containing lattice points at each corner and in the center of each face

Fahrenheit | unit of temperature; water freezes at 32 °F and boils at 212 °F on this scale

Faraday's constant (F) | charge on 1 mol of electrons; F = 96,485 C/mol e^-

First law of thermodynamics | internal energy of a system changes due to heat flow in or out of the system or work done on or by the system

First transition series | transition elements in the fourth period of the periodic table (first row of the *d*-block), atomic numbers 21–29

Fissile (or fissionable) | when a material is capable of sustaining a nuclear fission reaction

Fission | splitting of a heavier nucleus into two or more lighter nuclei, usually accompanied by the conversion of mass into large amounts of energy

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

Formula mass | sum of the average masses for all atoms represented in a chemical formula; for covalent compounds, this is also the molecular mass

Fourth transition series | transition elements in the seventh period of the periodic table (fourth row of the *d*-block), atomic numbers 89 and 104–111

Frasch process | important in the mining of free sulfur from enormous underground deposits

Free radical | molecule that contains an odd number of electrons

Freezing | change from a liquid state to a solid state

Freezing point | temperature at which the solid and liquid phases of a substance are in equilibrium; see also *melting point*

Freezing point depression | lowering of the freezing point of a liquid by addition of a solute

Freezing point depression constant | (also, cryoscopic constant) proportionality constant in the equation relating freezing point depression to solute molality

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

Frequency factor (A) | proportionality constant in the Arrhenius equation, related to the relative number of collisions having an orientation capable of leading to product formation

Functional group | part of an organic molecule that imparts a specific chemical reactivity to the molecule

Fundamental unit of charge | (also called the elementary charge) equals the magnitude of the charge of an electron (e) with $e = 1.602 \times 10^{-19}$ C

Fusion | combination of very light nuclei into heavier nuclei, accompanied by the conversion of mass into large amounts of energy

Fusion reactor | nuclear reactor in which fusion reactions of light nuclei are controlled

Galvanic cell | electrochemical cell that involves a spontaneous oxidation-reduction reaction; electrochemical cells with positive cell potentials; also called a voltaic cell

Galvanized iron | method for protecting iron by covering it with zinc, which will oxidize before the iron; zinc-plated iron

Gamma (γ) emission | decay of an excited-state nuclide accompanied by emission of a gamma ray

Gamma ray | (γ or ${}^{0}_{0}\gamma$) short wavelength, high-energy electromagnetic radiation that exhibits wave-particle duality

Gas | state in which matter has neither definite volume nor shape

Geiger counter | instrument that detects and measures radiation via the ionization produced in a Geiger-Müller tube

Gel | colloidal dispersion of a liquid in a solid

Geometric isomers | isomers that differ in the way in which atoms are oriented in space relative to each other, leading to different physical and chemical properties

Gibbs free energy change (G) | thermodynamic property defined in terms of system enthalpy and entropy; all spontaneous processes involve a decrease in G

Gravimetric analysis | quantitative chemical analysis method involving the separation of an analyte from a sample by a physical or chemical process and subsequent mass measurements of the analyte, reaction product, and/or sample

Gray (Gy) | SI unit for measuring radiation dose; 1 Gy = 1 J absorbed/kg tissue

Ground state | state in which the electrons in an atom, ion, or molecule have the lowest energy possible

Group | vertical column of the periodic table

Haber process | main industrial process used to produce ammonia from nitrogen and hydrogen; involves the use of an iron catalyst and elevated temperatures and pressures

Half-life ($t_{1/2}$) | time required for half of the atoms in a radioactive sample to decay

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

Half-reaction method | method that produces a balanced overall oxidation-reduction reaction by splitting the reaction into an oxidation "half" and reduction "half," balancing the two half-reactions, and then combining the oxidation half-reaction and reduction half-reaction in such a way that the number of electrons generated by the oxidation is exactly canceled by the number of electrons required by the reduction

Halide | compound containing an anion of a group 17 element in the 1− oxidation state (fluoride, F^-; chloride, Cl^-; bromide, Br^-; and iodide, I^-)

Hall–Héroult cell | electrolysis apparatus used to isolate pure aluminum metal from a solution of alumina in molten cryolite

Halogen | element in group 17

Heat (q) | transfer of thermal energy between two bodies

Heat capacity (C) | extensive property of a body of matter that represents the quantity of heat required to increase its temperature by 1 degree Celsius (or 1 kelvin)

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

Hemolysis | rupture of red blood cells due to the accumulation of excess water by osmosis

Henderson-Hasselbalch equation | equation used to calculate the pH of buffer solutions

Henry's law | law stating the proportional relationship between the concentration of dissolved gas in a solution and the partial pressure of the gas in contact with the solution

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

Hess's law | if a process can be represented as the sum of several steps, the enthalpy change of the process equals the sum of the enthalpy changes of the steps

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

Heterogeneous equilibria | equilibria between reactants and products in different phases

Heterogeneous mixture | combination of substances with a composition that varies from point to point

Hexagonal closest packing (HCP) | crystalline structure in which close packed layers of atoms or ions are stacked as a series of two alternating layers of different relative orientations (AB)

High-spin complex | complex in which the electrons maximize the total electron spin by singly populating all of the orbitals before pairing two electrons into the lower-energy orbitals

Hole | (also, interstice) space between atoms within a crystal

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

Homogeneous equilibria | equilibria within a single phase

Homogeneous mixture | (also, solution) combination of substances with a composition that is uniform throughout

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

Hydrocarbon | compound composed only of hydrogen and carbon; the major component of fossil fuels

Hydrogen bonding | occurs when exceptionally strong dipoles attract; bonding that exists when hydrogen is bonded to one of the three most electronegative elements: F, O, or N

Hydrogen carbonate | salt of carbonic acid, H_2CO_3 (containing the anion $\mathbf{HCO_3^-}$) in which one hydrogen atom has been replaced; an acid carbonate; also known as *bicarbonate ion*

Hydrogen halide | binary compound formed between hydrogen and the halogens: HF, HCl, HBr, and HI

Hydrogen sulfate | $\mathbf{HSO_4^-}$ ion

Hydrogen sulfite | $\mathbf{HSO_3^-}$ ion

Hydrogenation | addition of hydrogen (H_2) to reduce a compound

Hydrometallurgy | process in which a metal is separated from a mixture by first converting it into soluble ions, extracting the ions, and then reducing the ions to precipitate the pure metal

Hydrostatic pressure | pressure exerted by a fluid due to gravity

Hydroxide | compound of a metal with the hydroxide ion OH^- or the group −OH

Hypertonic | of greater osmotic pressure

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

Hypothesis | tentative explanation of observations that acts as a guide for gathering and checking information

Hypotonic | of less osmotic pressure

Ideal solution | solution that forms with no accompanying energy change

Immiscible | of negligible mutual solubility; typically refers to liquid substances

Indicator | substance added to the sample in a titration analysis to permit visual detection of the end point

Induced dipole | temporary dipole formed when the electrons of an atom or molecule are distorted by the instantaneous dipole of a neighboring atom or molecule

Inert electrode | electrode that allows current to flow, but that does not otherwise participate in the oxidation-reduction reaction in an electrochemical cell; the mass of an inert electrode does not change during the oxidation-reduction reaction; inert electrodes are often made of platinum or gold because these metals are chemically unreactive.

Inert gas | (also, noble gas) element in group 18

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

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

Inner transition metal | (also, lanthanide or actinide) element in the bottom two rows; if in the first row, also called lanthanide, or if in the second row, also called actinide

Instantaneous dipole | temporary dipole that occurs for a brief moment in time when the electrons of an atom or molecule are distributed asymmetrically

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

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

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

Intensive property | property of a substance that is independent of the amount of the substance

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

Interhalogen | compound formed from two or more different halogens

Intermolecular force | noncovalent attractive force between atoms, molecules, and/or ions

Internal energy (U) | total of all possible kinds of energy present in a substance or substances

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

Interstitial sites | spaces between the regular particle positions in any array of atoms or ions

Ion | electrically charged atom or molecule (contains unequal numbers of protons and electrons)

Ion pair | solvated anion/cation pair held together by moderate electrostatic attraction

Ion-dipole attraction | electrostatic attraction between an ion and a polar molecule

Ion-product constant for water (K_w) | equilibrium constant for the autoionization of water

Ionic bond | electrostatic forces of attraction between the oppositely charged ions of an ionic compound

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

Ionic compound | compound composed of cations and anions combined in ratios, yielding an electrically neutral substance

Ionic solid | solid composed of positive and negative ions held together by strong electrostatic attractions

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

Ionization isomer | (or coordination isomer) isomer in which an anionic ligand is replaced by the counter ion in the inner coordination sphere

Ionizing radiation | radiation that can cause a molecule to lose an electron and form an ion

Isoelectronic | group of ions or atoms that have identical electron configurations

Isomers | compounds with the same chemical formula but different structures

Isomorphous | possessing the same crystalline structure

Isotonic | of equal osmotic pressure

Isotopes | atoms that contain the same number of protons but different numbers of neutrons

Joule (J) | SI unit of energy; 1 joule is the kinetic energy of an object with a mass of 2 kilograms moving with a velocity of 1 meter per second, 1 J = 1 kg m^2/s and 4.184 J = 1 cal

K_c | equilibrium constant for reactions based on concentrations of reactants and products

Kelvin (K) | SI unit of temperature; 273.15 K = 0 ºC

Kilogram (kg) | standard SI unit of mass; 1 kg = approximately 2.2 pounds

Kinetic energy | energy of a moving body, in joules, equal to $\frac{1}{2}mv^2$ (where m = mass and v = velocity)

K_P | equilibrium constant for gas-phase reactions based on partial pressures of reactants and products

Lanthanide | inner transition metal in the top of the bottom two rows of the periodic table

Lanthanide series | (also, lanthanoid series) lanthanum and the elements in the first row or the *f*-block, atomic numbers 57–71

Lattice energy ($\Delta H_{lattice}$) | energy required to separate one mole of an ionic solid into its component gaseous ions

Law | statement that summarizes a vast number of experimental observations, and describes or predicts some aspect of the natural world

Law of conservation of matter | when matter converts from one type to another or changes form, there is no detectable change in the total amount of matter present

Law of constant composition | (also, law of definite proportions) all samples of a pure compound contain the same elements in the same proportions by mass

Law of definite proportions | (also, law of constant composition) all samples of a pure compound contain the same elements in the same proportions by mass

Law of mass action | when a reversible reaction has attained equilibrium at a given temperature, the reaction quotient remains constant

Law of multiple proportions | when two elements react to form more than one compound, a fixed mass of one element will react with masses of the other element in a ratio of small whole numbers

Le Chatelier's principle | when a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance

Length | measure of one dimension of an object

Leveling effect of water | any acid stronger than H_3O^+, or any base stronger than OH^- will react with water to form H_3O^+, or OH^-, respectively; water acts as a base to make all strong acids appear equally strong, and it acts as an acid to make all strong bases appear equally strong

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

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

Ligand | ion or neutral molecule attached to the central metal ion in a coordination compound

Limiting reactant | reactant present in an amount lower than required by the reaction stoichiometry, thus limiting the amount of product generated

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

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

Linkage isomer | coordination compound that possesses a ligand that can bind to the transition metal in two different ways (CN^- vs. NC^-)

Liquid | state of matter that has a definite volume but indefinite shape

Liter (L) | (also, cubic decimeter) unit of volume; 1 L = 1,000 cm^3

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

Low-spin complex | complex in which the electrons minimize the total electron spin by pairing in the lower-energy orbitals before populating the higher-energy orbitals

Macroscopic domain | realm of everyday things that are large enough to sense directly by human sight and touch

Magic number | nuclei with specific numbers of nucleons that are within the band of stability

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

Main-group element | (also, representative element) element in columns 1, 2, and 12–18

Manometer | device used to measure the pressure of a gas trapped in a container

Mass | fundamental property indicating amount of matter

Mass defect | difference between the mass of an atom and the summed mass of its constituent subatomic particles (or the mass "lost" when nucleons are brought together to form a nucleus)

Mass number (A) | sum of the numbers of neutrons and protons in the nucleus of an atom

Mass percentage | ratio of solute-to-solution mass expressed as a percentage

Mass-energy equivalence equation | Albert Einstein's relationship showing that mass and energy are equivalent

Mass-volume percent | ratio of solute mass to solution volume, expressed as a percentage

Matter | anything that occupies space and has mass

Melting | change from a solid state to a liquid state

Melting point | temperature at which the solid and liquid phases of a substance are in equilibrium; see also *freezing point*

Metal | element that is shiny, malleable, good conductor of heat and electricity

Metal (representative) | atoms of the metallic elements of groups 1, 2, 12, 13, 14, 15, and 16, which form ionic compounds by losing electrons from their outer *s* or *p* orbitals

Metallic solid | solid composed of metal atoms

Metalloid | element that conducts heat and electricity moderately well, and possesses some properties of metals and some properties of nonmetals

Metalloid | element that has properties that are between those of metals and nonmetals; these elements are typically semiconductors

Meter (m) | standard metric and SI unit of length; 1 m = approximately 1.094 yards

Method of initial rates | use of a more explicit algebraic method to determine the orders in a rate law

Microscopic domain | realm of things that are much too small to be sensed directly

Microstate (W) | possible configuration or arrangement of matter and energy within a system

Millicurie (mCi) | larger unit for rate of radioactive decay frequently used in medicine; 1 Ci = 3.7×10^{10} disintegrations/s

Milliliter (mL) | 1/1,000 of a liter; equal to 1 cm^3

Miscible | mutually soluble in all proportions; typically refers to liquid substances

Mixture | matter that can be separated into its components by physical means

Molality (m) | a concentration unit defined as the ratio of the numbers of moles of solute to the mass of the solvent in kilograms

Molar mass | mass in grams of 1 mole of a substance

Molar solubility | solubility of a compound expressed in units of moles per liter (mol/L)

Molarity (M) | unit of concentration, defined as the number of moles of solute dissolved in 1 liter of solution

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

Molecular compound | (also, covalent compound) composed of molecules formed by atoms of two or more different elements

Molecular equation | chemical equation in which all reactants and products are represented as neutral substances

Molecular formula | formula indicating the composition of a molecule of a compound and giving the actual number of atoms of each element in a molecule of the compound.

Molecular solid | solid composed of neutral molecules held together by intermolecular forces of attraction

Molecular structure | arrangement of atoms in a molecule or ion

Molecular structure | structure that includes only the placement of the atoms in the molecule

Molecule | bonded collection of two or more atoms of the same or different elements

Monatomic ion | ion composed of a single atom

Monodentate | ligand that attaches to a central metal through just one coordinate covalent bond

Monoprotic acid | acid containing one ionizable hydrogen atom per molecule

Multiple equilibrium | system characterized by more than one state of balance between a slightly soluble ionic solid and an aqueous solution of ions working simultaneously

Nernst equation | equation that relates the logarithm of the reaction quotient (Q) to nonstandard cell potentials; can be used to relate equilibrium constants to standard cell potentials

Net ionic equation | chemical equation in which only those dissolved ionic reactants and products that undergo a chemical or physical change are represented (excludes spectator ions)

Neutral | describes a solution in which $[H_3O^+] = [OH^-]$

Neutron | uncharged, subatomic particle located in the nucleus

Nitrate | NO_3^- ion; salt of nitric acid

Nitrogen fixation | formation of nitrogen compounds from molecular nitrogen

Noble gas | (also, inert gas) element in group 18

Node | any point of a standing wave with zero amplitude

Node | plane separating different lobes of orbitals, where the probability of finding an electron is zero

Nomenclature | system of rules for naming objects of interest

Nonelectrolyte | substance that does not produce ions when dissolved in water

Nonionizing radiation | radiation that speeds up the movement of atoms and molecules; it is equivalent to heating a sample, but is not energetic enough to cause the ionization of molecules

Nonmetal | element that appears dull, poor conductor of heat and electricity

Nonspontaneous process | process that requires continual input of energy from an external source

Normal boiling point | temperature at which a liquid's vapor pressure equals 1 atm (760 torr)

Nuclear binding energy | energy lost when an atom's nucleons are bound together (or the energy needed to break a nucleus into its constituent protons and neutrons)

Nuclear chemistry | study of the structure of atomic nuclei and processes that change nuclear structure

Nuclear fuel | fissionable isotope present in sufficient quantities to provide a self-sustaining chain reaction in a nuclear reactor

Nuclear moderator | substance that slows neutrons to a speed low enough to cause fission

Nuclear reaction | change to a nucleus resulting in changes in the atomic number, mass number, or energy state

Nuclear reactor | environment that produces energy via nuclear fission in which the chain reaction is controlled and sustained without explosion

Nuclear transmutation | conversion of one nuclide into another nuclide

Nucleon | collective term for protons and neutrons in a nucleus

Nucleus | massive, positively charged center of an atom made up of protons and neutrons

Nuclide | nucleus of a particular isotope

Nutritional calorie (Calorie) | unit used for quantifying energy provided by digestion of foods, defined as 1000 cal or 1 kcal

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

Octahedral hole | open space in a crystal at the center of six particles located at the corners of an octahedron

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

Optical isomer | (also, enantiomer) molecule that is a nonsuperimposable mirror image with identical chemical and physical properties, except when it reacts with other optical isomers

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

Organic compound | natural or synthetic compound that contains carbon

Osmosis | diffusion of solvent molecules through a semipermeable membrane

Osmotic pressure (*Π*) | opposing pressure required to prevent bulk transfer of solvent molecules through a semipermeable membrane

Ostwald process | industrial process used to convert ammonia into nitric acid

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

Overlap | coexistence of orbitals from two different atoms sharing the same region of space, leading to the formation of a covalent bond

Oxidation half-reaction | the "half" of an oxidation-reduction reaction involving oxidation; the half-reaction in which electrons appear as products; balanced when each atom type, as well as the charge, is balanced

Oxide | binary compound of oxygen with another element or group, typically containing O^{2-} ions or the group –O– or =O

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

Oxyacid | compound containing a nonmetal and one or more hydroxyl groups

Oxyanion | polyatomic anion composed of a central atom bonded to oxygen atoms

Ozone | allotrope of oxygen; O_3

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

Pairing energy (P) | energy required to place two electrons with opposite spins into a single orbital

Parent nuclide | unstable nuclide that changes spontaneously into another (daughter) nuclide

Partially miscible | of moderate mutual solubility; typically refers to liquid substances

Particle accelerator | device that uses electric and magnetic fields to increase the kinetic energy of nuclei used in transmutation reactions

Parts per billion (ppb) | ratio of solute-to-solution mass multiplied by 10^9

Parts per million (ppm) | ratio of solute-to-solution mass multiplied by 10^6

Pascal (Pa) | SI unit of pressure; 1 Pa = 1 N/m^2

Passivation | metals with a protective nonreactive film of oxide or other compound that creates a barrier for chemical reactions; physical or chemical removal of the passivating film allows the metals to demonstrate their expected chemical reactivity

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

Percent composition | percentage by mass of the various elements in a compound

Percent ionization | ratio of the concentration of the ionized acid to the initial acid concentration, times 100

Percent yield | measure of the efficiency of a reaction, expressed as a percentage of the theoretical yield

Period | (also, series) horizontal row of the periodic table

Periodic law | properties of the elements are periodic function of their atomic numbers.

Periodic table | table of the elements that places elements with similar chemical properties close together

Peroxide | molecule containing two oxygen atoms bonded together or as the anion, O_2^{2-}

PH | logarithmic measure of the concentration of hydronium ions in a solution

Phase diagram | pressure-temperature graph summarizing conditions under which the phases of a substance can exist

Photon | smallest possible packet of electromagnetic radiation, a particle of light

Photosynthesis | process whereby light energy promotes the reaction of water and carbon dioxide to form carbohydrates and oxygen; this allows photosynthetic organisms to store energy

Physical change | change in the state or properties of matter that does not involve a change in its chemical composition

Physical property | characteristic of matter that is not associated with any change in its chemical composition

Pi bond (π bond) | covalent bond formed by side-by-side overlap of atomic orbitals; the electron density is found on opposite sides of the internuclear axis

Pidgeon process | chemical reduction process used to produce magnesium through the thermal reaction of magnesium oxide with silicon

Plasma | gaseous state of matter containing a large number of electrically charged atoms and/or molecules

Platinum metals | group of six transition metals consisting of ruthenium, osmium, rhodium, iridium, palladium, and platinum that tend to occur in the same minerals and demonstrate similar chemical properties

Pnictogen | element in group 15

POH | logarithmic measure of the concentration of hydroxide ions in a solution

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

Polar molecule | (also, dipole) molecule with an overall dipole moment

Polarizability | measure of the ability of a charge to distort a molecule's charge distribution (electron cloud)

Polyatomic ion | ion composed of more than one atom

Polydentate ligand | ligand that is attached to a central metal ion by bonds from two or more donor atoms, named with prefixes specifying how many donors are present (e.g., hexadentate = six coordinate bonds formed)

Polymorph | variation in crystalline structure that results in different physical properties for the resulting compound

Position of equilibrium | concentrations or partial pressures of components of a reaction at equilibrium (commonly used to describe conditions before a disturbance)

Positron ($_{+1}^{0}\beta$ or $_{+1}^{0}e$) | antiparticle to the electron; it has identical properties to an electron, except for having the opposite (positive) charge

Positron emission | (also, β^+ decay) conversion of a proton into a neutron, which remains in the nucleus, and a positron, which is emitted

Potential energy | energy of a particle or system of particles derived from relative position, composition, or condition

Pounds per square inch (psi) | unit of pressure common in the US

Precision | how closely a measurement matches the same measurement when repeated

Pressure | force exerted per unit area

Principal quantum number (*n*) | quantum number specifying the shell an electron occupies in an atom

Product | substance formed by a chemical or physical change; shown on the right side of the arrow in a chemical equation

Proton | positively charged, subatomic particle located in the nucleus

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

Pure substance | homogeneous substance that has a constant composition

Quantitative analysis | the determination of the amount or concentration of a substance in a sample

Quantization | occurring only in specific discrete values, not continuous

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

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

Radiation absorbed dose (rad) | SI unit for measuring radiation dose, frequently used in medical applications; 1 rad = 0.01 Gy

Radiation dosimeter | device that measures ionizing radiation and is used to determine personal radiation exposure

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

Radioactive decay | spontaneous decay of an unstable nuclide into another nuclide

Radioactive decay series | chains of successive disintegrations (radioactive decays) that ultimately lead to a stable end-product

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

Radioactivity | phenomenon exhibited by an unstable nucleon that spontaneously undergoes change into a nucleon that is more stable; an unstable nucleon is said to be radioactive

Radiocarbon dating | highly accurate means of dating objects 30,000–50,000 years old that were derived from once-living matter; achieved by calculating the ratio of $^{14}_{6}C:\ ^{12}_{6}C$ in the object vs. the ratio of $^{14}_{6}C:\ ^{12}_{6}C$ in the present-day atmosphere

Radioisotope | isotope that is unstable and undergoes conversion into a different, more stable isotope

Radiometric dating | use of radioisotopes and their properties to date the formation of objects such as archeological artifacts, formerly living organisms, or geological formations

Raoult's law | the partial pressure exerted by a solution component is equal to the product of the component's mole fraction in the solution and its equilibrium vapor pressure in the pure state

Rare earth element | collection of 17 elements including the lanthanides, scandium, and yttrium that often occur together and have similar chemical properties, making separation difficult

Rate constant (*k*) | proportionality constant in the relationship between reaction rate and concentrations of reactants

Rate expression | mathematical representation relating reaction rate to changes in amount, concentration, or pressure of reactant or product species per unit time

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

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

Reactant | substance undergoing a chemical or physical change; shown on the left side of the arrow in a chemical equation

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

Reaction quotient (*Q*) | ratio of the product of molar concentrations (or pressures) of the products to that of the reactants, each concentration (or pressure) being raised to the power equal to the coefficient in the equation

Reactor coolant | assembly used to carry the heat produced by fission in a reactor to an external boiler and turbine where it is transformed into electricity

Reduction half-reaction | the "half" of an oxidation-reduction reaction involving reduction; the half-reaction in which electrons appear as reactants; balanced when each atom type, as well as the charge, is balanced

Relative biological effectiveness (RBE) | measure of the relative damage done by radiation

Representative element | (also, main-group element) element in columns 1, 2, and 12–18

Representative element | element where the *s* and *p* orbitals are filling

Representative metal | metal among the representative elements

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

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

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

Reversible process | process that takes place so slowly as to be capable of reversing direction in response to an infinitesimally small change in conditions; hypothetical construct that can only be approximated by real processes removed

Reversible reaction | chemical reaction that can proceed in both the forward and reverse directions under given conditions

Roentgen equivalent man (rem) | unit for radiation damage, frequently used in medicine; 1 rem = 1 Sv

Rounding | procedure used to ensure that calculated results properly reflect the uncertainty in the measurements used in the calculation

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

Sacrificial anode | more active, inexpensive metal used as the anode in cathodic protection; frequently made from magnesium or zinc

Saturated | of concentration equal to solubility; containing the maximum concentration of solute possible for a given temperature and pressure

Saturated hydrocarbon | molecule containing carbon and hydrogen that has only single bonds between carbon atoms

Scientific method | path of discovery that leads from question and observation to law or hypothesis to theory, combined with experimental verification of the hypothesis and any necessary modification of the theory

Scintillation counter | instrument that uses a scintillator—a material that emits light when excited by ionizing radiation—to detect and measure radiation

Second (s) | SI unit of time

Second law of thermodynamics | entropy of the universe increases for a spontaneous process

Second transition series | transition elements in the fifth period of the periodic table (second row of the *d*-block), atomic numbers 39–47

Selective precipitation | process in which ions are separated using differences in their solubility with a given precipitating reagent

Semipermeable membrane | a membrane that selectively permits passage of certain ions or molecules

Series | (also, period) horizontal row of the period table

Shell | set of orbitals with the same principal quantum number, *n*

SI units (International System of Units) | standards fixed by international agreement in the International System of Units (*Le Système International d'Unités*)

Sievert (Sv) | SI unit measuring tissue damage caused by radiation; takes into account energy and biological effects of radiation

Sigma bond (σ bond) | covalent bond formed by overlap of atomic orbitals along the internuclear axis

Significant figures | (also, significant digits) all of the measured digits in a determination, including the uncertain last digit

Silicate | compound containing silicon-oxygen bonds, with silicate tetrahedra connected in rings, sheets, or three-dimensional networks, depending on the other elements involved in the formation of the compounds

Simple cubic structure | crystalline structure with a cubic unit cell with lattice points only at the corners

Simple cubic unit cell | (also, primitive cubic unit cell) unit cell in the simple cubic structure

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

Skeletal structure | shorthand method of drawing organic molecules in which carbon atoms are represented by the ends of lines and bends in between lines, and hydrogen atoms attached to the carbon atoms are not shown (but are understood to be present by the context of the structure)

Smelting | process of extracting a pure metal from a molten ore

Solid | state of matter that is rigid, has a definite shape, and has a fairly constant volume

Solubility | extent to which a solute may be dissolved in water, or any solvent

Solubility product (K_{sp}) | equilibrium constant for the dissolution of a slightly soluble electrolyte

Solute | solution component present in a concentration less than that of the solvent

Solvation | exothermic process in which intermolecular attractive forces between the solute and solvent in a solution are established

Solvent | solution component present in a concentration that is higher relative to other components

Space lattice | all points within a crystal that have identical environments

Spatial isomers | compounds in which the relative orientations of the atoms in space differ

Specific heat capacity (c) | intensive property of a substance that represents the quantity of heat required to raise the temperature of 1 gram of the substance by 1 degree Celsius (or 1 kelvin)

Spectator ion | ion that does not undergo a chemical or physical change during a reaction, but its presence is required to maintain charge neutrality

Spectrochemical series | ranking of ligands according to the magnitude of the crystal field splitting they induce

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

Spontaneous change | process that takes place without a continuous input of energy from an external source

Spontaneous process | physical or chemical change that occurs without the addition of energy from an external source

Standard cell potential (E°_{cell}) | the cell potential when all reactants and products are in their standard states (1 bar or 1 atm or gases; 1 *M* for solutes), usually at 298.15 K; can be calculated by subtracting the standard reduction potential for the half-reaction at the anode from the standard reduction potential for the half-reaction occurring at the cathode

Standard enthalpy of combustion (ΔH°_c) | heat released when one mole of a compound undergoes complete combustion under standard conditions

Standard enthalpy of formation (ΔH°_f) | enthalpy change of a chemical reaction in which 1 mole of a pure substance is formed from its elements in their most stable states under standard state conditions

Standard entropy (S°) | entropy for a substance at 1 bar pressure; tabulated values are usually determined at 298.15 K and denoted S°_{298}

Standard entropy change (ΔS°) | change in entropy for a reaction calculated using the standard entropies, usually at room temperature and denoted ΔS°_{298}

Standard free energy change (ΔG°) | change in free energy for a process occurring under standard conditions (1 bar pressure for gases, 1 M concentration for solutions)

Standard free energy of formation (ΔG°_f) | change in free energy accompanying the formation of one mole of substance from its elements in their standard states

Standard hydrogen electrode (SHE) | the electrode consists of hydrogen gas bubbling through hydrochloric acid over an inert platinum electrode whose reduction at standard conditions is assigned a value of 0 V; the reference point for standard reduction potentials

Standard reduction potential (E°) | the value of the reduction under standard conditions (1 bar or 1 atm for gases; 1 *M* for solutes) usually at 298.15 K; tabulated values used to calculate standard cell potentials

Standard state | set of physical conditions as accepted as common reference conditions for reporting thermodynamic properties; 1 bar of pressure, and solutions at 1 molar concentrations, usually at a temperature of 298.15 K

Standing wave | (also, stationary wave) localized wave phenomenon characterized by discrete wavelengths determined by the boundary conditions used to generate the waves; standing waves are inherently quantized

State function | property depending only on the state of a system, and not the path taken to reach that state

Steel | material made from iron by removing impurities in the iron and adding substances that produce alloys with properties suitable for specific uses

Stepwise ionization | process in which an acid is ionized by losing protons sequentially

Stress | change to a reaction's conditions that may cause a shift in the equilibrium

Strong electrolyte | substance that dissociates or ionizes completely when dissolved in water

Strong nuclear force | force of attraction between nucleons that holds a nucleus together

Strong-field ligand | ligand that causes larger crystal field splittings

Structural formula | shows the atoms in a molecule and how they are connected

Structural isomer | one of two substances that have the same molecular formula but different physical and chemical properties because their atoms are bonded differently

Subcritical mass | amount of fissionable material that cannot sustain a chain reaction; less than a critical mass

Sublimation | change from solid state directly to gaseous state

Subshell | set of orbitals in an atom with the same values of *n* and *l*

Substituent | branch or functional group that replaces hydrogen atoms in a larger hydrocarbon chain

Substitution reaction | reaction in which one atom replaces another in a molecule

Sulfate | SO_4^{2-} ion

Sulfite | SO_3^{2-} ion

Superconductor | material that conducts electricity with no resistance

Supercritical fluid | substance at a temperature and pressure higher than its critical point; exhibits properties intermediate between those of gaseous and liquid states

Supercritical mass | amount of material in which there is an increasing rate of fission

Superoxide | oxide containing the anion O_2^-

Supersaturated | of concentration that exceeds solubility; a nonequilibrium state

Surface tension | energy required to increase the area, or length, of a liquid surface by a given amount

Surroundings | all matter other than the system being studied

Symbolic domain | specialized language used to represent components of the macroscopic and microscopic domains, such as chemical symbols, chemical formulas, chemical equations, graphs, drawings, and calculations

System | portion of matter undergoing a chemical or physical change being studied

t_{2g} orbitals | set of three *d* orbitals aligned between the Cartesian axes for coordination complexes; in octahedral complexes, they are lowered in energy compared to the e_g orbitals according to CFT

Temperature | intensive property of matter that is a quantitative measure of "hotness" and "coldness"

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

Tetrahedral hole | tetrahedral space formed by four atoms or ions in a crystal

Theoretical yield | amount of product that may be produced from a given amount of reactant(s) according to the reaction stoichiometry

Theory | well-substantiated, comprehensive, testable explanation of a particular aspect of nature

Thermal energy | kinetic energy associated with the random motion of atoms and molecules

Thermochemistry | study of measuring the amount of heat absorbed or released during a chemical reaction or a physical change

Third law of thermodynamics | entropy of a perfect crystal at absolute zero (0 K) is zero

Third transition series | transition elements in the sixth period of the periodic table (third row of the *d*-block), atomic numbers 57 and 72–79

Titrant | solution containing a known concentration of substance that will react with the analyte in a titration analysis

Titration analysis | quantitative chemical analysis method that involves measuring the volume of a reactant solution required to completely react with the analyte in a sample

Titration curve | plot of the pH of a solution of acid or base versus the volume of base or acid added during a titration

Torr | unit of pressure; $1\ \text{torr} = \frac{1}{760}\ \text{atm}$

***trans* configuration** | configuration of a geometrical isomer in which two similar groups are on opposite sides of an imaginary reference line on the molecule

Transition metal | element in columns 3–11

Transmutation reaction | bombardment of one type of nuclei with other nuclei or neutrons

Transuranium element | element with an atomic number greater than 92; these elements do not occur in nature

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

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

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

Triple point | temperature and pressure at which the vapor, liquid, and solid phases of a substance are in equilibrium

Triprotic acid | acid that contains three ionizable hydrogen atoms per molecule; ionization of triprotic acids occurs in three steps

Tyndall effect | scattering of visible light by a colloidal dispersion

Uncertainty | estimate of amount by which measurement differs from true value

Unified atomic mass unit (u) | alternative unit equivalent to the atomic mass unit

Unit | standard of comparison for measurements

Unit cell | smallest portion of a space lattice that is repeated in three dimensions to form the entire lattice

Unit conversion factor | ratio of equivalent quantities expressed with different units; used to convert from one unit to a different unit

Unsaturated | of concentration less than solubility

Vacancy | defect that occurs when a position that should contain an atom or ion is vacant

Valence bond theory | description of bonding that involves atomic orbitals overlapping to form σ or π bonds, within which pairs of electrons are shared

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

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

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

Van der Waals equation | modified version of the ideal gas equation containing additional terms to account for non-ideal gas behavior

Van der Waals force | attractive or repulsive force between molecules, including dipole-dipole, dipole-induced dipole, and London dispersion forces; does not include forces due to covalent or ionic bonding, or the attraction between ions and molecules

Van't Hoff factor (*i*) | the ratio of the number of moles of particles in a solution to the number of moles of formula units dissolved in the solution

Vapor pressure | (also, equilibrium vapor pressure) pressure exerted by a vapor in equilibrium with a solid or a liquid at a given temperature

Vaporization | change from liquid state to gaseous state

Vector | quantity having magnitude and direction

Viscosity | measure of a liquid's resistance to flow

Voltaic cell | another name for a galvanic cell

Volume | amount of space occupied by an object

Volume percentage | ratio of solute-to-solution volume expressed as a percentage

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

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

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

Wavelength (λ) | distance between two consecutive peaks or troughs in a wave

Weak electrolyte | substance that ionizes only partially when dissolved in water

Weak-field ligand | ligand that causes small crystal field splittings

Weight | force that gravity exerts on an object

Work (*w*) | energy transfer due to changes in external, macroscopic variables such as pressure and volume; or causing matter to move against an opposing force

X-ray crystallography | experimental technique for determining distances between atoms in a crystal by measuring the angles at which X-rays are diffracted when passing through the crystal



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