TEXTBOOK: MODERN APPLICATIONS OF CHEMISTRY (COX)



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CHEM 2010D: Modern Applications of Chemistry

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Detailed Licensing

Licensing

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CHAPTER OVERVIEW

1: Primer

Chemistry is all around us "from the air we breathe to the food we eat" to the items at the super market that say “no chemicals added”. In fact, it is impossible to create something without using chemistry because chemistry consists of all matter. It allows us to answer questions as simple as why a candle goes out when a glass is placed over it to more complex questions such as does a candle actually burn in zero gravity? Chemistry is the study of matter and the changes it undergoes such as ice changing from the solid to liquid to gas phase. People have used it for things such as creating metal from an ore, dying fabric, and making cheese. Chemistry deals with different substances and how they can interact with each other to create a product.

As you begin your study of college chemistry, those of you who do not intend to become professional chemists may well wonder why you need to study chemistry. You will soon discover that a basic understanding of chemistry is useful in a wide range of disciplines and career paths. You will also discover that an understanding of chemistry helps you make informed decisions about many issues that affect you, your community, and your world. A major goal of this text is to demonstrate the importance of chemistry in your daily life and in our collective understanding of both the physical world we occupy and the biological realm of which we are a part.

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SECTION OVERVIEW

1.1.1: Electrons in Atoms

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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.

Topic hierarchy

1.1.1.1: Electromagnetic Radiation

1.1.1.2: Atomic Spectra

1.1.1.3: Quantum Theory

1.1.1.4: The Bohr Atom

1.1.1.5: Leading to New Quantum Mechanics

1.1.1.6: Wave Mechanics

1.1.1.7: Electron Spin (A Fourth Quantum Number)

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1.1.1.1: Electromagnetic Radiation

Learning Objectives

- to learn about the characteristics of electromagnetic waves. Light, X-Rays, infrared and microwaves 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 **1.1.1.1.1**: 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.

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 **1.1.1.1.1**). 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.

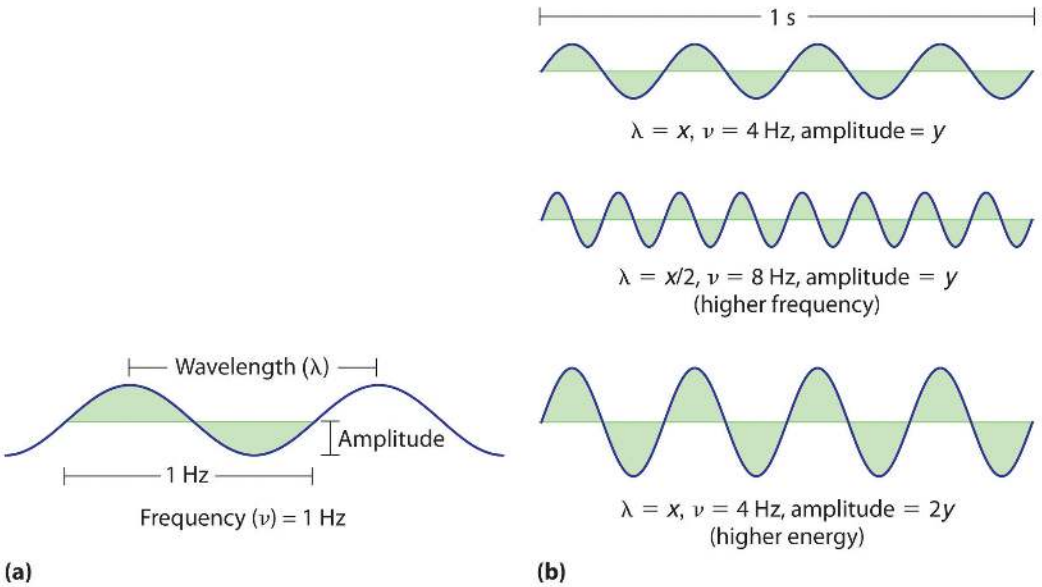


Figure **1.1.1.1.2**: Important Properties of Waves (a) Wavelength (λ in meters), frequency (ν, in Hz), and amplitude are indicated on this drawing of a wave. (b) The wave with the shortest wavelength has the greatest number of wavelengths per unit time (i.e., the highest frequency). If two waves have the same frequency and speed, the one with the greater amplitude has the higher energy.

Waves have characteristic properties (Figure **1.1.1.1.2**). As you may have noticed in Figure **1.1.1.1.1**, 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), distance between two corresponding points in a wave—between the midpoints of two peaks or two troughs. $\boldsymbol{\lambda}$ is the lowercase Greek lambda, and $\boldsymbol{u}$ is the lowercase Greek nu. Wavelengths are described by a unit of distance, typically meters. The frequency (ν), the number of oscillations (i.e., of a wave) that pass a particular point in a given period of time. of a wave is the number of oscillations that pass a particular point in a given period of time. The usual units are oscillations persecond (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 (the vertical height of a wave, which is defined as half the peak-to-trough height), 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 **1.1.1.1.2**, 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), the distance traveled by a wave per unit time, 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:

$$(\textbf{wavelength})(\textbf{frequency}) = \textit{speed} \tag{1.1.1.1.1}$$

$$\lambda u = v \tag{1.1.1.1.2}$$

$$\left(\frac{\textit{meters}}{\cancel{\textit{wave}}}\right)\left(\frac{\cancel{\textit{wave}}}{\textit{second}}\right) = \frac{\textit{meters}}{\textit{second}} \tag{1.1.1.1.3}$$

Be careful not to confuse the symbols for the speed, $\boldsymbol{v}$, with the frequency, $\boldsymbol{u}$. 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.

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, which is energy that is transmitted, or radiated, through space in the form of periodic oscillations of electric and magnetic fields. (Figure **1.1.1.1.3**). Some forms of electromagnetic radiation are shown in Figure **1.1.1.1.4**. In a vacuum, all forms of electromagnetic radiation—whether microwaves, visible light, or gamma rays—travel at the speed of light (c), which is the speed with which all forms of electromagnetic radiation travel in a vacuum, a fundamental physical constant with a value of 2.99792458 × 10^8 m/s (which is 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.

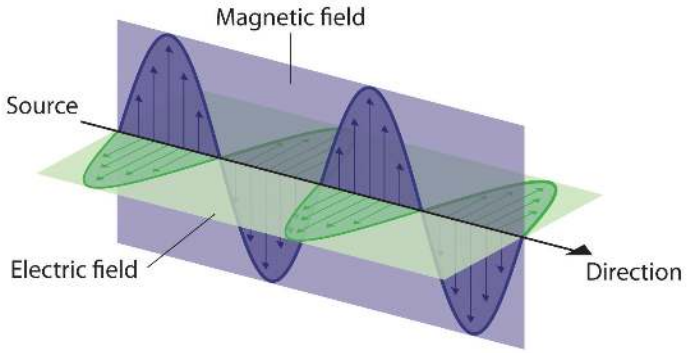


Figure **1.1.1.1.3**: The Nature of Electromagnetic Radiation. All forms of electromagnetic radiation consist of perpendicular oscillating electric and magnetic fields.

Because the various kinds of electromagnetic radiation all have the same speed (*c*), they differ in only wavelength and frequency. As shown in Figure **1.1.1.1.4** and Table **1.1.1.1.1**, 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 **1.1.1.1.1**, we can show that the frequency of electromagnetic radiation is inversely proportional to its wavelength:

$$c = \lambda u$$
$$u = \frac{c}{\lambda} \tag{1.1.1.1.4}$$

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.

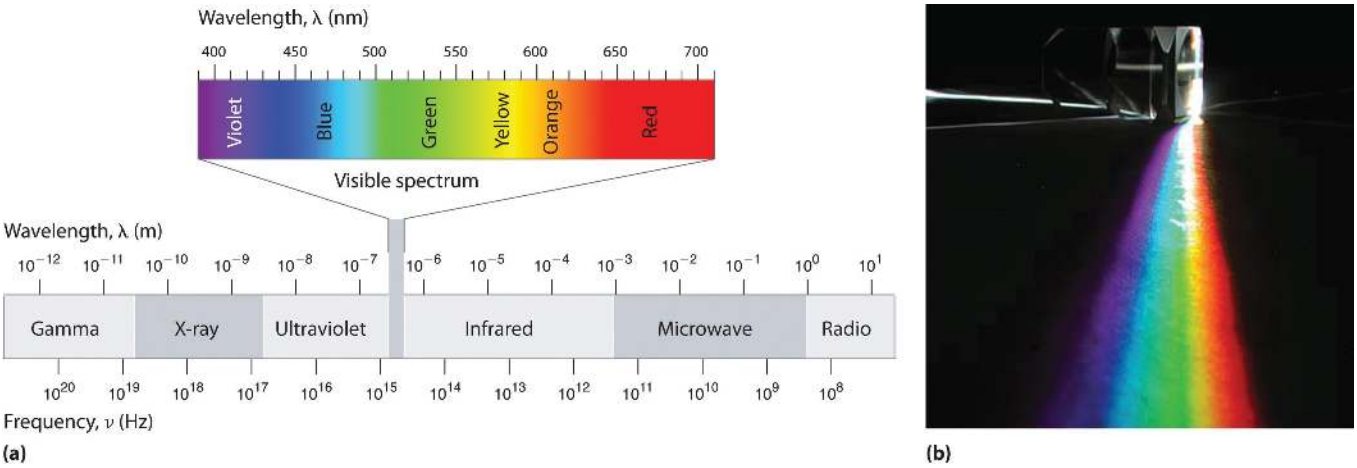


Figure 1.1.1.1.4: The Electromagnetic Spectrum. (a) This diagram shows the wavelength and frequency ranges of electromagnetic radiation. The visible portion of the electromagnetic spectrum is the narrow region with wavelengths between about 400 and 700 nm. (b) When white light is passed through a prism, it is split into light of different wavelengths, whose colors correspond to the visible spectrum. (CC BY-NC-SA; anonymous)

Within this 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 1.1.1.1.4. A similar phenomenon creates a rainbow, where water droplets suspended in the air act as tiny prisms.

Table 1.1.1.1.1: 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}	x-ray
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:

$$E \propto u \tag{1.1.1.1.5}$$
$$E \propto \frac{1}{\lambda} \tag{1.1.1.1.6}$$

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 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.

Example 1.1.1.1.1

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 **1.1.1.1.2** to calculate the wavelength in meters.

Solution:

From Equation 1.1.1.1.4, 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:

$$\lambda\nu = c = 2.998 \times 10^8 m/s \tag{1.1.1.1.7}$$

Thus the wavelength λ is given by

$$\lambda = \frac{c}{u} = \left(\frac{2.988 \times 10^8\ m/\cancel{s}}{101.1\ \cancel{MHz}}\right)\left(\frac{1\ \cancel{MHz}}{10^6\ \cancel{s^{-1}}}\right) = 2.965\ m \tag{1.1.1.1.8}$$

Exercise 1.1.1.1.1

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



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

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: **wavelength (λ)**, the distance between successive waves; **frequency (ν)**, 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.

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1.1.1.2: Atomic Spectra

Learning Objectives

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

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

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, called a line spectrum, which is a spectrum in which light of only a certain wavelength is emitted or absorbed, rather than a continuous range of wavelengths (Figure **1.1.1.2.1**), rather than a continuous range of colors. 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 **1.1.1.2.1**: The Emission of Light by Hydrogen Atoms. (a) A sample of excited hydrogen atoms emits a characteristic red light. (b) When the light emitted by a sample of excited hydrogen atoms is split into its component wavelengths by a prism, four characteristic violet, blue, green, and red emission lines can be observed, the most intense of which is at 656 nm.

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 the observation of only a few values of λ (or ν) 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:

$$u = constant\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \tag{1.1.1.2.1}$$

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*:

$$\frac{1}{\lambda} = \mathfrak{R}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \tag{1.1.1.2.2}$$

where n_1 and n_2 are positive integers, $n_2 > n_1$, and $\mathfrak{R}$ the *Rydberg constant*, has a value of 1.09737 × 10^7 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 described 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.



The Bohr Atom: https://youtu.be/GuFQEOzFOgA

Summary

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 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.

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. Bohr's model could not, however, explain the spectra of atoms heavier than hydrogen.

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1.1.1.3: Quantum Theory

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.

Blackbody Radiation

One phenomenon that seemed to contradict the theories of classical physics was blackbody radiation, which is electromagnetic radiation whose wavelength and color that depends on the temperature of the object. The wavelength of energy emitted by an object 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 **1.1.1.3.1**: 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 **1.1.1.3.2**. 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 **1.1.1.3.2**. 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 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 **1.1.1.3.2**, 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 (the smallest possible unit of energy). Energy can be gained or lost only in integral multiples of a quantum..

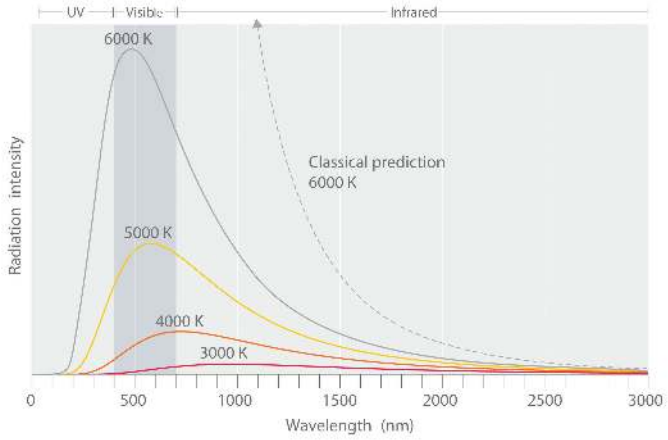
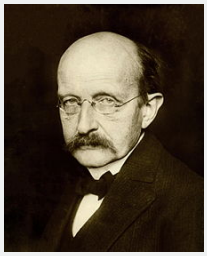


Figure **1.1.1.3.2**: Relationship between the Temperature of an Object and the Spectrum of Blackbody Radiation It Emits. At relatively low temperatures, most radiation is emitted at wavelengths longer than 700 nm, which is in the infrared portion of the spectrum. The dull red glow of the electric stove element in Figure **1.1.1.3.1** 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 **1.1.1.3.1**). 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 Max Planck (1858–1947) by the equation

$$E = hu \qquad (1.1.1.3.1)$$

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:

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

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 **1.1.1.3.2**. 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 **1.1.1.3.2**, 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.

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 **1.1.1.3.3**). 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).

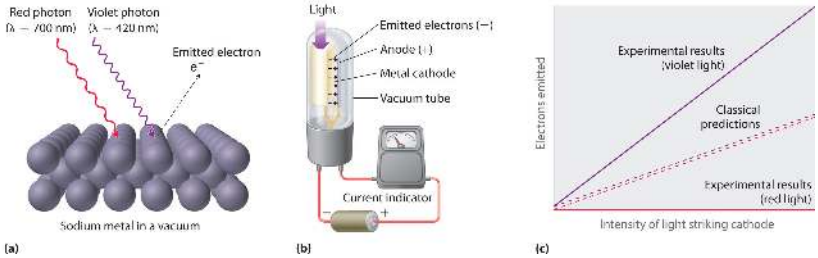


Figure **1.1.1.3.3**: The Photoelectric Effect *(a) Irradiating a metal surface with photons of sufficiently high energy causes electrons to be ejected from the metal. (b) A photocell that uses the photoelectric effect, similar to those found in automatic door openers. When light strikes the metal cathode, 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 8.3.1 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 ($E_o = h\nu_o$). 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:

$$\textit{kinetic energy of ejected electron} = E - E_o = hu - hu_o = h\,(u - u_o) \qquad (1.1.1.3.2)$$

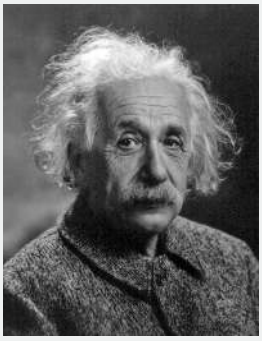
When a metal is struck by light with energy above the threshold energy E_o, the *number* of emitted electrons is proportional to the *intensity* of the light beam, which corresponds to the number of photons per square centimeter, but the *kinetic energy* of the emitted electrons is proportional to the *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.



Figure **1.1.1.3.4**: 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 1.1.1.3.1

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 **1.1.1.3.4**). What is the energy in joules of a single photon?

Given: wavelength

Asked for: energy of single photon.

Strategy:

A. Use Equation 6.1.2 and Equation 8.3.1 to calculate the energy in joules.

Solution:

The energy of a single photon is given by $E = h\nu = hc/\lambda$.

? Exercise 1.1.1.3.1

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. $1.287 \times 10^{-15}\ J/photon$
b. 4497 times



The Photoelectric Effect: https://youtu.be/mxBMxJLauQk

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.

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1.1.1.4: The Bohr Atom

Learning Objectives

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

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

$$E_n = \frac{-\mathfrak{R}hc}{n^2} \tag{1.1.1.4.1}$$

where $\mathfrak{R}$ 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.

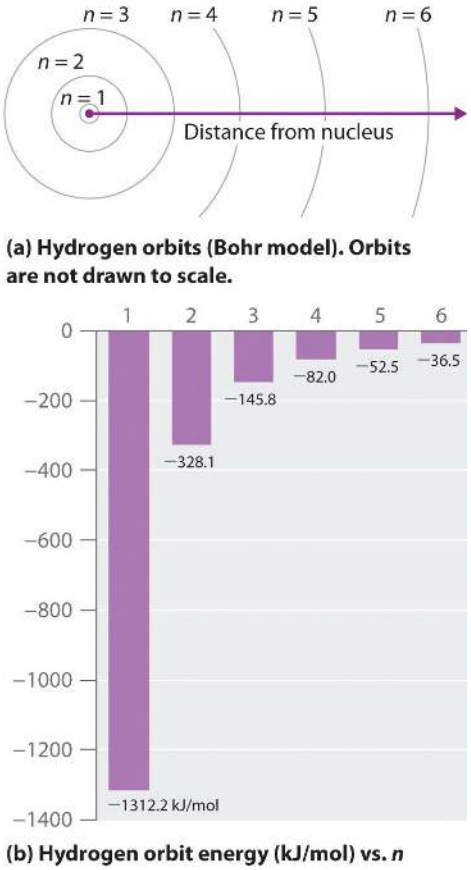
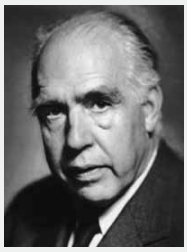


Figure **1.1.1.4.2** The Bohr Model of the Hydrogen Atom (a) The distance of the orbit from the nucleus increases with increasing n. (b) The energy of the orbit becomes increasingly less negative with increasing n.

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 **1.1.1.4.3** indicates that the electron-nucleus pair is more tightly bound 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), the most stable arrangement 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 2.10). A hydrogen atom with an electron in an orbit with n > 1 is therefore in an excited state. Any arrangement of electrons that is higher in energy than the ground state.: its energy is higher than the energy of 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 **1.1.1.4.1**).

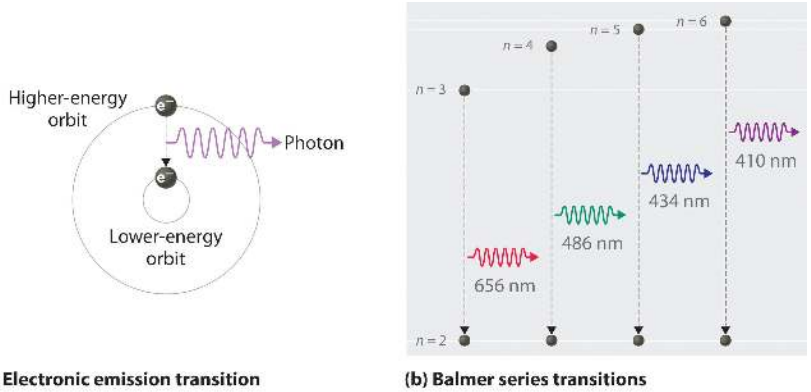


Figure **1.1.1.4.3**: The Emission of Light by a Hydrogen Atom in an Excited State. (a) Light is emitted when the electron undergoes a transition from an orbit with a higher value of *n* (at a higher energy) to an orbit with a lower value of *n* (at lower energy). (b) The Balmer series of emission lines 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 **1.1.1.4.3**) for each energy value gives

$$\Delta E = E_{final} - E_{initial} = -\frac{\Re hc}{n_2^2} - \left(-\frac{\Re hc}{n_1^2}\right) = -\Re hc\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \qquad (1.1.1.4.2)$$

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 **1.1.1.4.3**. Substituting hc/λ for ΔE gives

$$\Delta E = \frac{hc}{\lambda} = -\Re hc\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \qquad (1.1.1.4.3)$$

Canceling *hc* on both sides gives

$$\frac{1}{\lambda} = -\Re\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \tag{1.1.1.4.4}$$

Except for the negative sign, this is the same equation that Rydberg obtained experimentally. The negative sign in Equation **1.1.1.4.5** and Equation **1.1.1.4.6** 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 (part (b) in Figure 2.9). As shown in part (b) in Figure **1.1.1.4.3**, 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 (part (a) in Figure **1.1.1.4.3**). 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 (part (a) in Figure **1.1.1.4.1**). 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 **1.1.1.4.4**

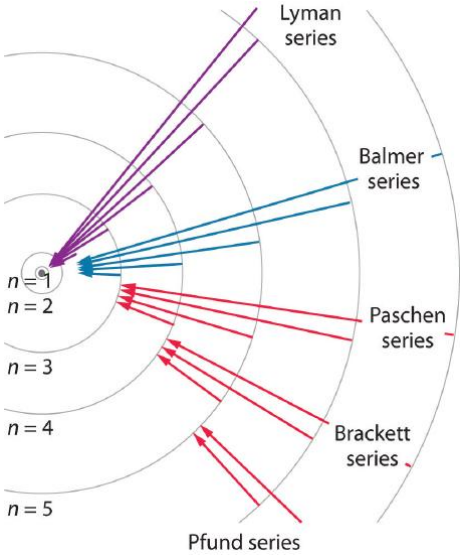


Figure **1.1.1.4.4**: Electron Transitions Responsible for the Various Series of Lines Observed in the Emission Spectrum of Hydrogen. The Lyman series of lines is due to transitions from higher-energy orbits to the lowest-energy orbit (*n* = 1); these transitions release a great deal of energy, corresponding 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.)

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 1.1.1.4.1: 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 **1.1.1.4.2** (the Rydberg equation) and solve for λ.
B. Use Figure **1.1.1.4.1** to locate the region of the electromagnetic spectrum corresponding to the calculated wavelength.

Solution:

We can use the Rydberg equation to calculate the wavelength:

$$\frac{1}{\lambda} = -\Re\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \tag{1.1.1.4.5}$$

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.

$$\frac{1}{\lambda} = -\Re\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) = 1.097 \times m^{-1}\left(\frac{1}{1} - \frac{1}{4}\right) = 8.228 \times 10^6\ m^{-1} \tag{1.1.1.4.6}$$

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, $E=h\nu$.

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}.

$$\varpi = \frac{1}{\lambda} = 8.228 \times 10^6\ \cancel{m^{-1}}\left(\frac{\cancel{m}}{100\ cm}\right) = 82,280\ cm^{-1} \tag{1.1.1.4.7}$$

and

$$\lambda = 1.215 \times 10^{-7}\ m = 122\ nm \tag{1.1.1.4.8}$$

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 1.1.1.4.1: 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:

- 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.

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 1.1.1.4.5). 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.

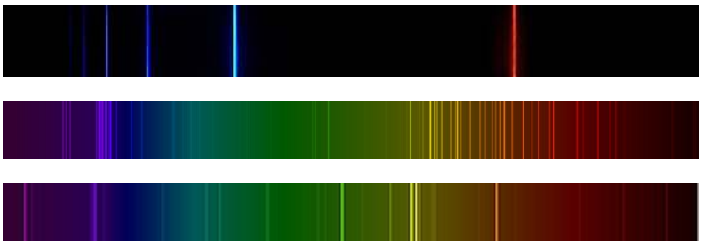


Figure 1.1.1.4.5: The Emission Spectra of Elements Compared with Hydrogen. These images show (a) hydrogen gas, which is atomized to hydrogen atoms in the discharge tube; (b) neon; and (c) mercury. The strongest lines in the hydrogen spectrum are in the far UV Lyman series starting at 124 nm and below. The strongest lines in the mercury spectrum are at 181 and 254 nm, also in the UV. These are not shown.

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). Because each element has characteristic emission and absorption spectra, scientists can use such spectra to analyze the composition of matter.

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.

The Energy States of the Hydrogen Atom

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.

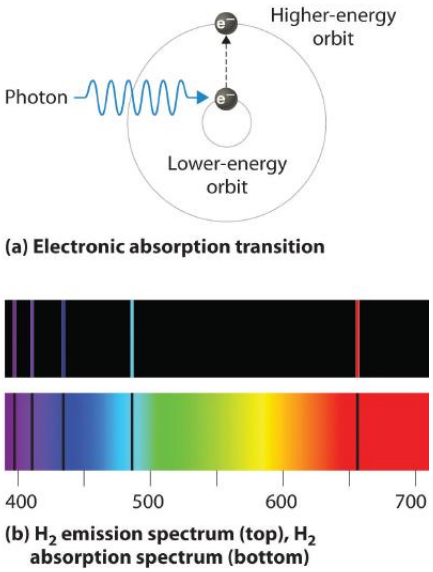


Figure 1.1.1.4.6: Absorption and Emission Spectra. Absorption of light by a hydrogen atom. (a) When a hydrogen atom absorbs a photon of light, an electron is excited to an orbit that has a higher energy and larger value of n. (b) Images of the emission and absorption spectra of hydrogen are shown here.

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 1.1.1.4.7 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.

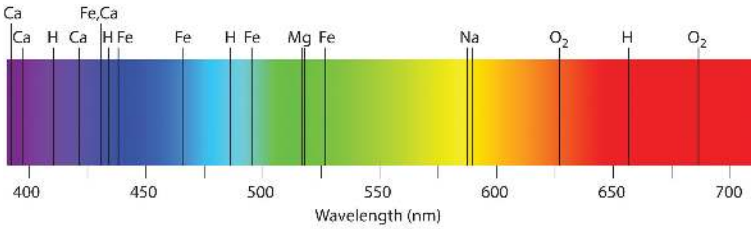


Figure 1.1.1.4.7: The Visible Spectrum of Sunlight. The characteristic dark lines are mostly due to the absorption of light by elements that are present in the cooler outer part of the sun’s atmosphere; specific elements are indicated by the labels. The lines at 628 and 687 nm, however, are due to the absorption of light by oxygen molecules in Earth’s atmosphere.

The familiar red color of “neon” signs used in advertising is due to the emission spectrum of neon shown in part (b) in Figure 1.1.1.4.5. 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 1.1.1.4.5). In the case of sodium, the most intense emission lines are at 589 nm, which produces an intense yellow light.

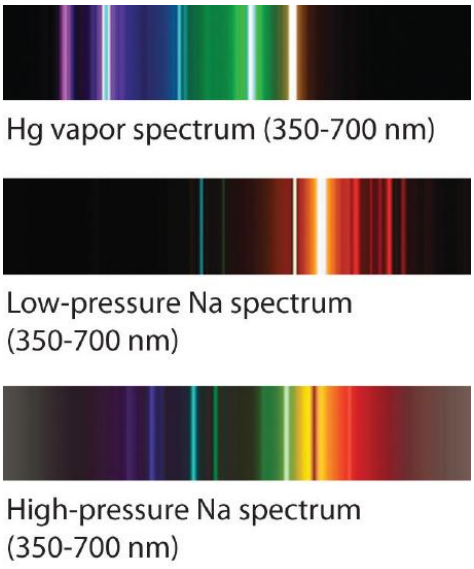


Figure **1.1.1.4.8**: The emission spectra of sodium and mercury. Sodium and mercury spectra. Many street lights use bulbs that contain sodium or mercury vapor. Due to the very different emission spectra of these elements, they emit light of different colors. The lines in the sodium lamp are broadened 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.



The Bohr Atom: https://youtu.be/GuFQEOzFOgA

The Chemistry of Fireworks

The colors of fireworks are also due to atomic emission spectra. As shown in part (a) in Figure **1.1.1.4.9**, a typical shell used in a fireworks display contains gunpowder to propel the shell into the air and a fuse to initiate a variety of reactions that produce heat and small explosions. Thermal energy excites the atoms to higher energy states; as they decay to lower energy states, the atoms emit light that gives the familiar colors.



Figure **1.1.1.4.9** :The Chemistry of Fireworks *(a) In the "multibreak" shell used for fireworks, the chambers contain mixtures of fuels and oxidizers plus compounds for special effects ("stars") connected by time-delay fuses so that the chambers explode in stages. (b) The finale of a fireworks display usually consists of many shells fired simultaneously to give a dazzling multicolor display. The labels indicate the substances that are responsible for the colors of some of the fireworks shown.*

When oxidant/reductant mixtures listed in Table **1.1.1.4.1** are ignited, a flash of white or yellow light is produced along with a loud bang. Achieving the colors shown in part (b) in Figure **1.1.1.4.9** requires adding a small amount of a substance that has an emission spectrum in the desired portion of the visible spectrum. For example, sodium is used for yellow because of its 589 nm emission lines. The intense yellow color of sodium would mask most other colors, so potassium and ammonium salts, rather than sodium salts, are usually used as oxidants to produce other colors, which explains the preponderance of such salts in Table **1.1.1.4.1**. Strontium salts, which are also used in highway flares, emit red light, whereas barium gives a green color. Blue is one of the most difficult colors to achieve. Copper(II) salts emit a pale blue light, but copper is dangerous to use because it forms highly unstable explosive compounds with anions such as chlorate. As you might guess, preparing fireworks with the desired properties is a complex, challenging, and potentially hazardous process. If you have the time here is a NOVA program about how fireworks are made.

Table **1.1.1.4.1**: Common Chemicals Used in the Manufacture of Fireworks*

Oxidizers	Fuels (reductants)	Special effects
ammonium perchlorate	aluminum	*blue flame*: copper carbonate, copper sulfate, or copper oxide
barium chlorate	antimony sulfide	*red flame*: strontium nitrate or strontium carbonate
barium nitrate	charcoal	*white flame*: magnesium or aluminum
potassium chlorate	magnesium	*yellow flame*: sodium oxalate or cryolite (Na_3AlF_6)
potassium nitrate	sulfur	*green flame*: barium nitrate or barium chlorate
potassium perchlorate	titanium	*white smoke*: potassium nitrate plus sulfur
strontium nitrate		*colored smoke*: potassium chlorate and sulfur, plus organic dye
		whistling noise: potassium benzoate or sodium salicylate
		white sparks: aluminum, magnesium, or titanium
		gold sparks: iron fillings or charcoal

*Almost any combination of an oxidizer and a fuel may be used along with the compounds needed to produce a desired special effect.



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. Bohr's model could not, however, explain the spectra of atoms heavier than hydrogen.

Contributors and Attributions

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1.1.1.5: Leading to New Quantum Mechanics

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.

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 following equation:

$$E = h\nu = h\frac{c}{\lambda} = mc^2 \tag{1.1.1.5.1}$$

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

$$m = \frac{E}{c^2} = \frac{h\nu}{c^2} = \frac{h}{\lambda c} \tag{1.1.1.5.2}$$

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

$$\lambda = \frac{h}{mv} \tag{1.1.1.5.3}$$

where

- 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 **1.1.1.5.1**, 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.

Example 1.1.1.5.1

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 8.5.3 and solve for the wavelength.

Solution:

The wavelength of a particle is given by λ = *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

$$\lambda = \frac{6.626 \times 10^{-34}\ J \cdot s}{(0.149\ kg)\,(44.69\ m \cdot s)} \tag{1.1.1.5.4}$$

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

(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 1.1.1.5.1

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 **1.1.1.5.1**, 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, 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 **1.1.1.5.1**).

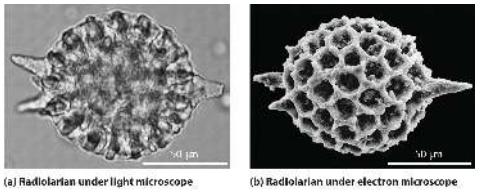


Figure **1.1.1.5.1**: A Comparison of Images Obtained Using a Light Microscope and an Electron Microscope**.** Because of their shorter wavelength, high-energy electrons have a higher resolving power than visible light. Consequently, an electron microscope (b) is able to resolve finer details than a light microscope (a). (Radiolaria, which are shown here, are unicellular planktonic organisms.)

An Important Wave Property: Phase

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 **1.1.1.5.2**a, on the right shows an arbitrary phase difference between two wave. Figure **1.1.1.5.2**b shows what happens when the two waves are 180 degrees out of phase. The green line is their sum. Figure **1.1.1.5.2**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.

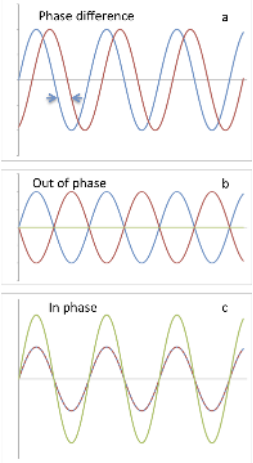


Figure 1.1.1.5.2: Phase. Two waves traveling together are displaced by a phase difference. If the phase difference is 0 then they lay on top of each other and reinforce. If the phase difference is 180 they completely cancel each other out.

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 1.1.1.5.3). If the length of the string is L, then the lowest-energy vibration (the fundamental (the lowest-energy standing wave) has wavelength

$$\frac{\lambda}{2} = L$$
$$\lambda = 2L \tag{1.1.1.5.5}$$

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

$$\lambda = \frac{2L}{n} \tag{1.1.1.5.6}$$

where n has any integral value. Thus the resonant vibrational energies of the string are quantized. When plucked, all other frequencies die out immediately. Only the resonant frequencies survive and are heard. By analogy we can think of the resonant frequencies as being quantized. Notice in Figure 1.1.1.5.3 that all overtones have one or more nodes (the points where the amplitude of a wave is zero), points where the string does not move. The amplitude of the wave at a node is zero.

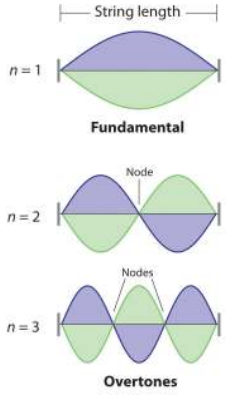


Figure 1.1.1.5.3 Standing Waves on a Vibrating String. The vibration with n = 1 is the fundamental and contains no nodes. Vibrations with higher values of n are called overtones; they contain n − 1 nodes.

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

$$2\pi r = n\lambda \tag{1.1.1.5.7}$$

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 **1.1.1.5.4**). 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 non resonant 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 8.5.2, one complete wavelength would close the circle. Higher energy levels would have successively higher values of n with a corresponding number of nodes.

Standing waves are often observed on rivers, reservoirs, ponds, and lakes when seismic waves from an earthquake travel through the area. The waves are called *seismic seiches*, a term first used in 1955 when lake levels in England and Norway oscillated from side to side as a result of the Assam earthquake of 1950 in Tibet. They were first described in the Proceedings of the Royal Society in 1755 when they were seen in English harbors and ponds after a large earthquake in Lisbon, Portugal. Seismic seiches were also observed in many places in North America after the Alaska earthquake of March 28, 1964. Those occurring in western reservoirs lasted for two hours or longer, and amplitudes reached as high as nearly 6 ft along the Gulf Coast. The height of seiches is approximately proportional to the thickness of surface sediments; a deeper channel will produce a higher seiche.

Still, as 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.

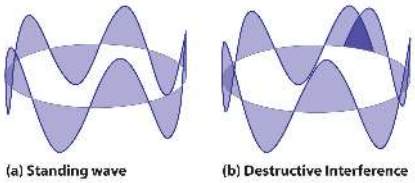


Figure **1.1.1.5.4** Standing Circular Wave and Destructive Interference.(a) In a standing circular wave with $n = 5$, the circumference of the circle corresponds to exactly five wavelengths, which results in constructive interference of the wave with itself when overlapping occurs. (b) If the circumference 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.

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 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.

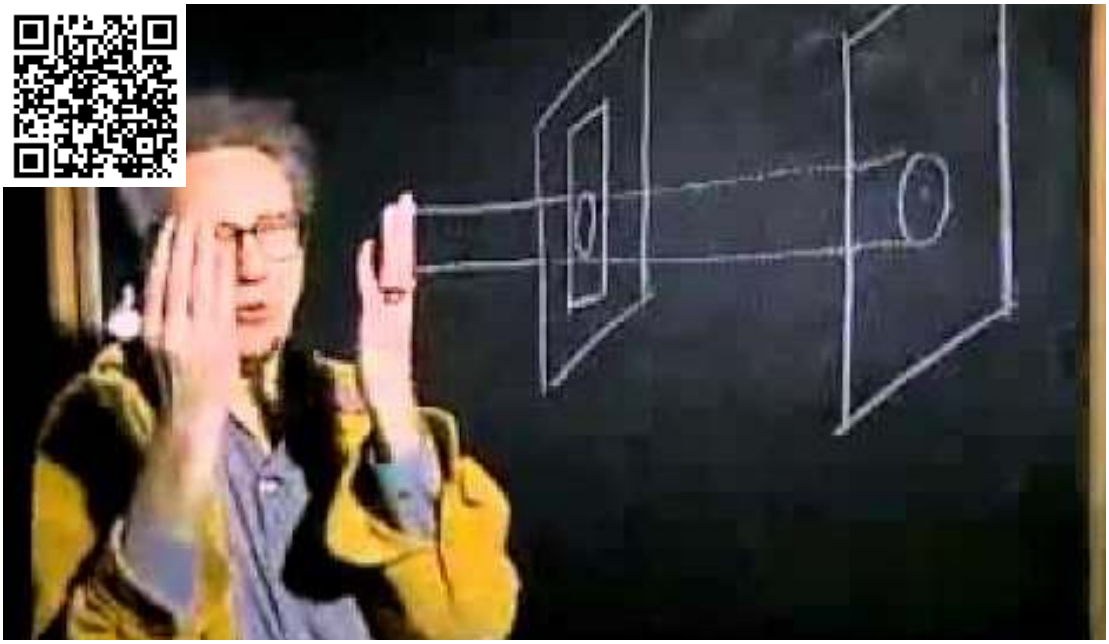


The de Broglie Equation: https://youtu.be/pz0zMHWtK7Q

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 as shown in the video below. 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. Heisenberg's uncertainty principle for light is, if you will, merely a conclusion about the nature of electromagnetic waves and nothing new. DeBroglie's idea of wave particle duality means that particles such as electrons which all exhibit wave like characteristics, will also undergo diffraction from slits whose size is of 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 is greater than or equal to Planck’s constant h divided by 4π: 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:

$$(\Delta x)\,(\Delta\,[mv]) \geqslant \frac{h}{4\pi} \tag{1.1.1.5.8}$$

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:

$$(\Delta\,[mv]) = \frac{h}{4\pi\,(\Delta x)} = \frac{h}{4\pi\,(0)} = \infty \tag{1.1.1.5.9}$$

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 8.5.8, 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 1.1.1.5.2

Calculate the minimum uncertainty in the position of the pitched baseball from Example **1.1.1.5.1** 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 8.5.7) 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 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

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

C Therefore,

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

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

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

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

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 1.1.1.5.2

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

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

Videos and Examples

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

Answers for these quizzes are included.

Summary

- 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.

$$\lambda = \frac{h}{mv} \tag{8.5.3}$$

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.

$$(\Delta x)\,(\Delta\,[mv]) \geqslant \frac{h}{4\pi} \tag{8.5.7}$$

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1.1.1.6: Wave Mechanics

Learning Objectives

- To apply the results of quantum mechanics to chemistry.

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. In doing so, Schrödinger developed the theory of quantum mechanics, which is used today to describe the energies and spatial distributions of electrons in atoms and molecules.

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.

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

Wave Functions

A wave function (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 wave function is associated with a particular energy E. The properties of wave functions derived from quantum mechanics are summarized here:

- **A wave function 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 wanted 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 **1.1.1.6.1**). 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.

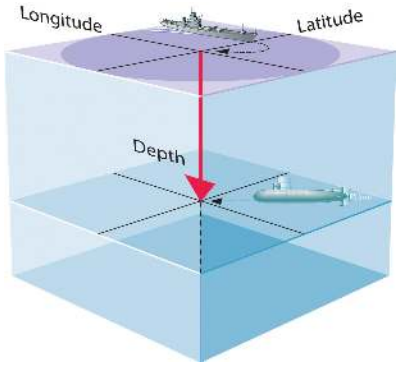


Figure **1.1.1.6.1**: The Four Variables (Latitude, Longitude, Depth, and Time) Required to Precisely Locate an Object

If you are the captain of a ship trying to intercept an enemy submarine, you need to deliver your depth charge to the right location at the right time.

- **The magnitude of the wave function at a particular point in space is proportional to the amplitude of the wave at that point.** Many wave functions 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 wave function (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 wave function should *not* be confused with a positive or negative electrical charge.
- **The square of the wave function 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 wave function (Ψ^2) is always a real quantity [recall that that $\sqrt{-1}^2 = -1$] is proportional to the probability of finding an electron at a given point. More accurately, the probability is given by the product of the wave function 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 1.1.1.6.2.

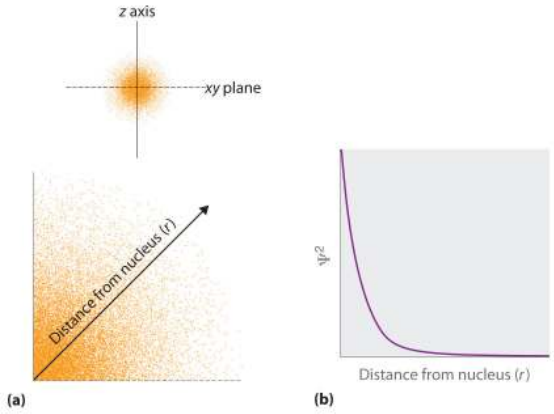


Figure 1.1.1.6.2: Probability of Finding the Electron in the Ground State of the Hydrogen Atom at Different Points in Space. (a) The density of the dots shows electron probability. (b) In this plot of Ψ^2 versus r for the ground state of the hydrogen atom, the electron probability density is greatest 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.

- **Describing the electron distribution as a standing wave leads to sets of *quantum numbers* that are characteristic of each wave function.** From the patterns of one- and two-dimensional standing waves shown in Figure 6.18 and Figure 6.19, 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 wave functions. 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 (wave functions), each of which is specified by a set of numbers called quantum numbers.
- **Each wave function 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.

Quantum Numbers

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



Introduction to Quantum Numbers: https://youtu.be/07JpBeaPxL8

The Principal Quantum Number

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

$$n = 1, 2, 3, 4, \ldots \tag{1.1.1.6.1}$$

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

The Azimuthal Quantum Number

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

$$l = 0, 1, 2, \ldots, n - 1 \tag{1.1.1.6.2}$$

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



Principal quantum number (n) & Orbital angular momentum (l): The Orbital Subshell: https://youtu.be/ms7WR149fAY

The Magnetic Quantum Number

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

$$m_l = -l, -l+1, \ldots, 0, \ldots, l-1, l \tag{1.1.1.6.3}$$

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

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

Example 1.1.1.6.1: n=4 Shell Structure

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

Given: value of n

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

Strategy:

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

Solution:

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

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

Exercise 1.1.1.6.1: n=3 Shell Structure

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

Answer: three subshells; nine orbitals

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

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

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

We can summarize the relationships between the quantum numbers and the number of subshells and orbitals as follows (Table 1.1.1.6.1):

- Each principal shell has n subshells. For $n = 1$, only a single subshell is possible (1s); for $n = 2$, there are two subshells (2s and 2p); for $n = 3$, there are three subshells (3s, 3p, and 3d); 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 2d subshell would require both $n = 2$ and $l = 2$, which is not an allowed value of l for $n = 2$, a 2d 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 **1.1.1.6.1** Values of n, l, and ml through n = 4

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



Magnetic Quantum Number (m_l) & Spin Quantum Number (m_s): https://youtu.be/gbmGVUXBOBk

Summary

- 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 **wave functions (Ψ)** to describe the mathematical relationship between the motion of electrons in atoms and molecules and their energies. Wave functions have five important properties:

1. the wave function uses three variables (Cartesian axes *x*, *y*, and *z*) to describe the position of an electron;
2. the magnitude of the wave function is proportional to the intensity of the wave;
3. the probability of finding an electron at a given point is proportional to the square of the wave function at that point, leading to a distribution of probabilities in space that is often portrayed as an **electron density** plot;
4. describing electron distributions as standing waves leads naturally to the existence of sets of **quantum numbers** characteristic of each wave function; and
5. each spatial distribution of the electron described by a wave function with a given set of quantum numbers has a particular energy.

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

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1.1.1.7: Electron Spin (A Fourth Quantum Number)

Learning Objectives

- To introduce the concept of electron spin and demonstrated it is quantized

The process of describing each atom's electronic structure consists, essentially, of beginning with hydrogen and adding one proton and one electron at a time to create the next heavier element in the table. All stable nuclei other than hydrogen also contain one or more neutrons. Because neutrons have no electrical charge, however, they can be ignored in the following discussion. Before demonstrating how to do this, however, we must introduce the concept of electron spin.

The Stern-Gerlach Experiment

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 8.9.1. 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.

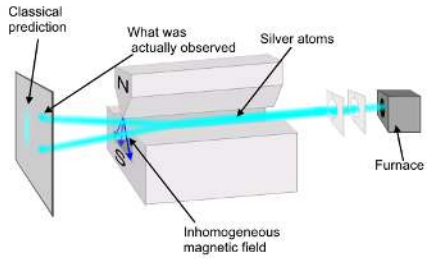


Figure **1.1.1.7.1**: The Stern-Gerlach apparatus. from Wikipedia

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.

Electron Spin

When scientists analyzed the emission and absorption spectra of the elements more closely, they saw that for elements having more than one electron, nearly all the lines in the spectra were actually *pairs* of very closely spaced lines. Because each line represents an energy level available to electrons in the atom, there are twice as many energy levels available as would be predicted solely based on the quantum numbers n, l, and m_l. Scientists also discovered that applying a magnetic field caused the lines in the pairs to split farther apart. In 1925, two graduate students in physics in the Netherlands, George Uhlenbeck (1900–1988) and Samuel Goudsmit (1902–1978), proposed that the splittings were caused by an electron spinning about its axis, much as Earth spins about its axis. When an electrically charged object spins, it produces a magnetic moment parallel to the axis of rotation, making it behave like a magnet. Although the electron cannot be viewed solely as a particle, spinning or otherwise, it is indisputable that it does have a magnetic moment. This magnetic moment is called electron spin.

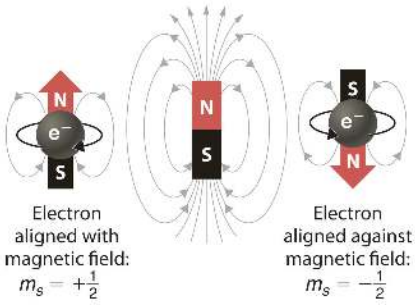


Figure **1.1.1.7.2**: Electron Spin. In a magnetic field, an electron has two possible orientations with different energies, one with spin up, aligned with the magnetic field, and one with spin down, aligned against it. All other orientations are forbidden.

In an external magnetic field, the electron has two possible orientations (Figure **1.1.1.7.2**). These are described by a fourth quantum number (m_s), which for any electron can have only two possible values, designated +½ (up) and −½ (down) to indicate that the two orientations are opposites; the subscript *s* is for spin. An electron behaves like a magnet that has one of two possible orientations, aligned either with the magnetic field or against it.

The 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 1.1.1.7.2

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 $m_l = -l, (-l + 1),\ldots, (l - 1), l$. There are only three possible combinations of (n, l, m_l): (2, 1, 1), (2, 1, 0), and (2, 1, −1).

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

C Hence the 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 1.1.1.7.2

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

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SECTION OVERVIEW

1.1.2: The Periodic Table

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The periodic table is a tabular arrangement of the chemical elements, ordered by their atomic number (number of protons in the nucleus), electron configurations, and recurring chemical properties. The periodic table can be used to derive relationships between the properties of the elements, and predict the properties of new elements yet to be discovered or synthesized. The periodic table provides a useful framework for analyzing chemical behavior, and is widely used in chemistry and other sciences.

Topic hierarchy

1.1.2.1: Classifying the Elements (Periodicity)

1.1.2.2: Sizes of Atoms and Ions

1.1.2.3: Ionization Energy

1.1.2.4: Electron Affinity

1.1.2.5: Magnetic Properties

1.1.2.6: Periodic Properties of the Elements

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1.1.2.1: Classifying the Elements (Periodicity)

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.

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 **1.1.2.1.1**). (The noble gases were still unknown.) Newlands therefore suggested that the elements could be classified into octaves A group of seven elements, corresponding to the horizontal rows in the main group elements (not counting the noble gases, which were unknown at the time)., corresponding to the *horizontal* rows in the main group elements. 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.

Note: 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.



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 **1.1.2.1.1**: 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."

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 **1.1.2.1.2**), 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):

$$\frac{molar\ mass\ \left(g/mol\right)}{density\ \left(g/cm^3\right)} = molar\ volume\ \left(cm^3/mol\right) \tag{1.1.2.1.1}$$

As shown in Figure **1.1.2.1.2**, 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.

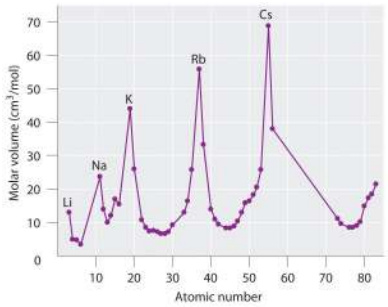
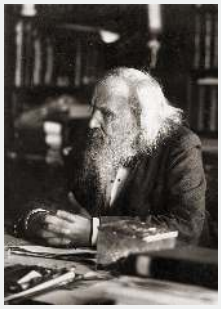


Figure **1.1.2.1.2**: Variation of Atomic Volume with Atomic Number, Adapted from Meyer's Plot of 1870**.** *Note the periodic increase and decrease in atomic volume. Because the noble gases had not yet been discovered at the time this graph was formulated, the peaks correspond to the alkali metals (group 1).*

Note: Dimitri Mendeleev (1834–1907)

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



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

Mendeleev's Periodic Table

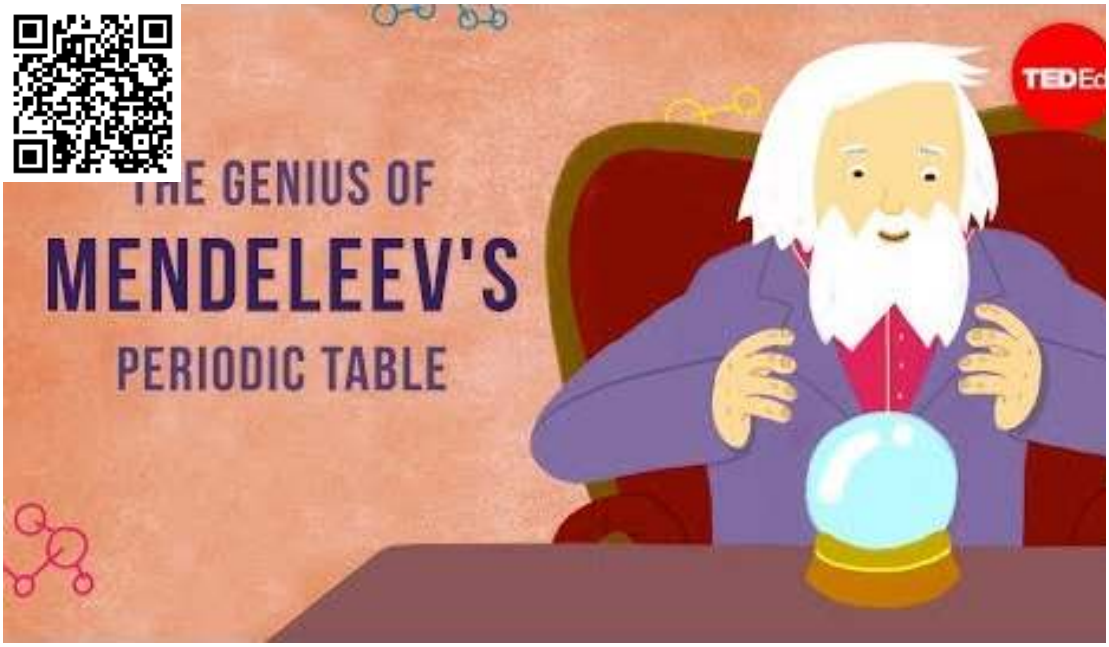
Mendeleev, who first published his periodic table in 1869 (Figure **1.1.2.1.3**), is usually credited with the origin of the modern periodic table. The key difference between his arrangement of the elements and that of Meyer and others is that Mendeleev did not assume that all the elements had been discovered (actually, only about two-thirds of the naturally occurring elements were known at the time). Instead, he deliberately left blanks in his table at atomic masses 44, 68, 72, and 100, in the expectation that elements with those atomic masses would be discovered. Those blanks correspond to the elements we now know as scandium, gallium, germanium, and technetium.

Reihen	Gruppe I. — R^2O	Gruppe II. — RO	Gruppe III. — R^2O^3	Gruppe IV. RH^4 RO^2	Gruppe V. RH^3 R^2O^5	Gruppe VI. RH^2 RO^3	Gruppe VII. RH R^2O^7	Gruppe VIII. — RO^4
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	— =44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63.
5	(Cu=63)	Zn=65	68	72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	—=100	Ru=104, Rh=104, Pd=106, Ag=108.
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce=140	—	—	—	— — — —
9	(—)	—				—	—	
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199.
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
12	—	—	—	Th=231	—	U=240	—	— — — —

Figure **1.1.2.1.3**: Mendeleev's Periodic Table, as Published in the German Journal *Annalen der Chemie und Pharmacie* in 1872. The column headings "Reihen" and "Gruppe" are German for "row" and "group." Formulas indicate the type of compounds formed by each group, with "R" standing for "any element" and superscripts used where we now use subscripts. Atomic masses are shown after equal signs and increase across each row from left to right.

The groups in Mendeleev's table are determined by how many oxygen or hydrogen atoms are needed to form compounds with each element. For example, in Group I, two atoms of hydrogen, lithium, Li, sodium, Na, and potassium form compounds with one atom of oxygen. In Group VII, one atom of fluorine, F, chlorine, Cl, and bromine, Br, react with one atom of hydrogen. Notice how this approach has trouble with the transition metals. Until roughly 1960, a rectangular table developed from Mendeleev's table and based on reactivity was standard at the front of chemistry lecture halls.

The most convincing evidence in support of Mendeleev's arrangement of the elements was the discovery of two previously unknown elements whose properties closely corresponded with his predictions (Table **1.1.2.1.1**). Two of the blanks Mendeleev had left in his original table were below aluminum and silicon, awaiting the discovery of two as-yet-unknown elements, *eka*-aluminum and *eka*-silicon (from the Sanskrit *eka*, meaning "one," as in "one beyond aluminum"). The observed properties of gallium and germanium matched those of *eka*-aluminum and *eka*-silicon so well that once they were discovered, Mendeleev's periodic table rapidly gained acceptance.



Video* 1.1.2.1.1: The genius of Mendeleev's periodic table.*

When the chemical properties of an element suggested that it might have been assigned the wrong place in earlier tables, Mendeleev carefully reexamined its atomic mass. He discovered, for example, that the atomic masses previously reported for beryllium, indium, and uranium were incorrect. The atomic mass of indium had originally been reported as 75.6, based on an assumed stoichiometry of InO for its oxide. If this atomic mass were correct, then indium would have to be placed in the middle of the nonmetals, between arsenic (atomic mass 75) and selenium (atomic mass 78). Because elemental indium is a silvery-white *metal*, however, Mendeleev postulated that the stoichiometry of its oxide was really In_2O_3 rather than InO. This would mean that indium's atomic mass was actually 113, placing the element between two other metals, cadmium and tin.

Table **1.1.2.1.1**: Comparison of the Properties Predicted by Mendeleev in 1869 for eka-Aluminum and eka-Silicon with the Properties of Gallium (Discovered in 1875) and Germanium (Discovered in 1886)

Property	*eka*-Aluminum (predicted)	Gallium (observed)	*eka*-Silicon (predicted)	Germanium (observed)
atomic mass	68	69.723	72	72.64
element	metal	metal	dirty-gray metal	gray-white metal
	low mp*	mp = 29.8°C	high mp	mp = 938°C
	ρ = 5.9 g/cm^3	ρ = 5.91 g/cm^3	ρ = 5.5 g/cm^3	ρ = 5.323 g/cm^3
oxide	E_2O_3	Ga_2O_3	EO_2	GeO_2
	ρ = 5.5 g/cm^3	ρ = 6.0 g/cm^3	ρ = 4.7 g/cm^3	ρ = 4.25 g/cm^3
chloride	ECl_3	$GaCl_3$	ECl_4	$GeCl_4$
	volatile	mp = 78°C bp* = 201°C	bp < 100°C	bp = 87°C

*mp = melting point; bp = boiling point.

One group of elements that absent from Mendeleev's table is the noble gases, all of which were discovered more than 20 years later, between 1894 and 1898, by Sir William Ramsay (1852–1916; Nobel Prize in Chemistry 1904). Initially, Ramsay did not know where to place these elements in the periodic table. Argon, the first to be discovered, had an atomic mass of 40. This was greater than chlorine's and comparable to that of potassium, so Ramsay, using the same kind of reasoning as Mendeleev, decided to place the noble gases between the halogens and the alkali metals.

The Role of the Atomic Number in the Periodic Table

Despite its usefulness, Mendeleev's periodic table was based entirely on empirical observation supported by very little understanding. It was not until 1913, when a young British physicist, H. G. J. Moseley (1887–1915), while analyzing the frequencies of x-rays emitted by the elements, discovered that the underlying foundation of the order of the elements was by the *atomic number*, not the atomic mass. Moseley hypothesized that the placement of each element in his series corresponded to its atomic number *Z*, which is the number of positive charges (protons) in its nucleus. Argon, for example, although having an atomic mass greater than that of potassium (39.9 amu versus 39.1 amu, respectively), was placed *before* potassium in the periodic table. While analyzing the frequencies of the emitted x-rays, Moseley noticed that the atomic number of argon is 18, whereas that of potassium is 19, which indicated that they were indeed placed correctly. Moseley also noticed three gaps in his table of x-ray frequencies, so he predicted the existence of three unknown elements: technetium (Z = 43), discovered in 1937; promethium (Z = 61), discovered in 1945; and rhenium (Z = 75), discovered in 1925.

Note: H. G. J. Moseley (1887–1915)

Moseley left his research work at the University of Oxford to join the British army as a telecommunications officer during World War I. He was killed during the Battle of Gallipoli in Turkey.



Example 1.1.2.1.1

Before its discovery in 1999, some theoreticians believed that an element with a Z of 114 existed in nature. Use Mendeleev's reasoning to name element 114 as *eka*-_____; then identify the known element whose chemistry you predict would be most similar to that of element 114.

Given: atomic number

Asked for: name using prefix *eka*-

Strategy:

A. Using the periodic table locate the n = 7 row. Identify the location of the unknown element with Z = 114; then identify the known element that is directly above this location.
B. Name the unknown element by using the prefix *eka*- before the name of the known element.

Solution:

A The $n = 7$ row can be filled in by assuming the existence of elements with atomic numbers greater than 112, which is underneath mercury (Hg). Counting three boxes to the right gives element 114, which lies directly below lead (Pb). **B** If Mendeleev were alive today, he would call element 114 *eka*-lead.

? Exercise 1.1.2.1.1

Use Mendeleev's reasoning to name element 112 as *eka*-_____; then identify the known element whose chemistry you predict would be most similar to that of element 112.

Answer: *eka*-mercury

Summary

- The elements in the periodic table are arranged according to their properties, and the periodic table serves as an aid in predicting chemical behavior.

The periodic table arranges the elements according to their electron configurations, such that elements in the same column have the same valence electron configurations. Periodic variations in size and chemical properties are important factors in dictating the types of chemical reactions the elements undergo and the kinds of chemical compounds they form. The modern periodic table was based on empirical correlations of properties such as atomic mass; early models using limited data noted the existence of **triads** and **octaves** of elements with similar properties. The periodic table achieved its current form through the work of Dimitri Mendeleev and Julius Lothar Meyer, who both focused on the relationship between atomic mass and chemical properties. Meyer arranged the elements by their atomic volume, which today is equivalent to the **molar volume**, defined as molar mass divided by molar density. The correlation with the electronic structure of atoms was made when H. G. J. Moseley showed that the periodic arrangement of the elements was determined by atomic number, not atomic mass.

Contributors and Attributions

Modified by Joshua Halpern (Howard University)

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1.1.2.2: 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. In this section, we discuss how atomic and ion "sizes" are defined and obtained.

Atomic Radii

Recall that the probability of finding an electron in the various available orbitals falls off slowly as the distance from the nucleus increases. This point is illustrated in Figure **1.1.2.2.1** 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.

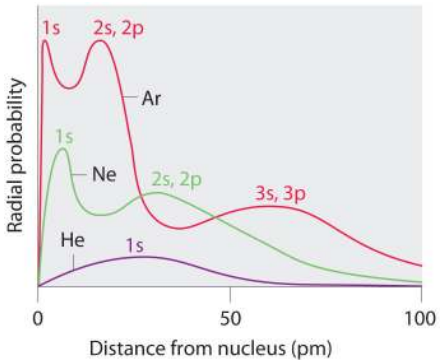


Figure **1.1.2.2.1**: Plots of Radial Probability as a Function of Distance from the Nucleus for He, Ne, and Ar. In He, the 1*s* electrons have a maximum radial probability at ≈30 pm from the nucleus. In Ne, the 1*s* electrons have a maximum at ≈8 pm, and the 2*s* and 2*p* electrons combine to form another 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 **1.1.2.2.1** 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 **1.1.2.2.1** 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 (part (a) in Figure **1.1.2.2.2**). Atomic radii are often measured in angstroms (Å), a non-SI unit: $1 Å = 1 \times 10^{-10}$ m = 100 pm.

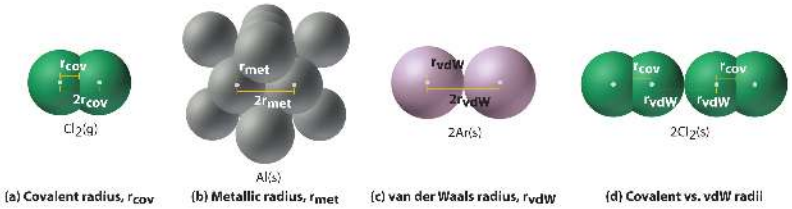


Figure **1.1.2.2.2**: Definitions of the Atomic Radius. (a) The covalent atomic radius, r_{cov}, is half the distance between the nuclei of two like atoms joined by a covalent bond in the same molecule, such as Cl_2. (b) The metallic atomic radius, r_{met}, is half the distance between the nuclei of 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 the distance between the two chlorine atoms in a single molecule of Cl_2. The van der Waals radius is 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 (part (b) in Figure **1.1.2.2.2**). 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 (part (c) in Figure **1.1.2.2.2**). 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 (part (d) in Figure **1.1.2.2.2**).

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 **1.1.2.2.3**).

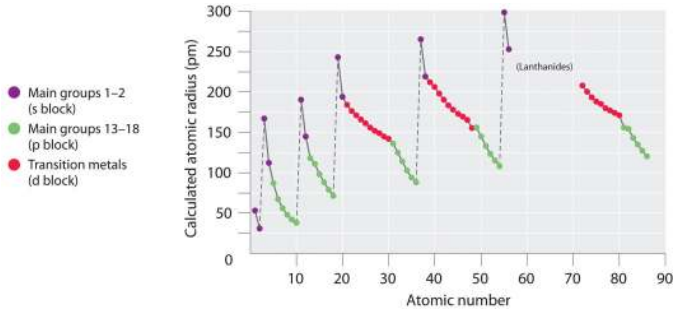


Figure **1.1.2.2.3**: A Plot of Periodic Variation of Atomic Radius with Atomic Number for the First Six Rows of the Periodic Table.

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 **1.1.2.2.4**).

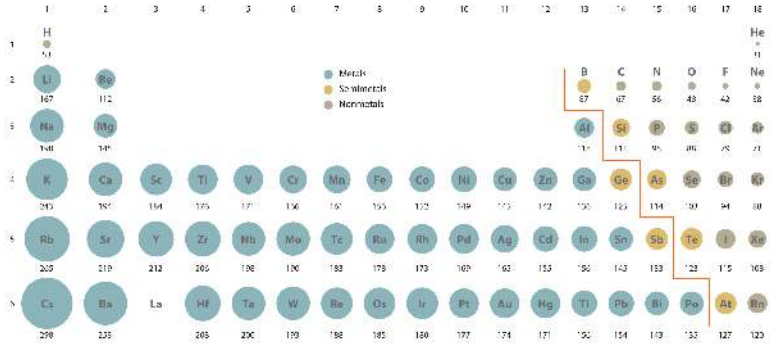


Figure **1.1.2.2.4** *Calculated Atomic Radii (in Picometers) of the s-, p-, and d-Block Elements. The sizes of the circles illustrate the relative sizes of the atoms. The calculated values are based on quantum mechanical wave functions. Source: http://www.webelements.com. Web Elements is an excellent on line source for looking up atomic properties.*

Note

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

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.

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.

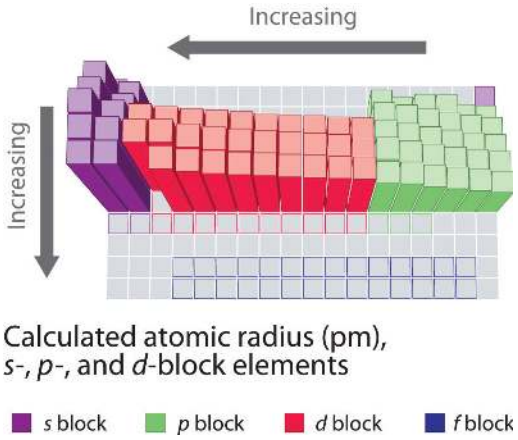


Figure **1.1.2.2.5**: *The Atomic Radius of the Elements. The atomic radius of the elements increases as we go from right to left across a period and as we go down the periods in a group.*

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.

Note

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 1.1.2.2.1

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 1.1.2.2.1

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: https://youtu.be/ZYKB8SNrGVY

Ionic Radii and Isoelectronic Series

An ion is formed when either one or more electrons are removed from a neutral atom (cations) to form a positive ion or when additional electrons attach themselves to neutral atoms (anions) to form a negative one. 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.

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 **1.1.2.2.6**, 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.

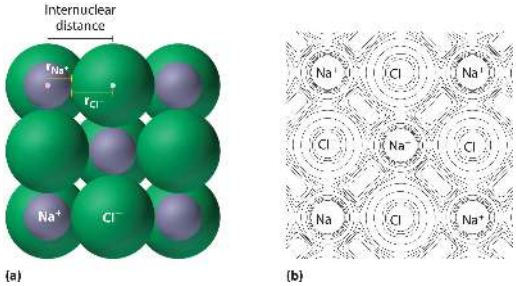


Figure **1.1.2.2.6**: Definition of Ionic Radius. (a) The internuclear distance is apportioned between adjacent cations (positively charged ions) and anions (negatively charged ions) in the ionic structure, as shown here for Na^+ and Cl^- in sodium chloride. (b) This depiction of electron density contours 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^+.

A comparison of ionic radii with atomic radii (Figure **1.1.2.2.7**) *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 (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 (compare F at 42 pm with F^- at 133 pm).

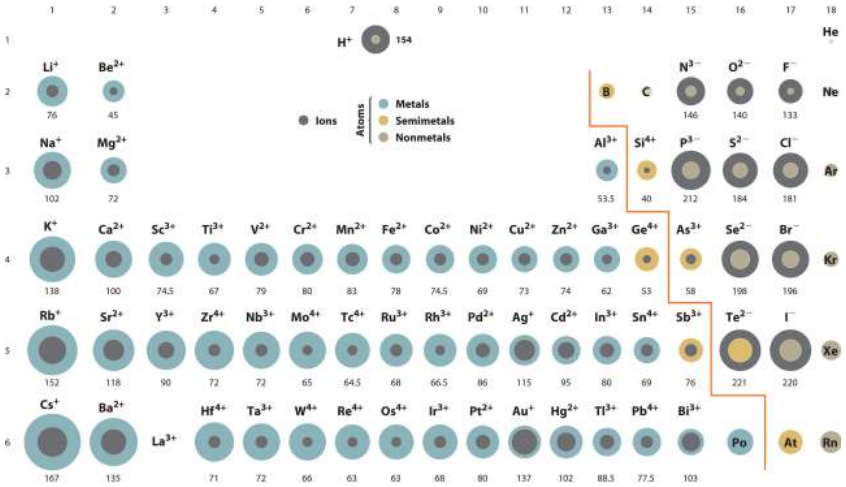


Figure 3.7. Source: Ionic radius data from R. D. Shannon, "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides," *Acta Crystallographica* 32, no. 5 (1976): 751–767.

Note

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 **1.1.2.2.1**. 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 **1.1.2.2.1**: Experimentally Measured Values for the Radius of Sodium in Its Three Known Oxidation States

	Na^+	Na^0	Na^-
Electron Configuration	$1s^22s^22p^6$	$1s^22s^22p^63s^1$	$1s^22s^22p^63s^2$
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 ($1s^22s^22p^6$) is shown in Table 7.3



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 **1.1.2.2.3**, because neon forms no covalent or ionic compounds and hence its radius is difficult to measure.

Table 9.3.3 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 1.1.2.2.2

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 1.1.2.2.2

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

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

Summary

- Ionic radii share the same vertical trend as atomic radii, but the horizontal trends differ due to differences in ionic charges.

A variety of methods have been established to measure the size of a single atom or ion. The **covalent atomic radius (r_{cov})** is half the internuclear distance in a molecule with two identical atoms bonded to each other, whereas the **metallic atomic radius (r_{met})** is defined as half the distance between the nuclei of two adjacent atoms in a metallic element. The **van der Waals radius (r_{vdW})** of an element is half the internuclear distance between two nonbonded atoms in a solid. Atomic radii decrease from left to right across a row because of the increase in effective nuclear charge due to poor electron screening by other electrons in the same principal shell. Moreover, atomic radii increase from top to bottom down a column because the effective nuclear charge remains relatively constant as the principal quantum number increases. The **ionic radii** of cations and anions are always smaller or larger, respectively, than the parent atom due to changes in electron–electron repulsions, and the trends in ionic radius parallel those in atomic size. A comparison of the dimensions of atoms or ions that have the same number of electrons but different nuclear charges, called an **isoelectronic series**, shows a clear correlation between increasing nuclear charge and decreasing size.

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1.1.2.3: 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. In this section, we develop a more quantitative approach to predicting such reactions by examining periodic trends in the energy changes that accompany ion formation.

Ionization Energies

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

$$E_{(g)} \rightarrow E^+_{(g)} + e^- \qquad \text{energy required=I} \tag{1.1.2.3.1}$$

Because an input of energy is required, the ionization energy is always positive ($I > 0$) for the reaction as written in Equation 9.4.1. 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):

$$1\ eV/atom = 96.49\ kJ/mol \tag{1.1.2.3.2}$$

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:

$$E_{(g)} \rightarrow E^+_{(g)} + e^- \qquad I_1 = \text{1st ionization energy} \tag{1.1.2.3.3}$$

$$E_{(g)} \rightarrow E^+_{(g)} + e^- \qquad I_2 = \text{2nd ionization energy} \tag{1.1.2.3.4}$$

$$E^+_{(g)} \rightarrow E^{2+}_{(g)} + e^- \qquad I_3 = \text{3rd ionization energy} \tag{1.1.2.3.5}$$

Values for the ionization energies of Li and Be listed in Table **1.1.2.3.1** show that successive ionization energies for an element increase steadily; 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.

Note

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

Table **1.1.2.3.1**: 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 (1.1.2.3.6)	Reaction	Electronic Transition	I (1.1.2.3.7)
$Li_{(g)} \rightarrow Li^+_{(g)} + e^-$	$1s^22s^1 \rightarrow 1s^2$	I_1 = 520.2	$Be_{(g)} \rightarrow Be^+_{(g)} + e^-$	$1s^22s^2 \rightarrow 1s^22s^1$	I_1 = 899.5
$Li^+_{(g)} \rightarrow Li^{2+}_{(g)} + e^-$	$1s^2 \rightarrow 1s^1$	I_2 = 7298.2	$Be^+_{(g)} \rightarrow Be^{2+}_{(g)} + e^-$	$1s^22s^1 \rightarrow 1s^2$	I_2 = 1757.1
$Li^{2+}_{(g)} \rightarrow Li^{3+}_{(g)} + e^-$	$1s^1 \rightarrow 1s^0$	I_3 = 11,815.0	$Be^{2+}_{(g)} \rightarrow Be^{3+}_{(g)} + e^-$	$1s^2 \rightarrow 1s^1$	I_3 = 14,848.8
			$Be^{3+}_{(g)} \rightarrow Be^{4+}_{(g)} + e^-$	$1s^1 \rightarrow 1s^0$	I_4 = 21,006.6

The most important consequence of the values listed in Table **1.1.2.3.1** is that the chemistry of Li is dominated by the Li^+ ion, while the chemistry of Be is dominated by the +2 oxidation state. The energy required to remove the *second* electron from Li

$$Li^+_{(g)} \rightarrow Li^{2+}_{(g)} + e^- \tag{1.1.2.3.8}$$

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

$$Be^{2+}_{(g)} \rightarrow Be^{3+}_{(g)} + e^- \tag{1.1.2.3.9}$$

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.*

Note

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

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 **1.1.2.3.2**): 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 **1.1.2.3.2**. 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 **1.1.2.3.2**: 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	579.4.4	1816.7	2744.8	**11,579.4.4**	—	—	—
Si	786.5	1577.1	3231.6	4355.5	**16,090.6**	—	—
P	1011.8	1909.4.4	2914.1	4963.6	6274.0	**21,269.4.3**	—
S	999.6	2251.8	3357	4556.2	7004.3	8495.8	**27,109.4.3**
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 1.1.2.3.1: 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:

$$E_{(g)}^{3+} \rightarrow E_{(g)}^{4+} + e^- \tag{1.1.2.3.10}$$

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 1.1.2.3.1: 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 1.1.2.3.2 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.

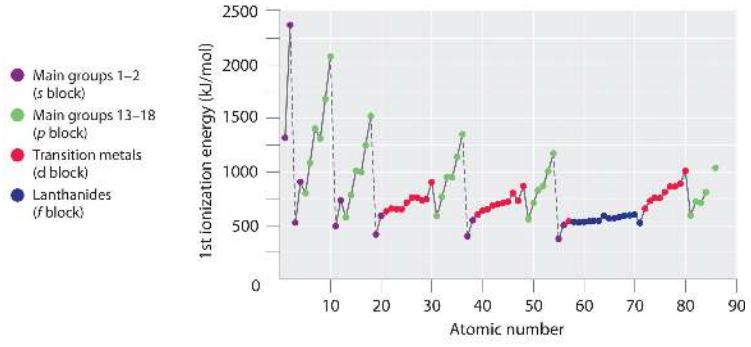


Figure 1.1.2.3.1: A Plot of Periodic Variation of First Ionization Energy with Atomic Number for the First Six Rows of the Periodic Table. There is a decrease in ionization energy within a group (most easily seen here for groups 1 and 18).

However, the first ionization energy decreases at Al ($[Ne]3s^2 3p^1$) and at S ($[Ne]3s^2 3p^4$). 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. 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.

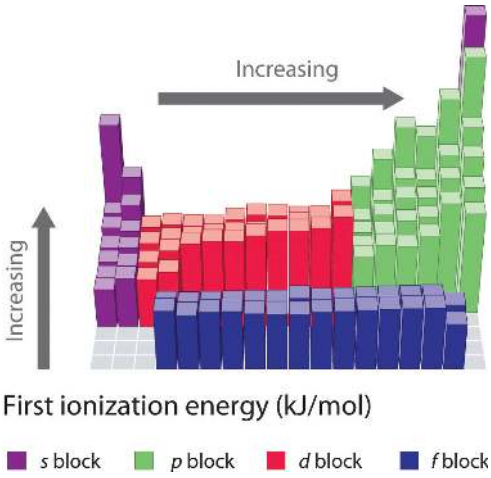


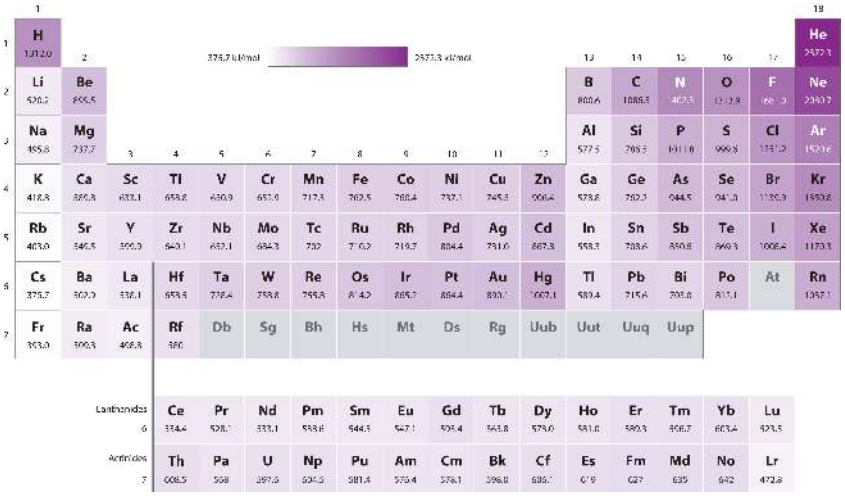
Figure* 1.1.2.3.2*: *First Ionization Energies of the s-, p-, d-, and f-Block Elements*

The first ionization energies of the elements in the first six rows of the periodic table are plotted in Figure **1.1.2.3.1** and are presented numerically and graphically in Figure **1.1.2.3.2**. 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) electron configurations.
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 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).

Note

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



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).

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

Ionization Energies of Transition Metals & Lanthanides

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

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

Because their first, second, and third ionization energies change so little across a row, these elements have important *horizontal* similarities in chemical properties in addition to the expected vertical similarities. For example, all the first-row transition metals except scandium form stable compounds as M^{2+} ions, whereas the lanthanides primarily form compounds in which they exist as M^{3+} ions.

Example 1.1.2.3.2: 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 1.1.2.3.2: 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



Ionization Energy: https://youtu.be/k7j-u02ifzo

Summary

- Generally, the first ionization energy and electronegativity values increase diagonally from the lower left of the periodic table to the upper right, and electron affinities become more negative across a row.

The tendency of an element to lose 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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1.1.2.4: Electron Affinity

Learning Objectives

- To master the concept of electron affinity as a measure of the energy required to 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 ***E*** is defined as the energy change that occurs when an electron is added to a gaseous atom:

$$E_{(g)} + e^- \rightarrow E^-_{(g)} \qquad \text{energy change} = EA \tag{1.1.2.4.1}$$

Unlike ionization energies, which are always positive for a neutral atom because energy is required to remove an electron, electron affinities can be negative (energy is released when an electron is added), positive (energy must be added to the system to produce an anion), or zero (the process is energetically neutral). This sign convention is consistent with a negative value corresponded to the energy change for an exothermic process, which is one in which heat is released.

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

$$Cl_{(g)} + e^- \rightarrow Cl^-_{(g)} \qquad EA = -346\ kJ/mol \tag{1.1.2.4.2}$$

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

$$Be_{(g)} + e^- \rightarrow Be^-_{(g)} \qquad EA \geq 0 \tag{1.1.2.4.3}$$

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:

$$N_{(g)} + e^- \rightarrow N^-_{(g)} \qquad EA \approx 0 \tag{1.1.2.4.4}$$

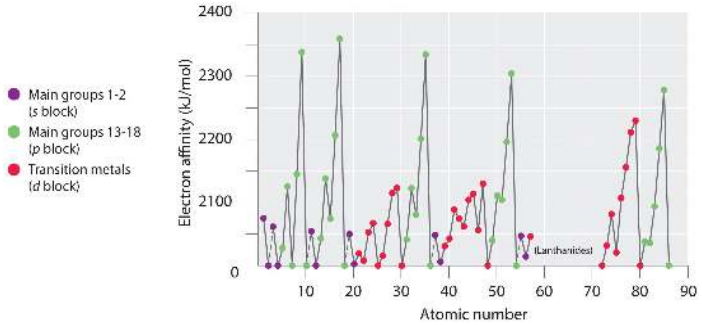


Figure 1.1.2.4.1: A Plot of Periodic Variation of Electron Affinity with Atomic Number for the First Six Rows of the Periodic Table

Note

Generally, electron affinities become more negative across a row of the periodic table.

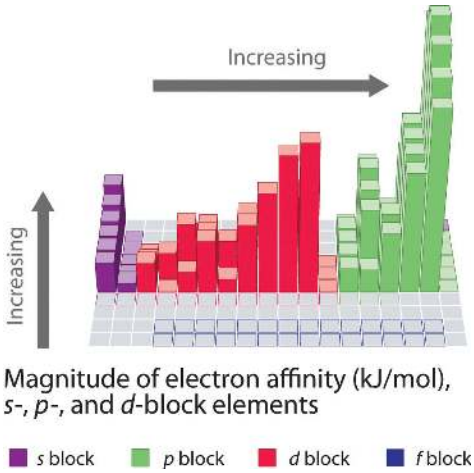
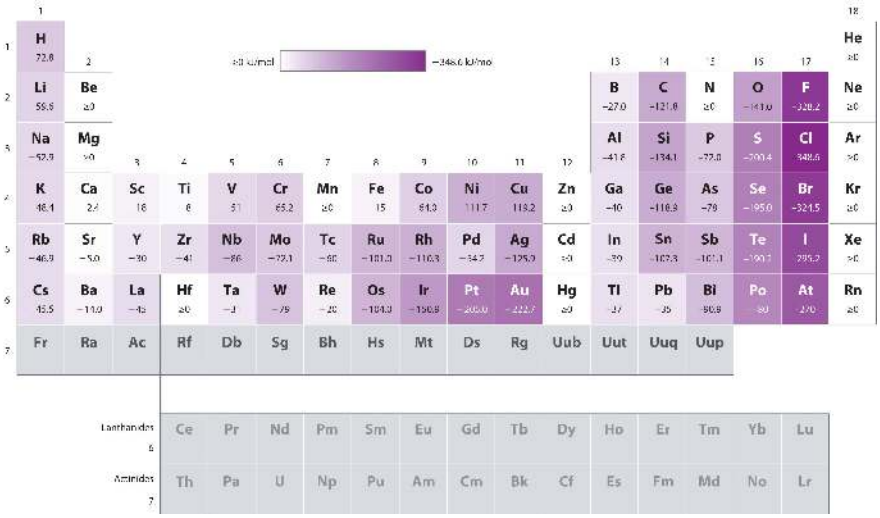


Figure **1.1.2.4.2** Electron Affinities (in kJ/mol) of the *s*-, *p*-, and *d*-Block Elements.

In general, electron affinities of the main-group elements become less negative as we proceed down a column. This is because as *n* increases, the extra electrons enter orbitals that are increasingly far from the nucleus. Atoms with the largest radii, which have the lowest ionization energies (affinity for their own valence electrons), also have the lowest affinity for an added electron. There are, however, two major exceptions to this trend:

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



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).

Note

In general, electron affinities become more negative across a row and less negative down a column.

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

$$E_{(g)} + e^- \rightarrow E^-_{(g)} \qquad \text{energy change} = EA_1 \tag{1.1.2.4.5}$$

$$E^-_{(g)} + e^- \rightarrow E^{2-}_{(g)} \qquad \text{energy change} = EA_2 \tag{1.1.2.4.6}$$

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:

$$O_{(g)} + e^- \rightarrow O^-_{(g)} \qquad EA_1 = -141\ kJ/mol \tag{1.1.2.4.7}$$

$$O^-_{(g)} + e^- \rightarrow O^{2-}_{(g)} \qquad EA_2 = +744\ kJ/mol \tag{1.1.2.4.8}$$

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

$$O_{(g)} + 2e^- \rightarrow O^{2-}_{(g)} \qquad EA = +603\ kJ/mol \tag{1.1.2.4.9}$$

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

Note

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

If energy is required to form both positively charged ions 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 1.1.2.4.1: Contrasting Electron Affinities of Sb, Se, and Te

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

Given: three elements

Asked for: element with most negative electron affinity

Strategy:

A. Locate the elements in the periodic table. Use the trends in electron affinities going down a column for elements in the same group. Similarly, use the trends in electron affinities from left to right for elements in the same row.
B. Place the elements in order, listing the element with the most negative electron affinity first.

Solution:

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

Exercise 1.1.2.4.1: 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



Electron Affinity: https://youtu.be/M5MsRM2Xtds

Summary

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

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1.1.2.5: Magnetic Properties

Learning Objectives

- To predict the magnetic properties of atoms and molecules based on their electronic configurations.

The magnetic moment of a system measures the strength and the direction of its magnetism. The term itself usually refers to the magnetic dipole moment. Anything that is magnetic, like a bar magnet or a loop of electric current, has a magnetic moment. A magnetic moment is a vector quantity, with a magnitude and a direction. An electron has an electron magnetic dipole moment, generated by the electron's intrinsic spin property, making it an electric charge in motion. There are many different magnetic forms: including paramagnetism, and diamagnetism, ferromagnetism, and anti-ferromagnetism. Only paramagnetism, and diamagnetism are discussed here.

Paramagnetism

Paramagnetism refers to the magnetic state of an atom with one or more unpaired electrons. The unpaired electrons are attracted by a magnetic field due to the electrons' magnetic dipole moments. Hund's Rule states that electrons must occupy every orbital singly before any orbital is doubly occupied. This may leave the atom with many unpaired electrons. Because unpaired electrons can orient in either direction, they exhibit magnetic moments that can align with a magnet. This capability allows paramagnetic atoms to be attracted to magnetic fields. Diatomic oxygen, O_2 is a good example of paramagnetism (that is best understood with molecular orbital theory). The following video shows liquid oxygen attracted into a magnetic field created by a strong magnet:



Video* 1.1.2.5.1*: *A chemical demonstration of the paramagnetism of molecular oxygen, as shown by the attraction of liquid oxygen to magnets.*

As shown in Video 1.1.2.5.1, since molecular oxygen (O_2 is paramagnetic, it is attracted to the magnet. In contrast, molecular nitrogen, N_2, has no unpaired electrons and it is diamagnetic (discussed below); it is therefore unaffected by the magnet.

Note

Paramagnetism is a form of magnetism whereby materials are **attracted** by an externally applied magnetic field.

There are some exceptions to the paramagnetism rule; these concern some transition metals, in which the unpaired electron is not in a d-orbital. Examples of these metals include Sc^{3+}, Ti^{4+}, Zn^{2+}, and Cu^{+}. These metals are the not defined as paramagnetic: they are considered diamagnetic because all d-electrons are paired. Paramagnetic compounds sometimes display bulk magnetic properties due to the clustering of the metal atoms. This phenomenon is known as ferromagnetism, but this property is not discussed here.

Diamagnetism

Diamagnetic substances are characterized by paired electrons—except in the previously-discussed case of transition metals, there are no unpaired electrons. According to the Pauli Exclusion Principle which states that no two identical electrons may take up the same quantum state at the same time, the electron spins are oriented in opposite directions. This causes the magnetic fields of the electrons to cancel out; thus there is no net

magnetic moment, and the atom cannot be attracted into a magnetic field. In fact, diamagnetic substances are weakly ***repelled*** by a magnetic field as demonstrated with the pyrolytic carbon sheet in Figure **1.1.2.5.1**.

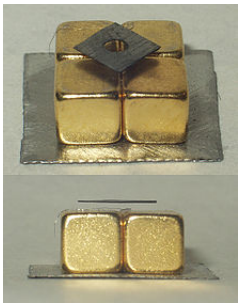


Figure **1.1.2.5.1**: Levitating pyrolytic carbon: A small (~6 mm) piece of pyrolytic graphite levitating over a permanent neodymium magnet array (5 mm cubes on a piece of steel). Note that the poles of the magnets are aligned vertically and alternate (two with north facing up, and two with south facing up, diagonally). from Wikipedia.

Note

Diamagnetic materials are **repelled** by the applied magnetic field.

Diamagnetism, to a greater or lesser degree, is a property of all materials and always makes a weak contribution to the material's response to a magnetic field. For materials that show some other form of magnetism (such paramagntism), the diamagnetic contribution becomes negligible.

How to tell if a substance is paramagnetic or diamagnetic

The magnetic form of a substance can be determined by examining its electron configuration: if it shows unpaired electrons, then the substance is paramagnetic; if all electrons are paired, the substance is diamagnetic. This process can be broken into four steps:

1. Find the electron configuration
2. Draw the valence orbitals
3. Look for unpaired electrons
4. Determine whether the substance is paramagnetic (one or more electrons unpaired) or diamagnetic (all electrons paired)



Determining Magnetic Properties from Orbital Diagrams: https://youtu.be/lun_w5VKD8k

Example 1.1.2.5.1: Chlorine atoms

Are chlorine atoms paramagnetic or diamagnetic?

Solution

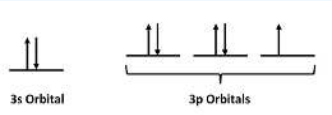
Follow the four steps outlines above.

Step 1: Find the electron configuration

For Cl atoms, the electron configuration is $3s^2 3p^5$

Step 2: Draw the valence orbitals

Ignore the core electrons and focus on the valence electrons only.



Step 3: Look for unpaired electrons

There is one unpaired electron.

Step 4: Determine whether the substance is paramagnetic or diamagnetic

Since there is an unpaired electron, Cl atoms are paramagnetic (but weakly since only one electron is unpaired).

? Exercise 1.1.2.5.1

Indicate whether boron atoms are paramagnetic or diamagnetic.

Answer:

The B atom has $2s^2 2p^1$ as the electron configuration. Because it has one unpaired electron, it is paramagnetic.

✓ Example 1.1.2.5.2: Zinc Atoms

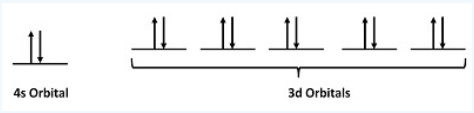
Are zinc atoms paramagnetic or diamagnetic?

Solution

Step 1: Find the electron configuration

For Zn atoms, the electron configuration is $4s^2 3d^{10}$

Step 2: Draw the valence orbitals



Step 3: Look for unpaired electrons

There are no unpaired electrons.

Step 4: Determine whether the substance is paramagnetic or diamagnetic

Because there are no unpaired electrons, Zn atoms are diamagnetic.

? Exercise 1.1.2.5.2

Indicate whether F^- ions are paramagnetic or diamagnetic.

Answer

The F^- ion has $2s^2 2p^6$ has the electron configuration. Because it has no unpaired electrons, it is diamagnetic.

Problems

1. How many unpaired electrons are found in oxygen atoms ?
2. How many unpaired electrons are found in bromine atoms?
3. Indicate whether Fe^{2+} ions are paramagnetic or diamagnetic.

Answers

1. The O atom has $2s^2 2p^4$ as the electron configuration. Therefore, O has 2 unpaired electrons.
2. The Br atom has $4s^2 3d^{10} 4p^5$ as the electron configuration. Therefore, Br has 1 unpaired electron.
3. The Fe^{2+} ion has $3d^6$ has the electron configuration. Because it has 4 unpaired electrons, it is paramagnetic.

References

1. Pettrucci, Ralph H. General Chemistry: Principles and Modern Applications. 9th. Upper Saddle River: Pearson Prentice Hall, 2007

2. Sherman, Alan, Sharon J. Sherman, and Leonard Russikoff. Basic Concepts of Chemistry Fifth Edition. Boston, MA: Houghton Mifflin Company, 1992. Print.

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1.1.2.6: Periodic Properties of the Elements

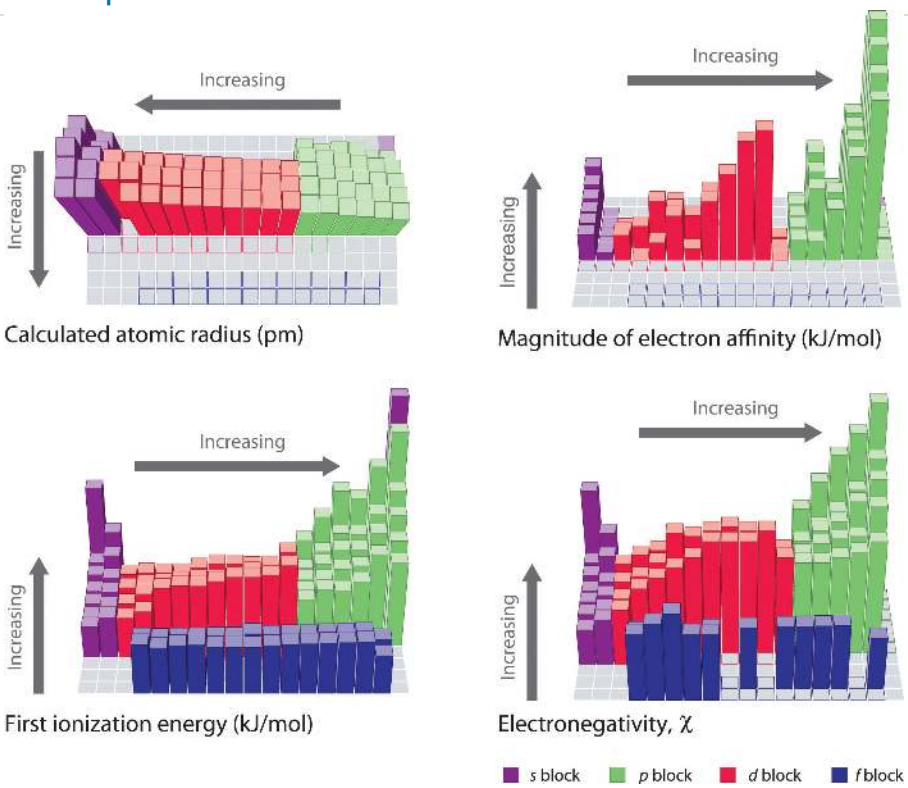


Figure **1.1.2.6.1** Summary of Major Periodic Trends. The general trends for the first ionization energy, electron affinity, and electronegativity are opposite to the general trend for covalent atomic radius.

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SECTION OVERVIEW

1.1.3: Chemical Bonding I- Basic Concepts

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We defined a chemical bond as the force that holds atoms together in a chemical compound. We also introduced two idealized types of bonding: **covalent bonding**, in which electrons are shared between atoms in a molecule or polyatomic ion, and **ionic bonding**, in which positively and negatively charged ions are held together by electrostatic forces. The concepts of covalent and ionic bonding were developed to explain the properties of different kinds of chemical substances.

Topic hierarchy

1.1.3.1: Lewis Theory- An Overview

1.1.3.2: Covalent Bonding- An Introduction

1.1.3.3: Polar Covalent Bonds and Electrostatic Maps

1.1.3.4: Writing Lewis Structures

1.1.3.5: Resonance

1.1.3.6: Exceptions to the Octet Rule

1.1.3.7: The Shapes of Molecules

1.1.3.8: Bond Order and Bond Lengths

1.1.3.9: Bond Energies

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1.1.3.1: Lewis Theory- An Overview

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.

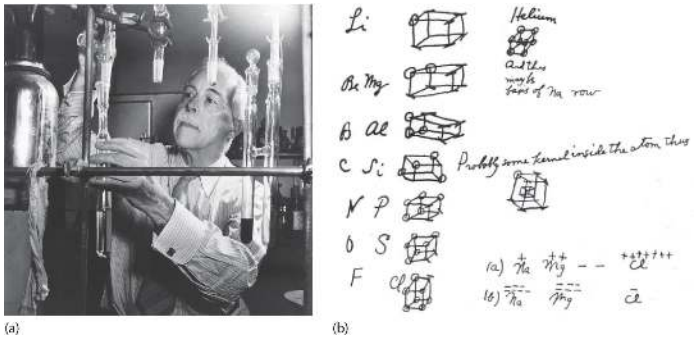


Figure **1.1.3.1.1**: G. N. Lewis and the Octet Rule. (a) Lewis is working in the laboratory. (b) In Lewis's original sketch for the octet rule, he initially placed the electrons at the corners of a cube rather than placing them as we do now.

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.

Note

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:

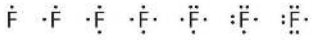


Figure **1.1.3.1.2**.

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 **1.1.3.1.2**. 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 **1.1.3.1.2**: Lewis Dot Symbols for the Elements in Period 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.

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., H_2
2. For most atoms there will be a maximum of eight electrons in the valence shell (octet structure), e.g., CH_4

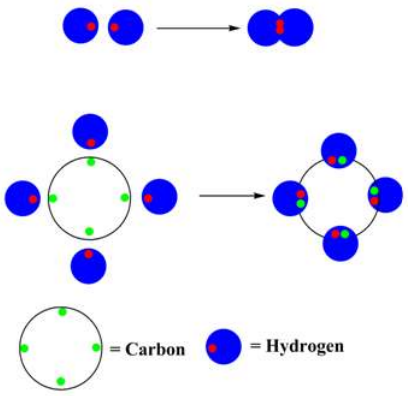


Figure 1: Bonding in H_2 and methane (CH_4)

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.

Note

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 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.

Note

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.



Lewis Theory of Bonding: https://youtu.be/TZ6C5_k-SPs

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.

Contributors and Attributions

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1.1.3.2: Covalent Bonding- An Introduction

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

Note

A chemical bond formed by sharing a pair of electrons is called a covalent bond

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 **1.1.3.2.1**):

- 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.

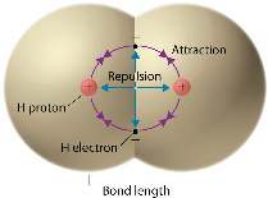


Figure **1.1.3.2.1**: Attractive and Repulsive Interactions between Electrons and Nuclei in the Hydrogen Molecule. Electron–electron and proton–proton interactions are repulsive; electron–proton interactions are attractive. At the observed bond distance, the repulsive and attractive interactions are balanced.

A plot of the potential energy of the system as a function of the internuclear distance (Figure **1.1.3.2.2**) 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 Figure **1.1.3.2.2** and Figure 8.1, 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.

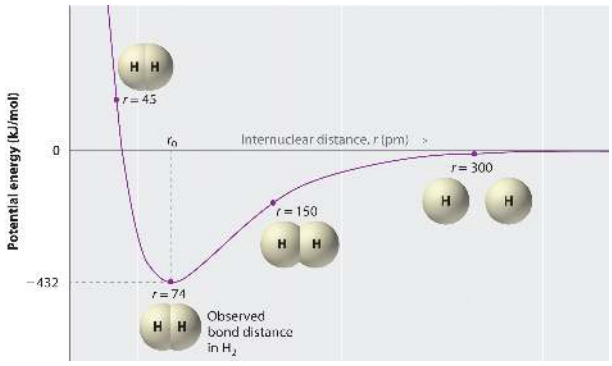


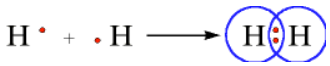
Figure **1.1.3.2.2**: A Plot of Potential Energy versus Internuclear Distance for the Interaction between Two Gaseous Hydrogen Atoms.

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.

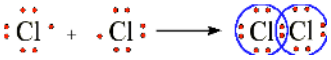
Lewis Structures

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:



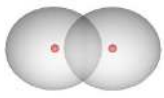
The ***shared pair*** of electrons provides ***each*** hydrogen atom with two electrons in its valence shell (the 1*s*) orbital. In a sense, each hydrogen atoms has the electron configuration of the noble gas helium (the octet rule). When two chlorine atoms covalently bond to form Cl_2, the following sharing of electrons occurs:



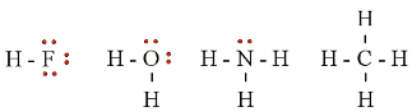
Each chlorine atom shared the bonding pair of electrons and achieves the electron configuration of the noble gas argon. In Lewis structures the bonding pair of electrons is usually displayed as a line, and the unshared electrons as dots:



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:



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***



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

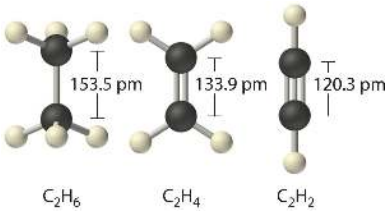
For the nonmetals (and the 's' block metals) the number of valence electrons is equal to the group number:

Element	Group	Valence electrons	Bonds needed to form valence octet
F	17	7	1
O	16	6	2
N	15	5	3
C	14	4	4



Lewis Structure of Molecules: https://youtu.be/xWiFCqA9Ur0

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 **1.1.3.2.1**, 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 **1.1.3.2.1**: 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); http://cccbdb.nist.gov.

Note

As a general rule, the distance between bonded atoms decreases as the number of shared electron pairs increases



Bond Lengths: https://youtu.be/9xn04FNkq9I

The Relationship between Bond Order & Bond Energy

As shown in Table **1.1.3.2.1**, 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 **1.1.3.2.2**: 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 **1.1.3.2.2** 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 **1.1.3.2.1**).
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 **1.1.3.2.1**. 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\[\ce{Cl\bond{-}Cl > Br\bond{-}Br > F\bond{-}F > I–I}\] Similar effects are also seen for the O–O versus S–S and for N–N versus P–P single bonds.

Note

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.

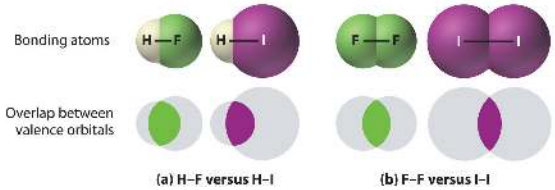


Figure **1.1.3.2.1** The Strength of Covalent Bonds Depends on the Overlap between the Valence Orbitals of the Bonded Atoms. The relative sizes of the region of space in which electrons are shared between (a) a hydrogen atom and lighter (smaller) vs. heavier (larger) atoms in the same periodic group; 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.

Note

Bond strengths increase as bond order **increases**, while bond distances **decrease**.

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 **1.1.3.2.3**); that is, the C–H bond energy depends on its molecular environment. Except for diatomic molecules, the bond energies listed in Table **1.1.3.2.2** 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 **1.1.3.2.3**: 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 ($\Delta H_{rxn} < 0$):

$$\Delta H_{rxn} \approx \sum(\text{bond energies of bonds broken}) - \sum(\text{bond energies of bonds formed}) \quad (1.1.3.2.1)$$

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:

$$CH_3(CH_2)_5CH_{3(l)} + 11O_{2(g)} \rightarrow 7CO_{2(g)} + 8H_2O_{(g)} \quad (1.1.3.2.2)$$

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:

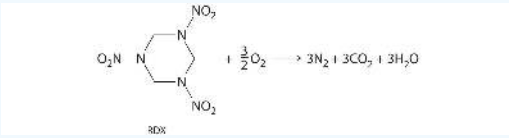
Bonds Broken (kJ/mol)		Bonds Formed (kJ/mol)	
6 C–C	346 × 6 = 2076	14 C=O	799 × 14 = 11,186
16 C–H	411 × 16 = 6576	16 O–H	459 × 16 = 7344
11 O=O	494 × 11 = 5434		**Total** = 18,530
	Total = 14,086		

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).

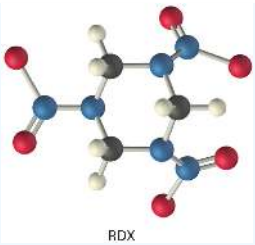
If we compare this approximation with the value obtained from measured ΔH_f^o values ($\Delta H_{rxn} = -481\ 7kJ/mol$), we find a discrepancy of only about 8%, less than the 10% typically encountered. Chemists find this method useful for calculating approximate enthalpies of reaction for molecules whose 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 1.1.3.2.1

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 **1.1.3.2.2** to estimate the ΔH_{rxn} per mole of RDX.



RDX


RDX

Given: chemical reaction, structure of reactant, and Table **1.1.3.2.2**.

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)	
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

$$\Delta H_{rxn} \approx \sum(\text{bond energies of bonds broken}) - \sum(\text{bond energies of bonds formed}) \tag{1.1.3.2.3}$$

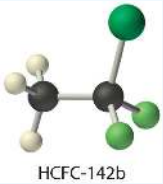
$$= 7962\ kJ/mol - 10,374\ kJ/mol \tag{1.1.3.2.4}$$

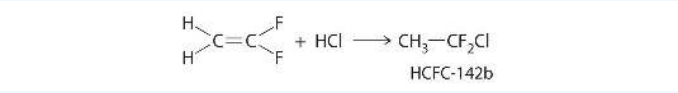
\[=−2412 \;kJ/mol]

Thus this reaction is also highly exothermic.

? Exercise 1.1.3.2.1

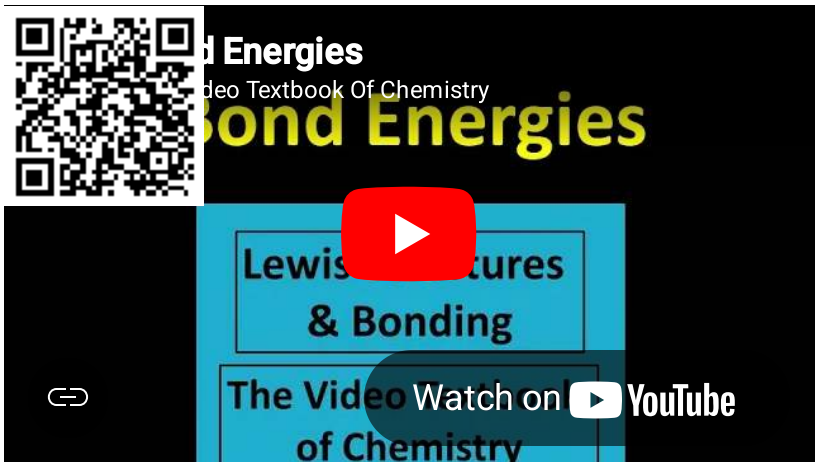
The molecule HCFC-142b, a hydrochlorofluorocarbon used in place of chlorofluorocarbons (CFCs) such as the Freons, can be prepared by adding HCl to 1,1-difluoroethylene:





Use tabulated bond energies to calculate ΔH_{rxn}.

Answer: −54 kJ/mol



Bond Energies: https://youtu.be/Prc6fbLXi5M

Summary

- The strength of a covalent bond depends on the overlap between the valence orbitals of the bonded atoms.

Formal charge on an atom:

Label '8.3.1' multiply defined

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.

Contributors and Attributions

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1.1.3.3: Polar Covalent Bonds and Electrostatic Maps

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 shared electron pairs 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. We 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.***

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 (compare Figure **1.1.3.3.2** and Figure **1.1.3.3.2**). 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.

Note

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 that is will be *highly electronegative* has:

- a large (negative) electron affinity
- a high ionization energy (always endothermic, or positive for neutral atoms)

and will

- attract electrons from other atoms
- resist having its own electrons attracted away.

The Pauling Electronegativity Scale

The original electronegativity scale, developed in the 1930s by Linus Pauling (1901– 1994) was based on measurements of the strengths of covalent bonds between different elements. Pauling arbitrarily set the electronegativity of fluorine at 4.0 (although today it has been refined to 3.98), thereby creating a scale in which all elements have values between 0 and 4.0.

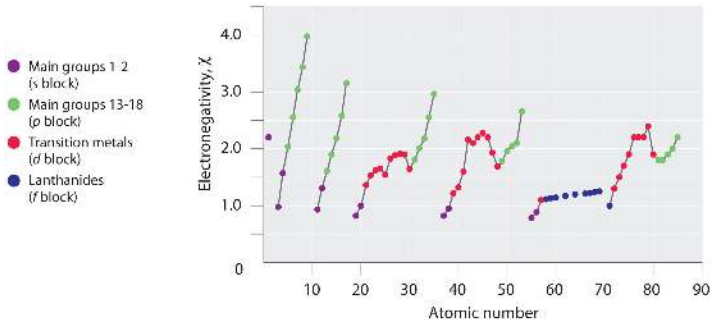


Figure 1.1.3.3.1: A Plot of Periodic Variation of Electronegativity with Atomic Number for the First Six Rows of the Periodic Table

Periodic variations in Pauling's electronegativity values are illustrated in Figure 1.1.3.3.1 and Figure 1.1.3.3.2. If we ignore the inert gases and elements for which no stable isotopes are known, we see that fluorine ($\chi = 3.98$) is the most electronegative element and cesium is the least electronegative nonradioactive element ($\chi = 0.79$). Because electronegativities generally increase diagonally from the lower left to the upper right of the periodic table, elements lying on diagonal lines running from upper left to lower right tend to have comparable values (e.g., O and Cl and N, S, and Br).

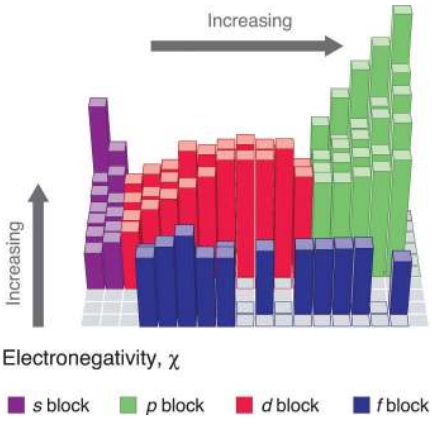
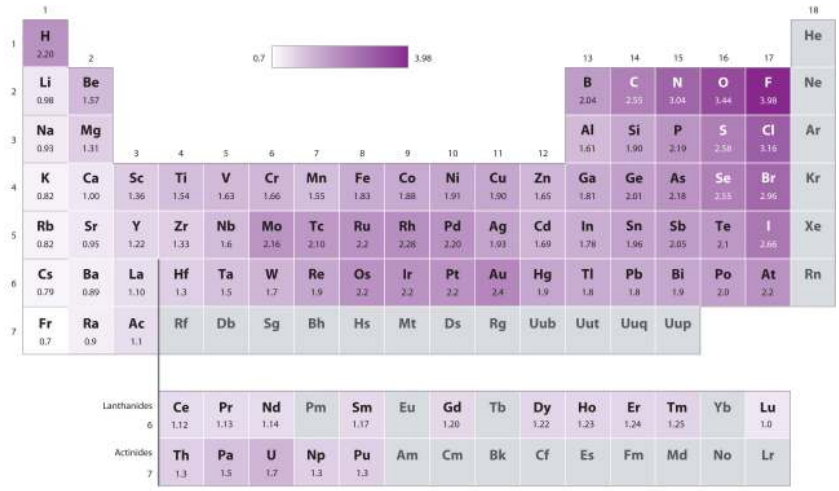


Figure* 1.1.3.3.2*: *Pauling Electronegativity Values of the s-, p-, d-, and f-Block Elements. Values for most of the actinides are approximate. Elements for which no data are available are shown in gray. Source: Data from L. Pauling, The Nature of the Chemical Bond, 3rd ed. (1960).*

Linus Pauling (1901-1994)

Pauling won two Nobel Prizes, one for chemistry in 1954 and one for peace in 1962. 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 denied a high school degree because of his refusal to take a civics class.



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 electronegativity scale).

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 ($\chi \geq 2.2$) 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 **semimetals** (or metalloids), 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 **1.1.3.3.3** shows the strong correlation between electronegativity values, metallic versus nonmetallic character, and location in the periodic table.

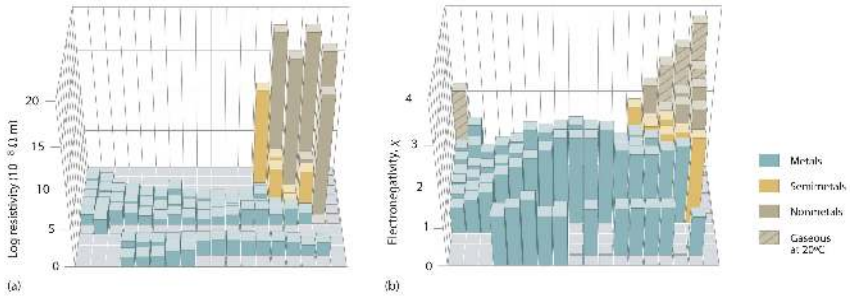


Figure **1.1.3.3.3**: Three-Dimensional Plots Demonstrating the Relationship between Electronegativity and the Metallic/Nonmetallic Character of the Elements. (a) A plot of electrical resistivity (measured resistivity to electron flow) at or near room temperature shows that substances with high resistivity (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).

Note

Electronegativity values *increase* from lower left to upper right in the periodic table.

The rules for assigning oxidation states are based on the relative electronegativities of the elements; the more electronegative element in a binary compound is assigned a negative oxidation state. As we shall see, electronegativity values are also used to

predict bond energies, bond polarities, and the kinds of reactions that compounds undergo.

Example 1.1.3.3.1

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 semimetal.

Given: four elements

Asked for: order by increasing electronegativity and classification

<p">**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 semimetal according to its location about the diagonal belt of semimetals running from B to At.

Solution:

A Electronegativity increases from lower left to upper right in the periodic table (Figure **1.1.3.3.2**). 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 semimetals 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 semimetal, and Se and Cl are nonmetals.

Exercise 1.1.3.3.1

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 semimetal.

Answer: Rb < Zr < Ge < N < O; metals (Rb, Zr); semimetal (Ge); nonmetal (N, O)



Electronegativity: https://youtu.be/3Pe0iShCdhM

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 **1.1.3.3.4** 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.

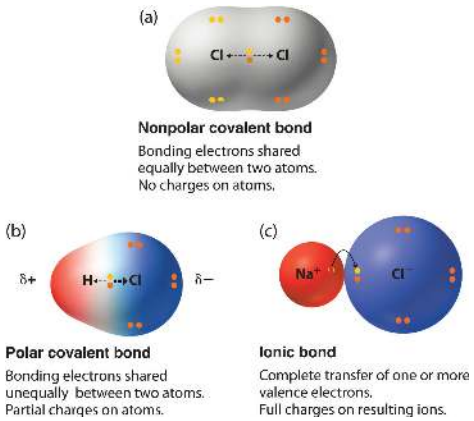


Figure **1.1.3.3.4**: The Electron Distribution in a Nonpolar Covalent Bond, a Polar Covalent Bond, and an Ionic Bond Using Lewis Electron Structures. In a purely covalent bond (a), the bonding electrons are shared equally between the atoms. In a purely ionic bond (c), an electron has been transferred 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.

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:

$$\underset{\delta^+}{\overset{\text{less electronegative}}{A}} - \underset{\delta^-}{\overset{\text{more electronegative}}{B}}$$

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 $\chi_{Na} = 0.93$ (see Figure **1.1.3.3.2**). 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.

Note

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.

Dipole Moments as a Measure of Bond Polarity

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:

$$\mu = Qr \tag{1.1.3.3.1}$$

where Q is measured in coulombs (C) and r in meters. The unit for dipole moments is the debye (D):

$$1\ D = 3.3356 \times 10^{-30}\ C \cdot m \tag{1.1.3.3.2}$$

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 **1.1.3.3.2**).

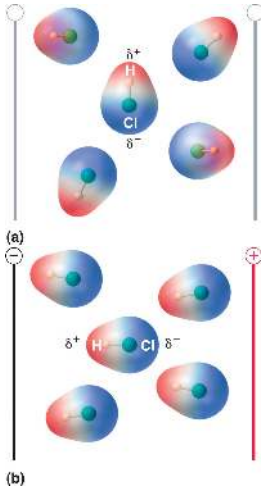


Figure **1.1.3.3.5**: Molecules That Possess a Dipole Moment Partially Align Themselves with an Applied Electric Field In the absence of a field (a), the HCl molecules are randomly oriented. When an electric field is applied (b), the molecules tend to align themselves with the field, such that the positive 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 10.3.2 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

$$Q = \frac{\mu}{r} = 1.109\ \cancel{D}\left(\frac{3.3356 \times 10^{-30}\ C \cdot \cancel{m}}{1\ \cancel{D}}\right)\left(\frac{1}{127.8\ \cancel{pm}}\right)\left(\frac{1\ \cancel{pm}}{10^{-12}\ \cancel{m}}\right) = 2.901 \times 10^{-20}\ C \tag{1.1.3.3.3}$$

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.

$$\frac{2.901 \times 10^{-20}\ \cancel{C}}{1.6022 \times 10^{-19}\ \cancel{C}} = 0.1811\ e^- \tag{1.1.3.3.4}$$

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 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 **1.1.3.3.6** 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 **1.1.3.3.6** 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 11.

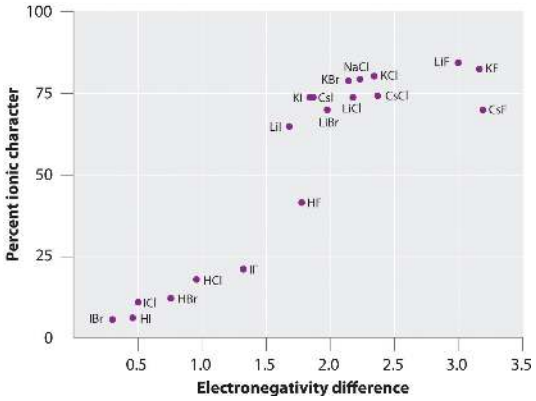


Figure **1.1.3.3.6**: A Plot of the Percent Ionic Character of a Bond as Determined from Measured Dipole Moments versus the Difference in Electronegativity of the Bonded Atoms.In the gas phase, even CsF, which has the largest possible difference in electronegativity between atoms, is not 100% ionic. Solid CsF, however, is best viewed as 100% ionic because of the additional electrostatic interactions in the lattice.

Example 1.1.3.3.2

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 10.3.2.

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

$$Q = \frac{\mu}{r} \tag{1.1.3.3.5}$$
$$= 9.001 \cancel{D} \left(\frac{3.3356 \times 10^{-30} \ C \cdot \cancel{m}}{1 \cancel{D}} \right) \left(\frac{1}{236.1 \cancel{pm}} \right) \left(\frac{1 \cancel{pm}}{10^{-12} \cancel{m}} \right)$$
$$= 1.272 \times 10^{-19} \ C$$

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):

$$\% \ ionic \ character = \left(\frac{1.272 \times 10^{-19} \cancel{C}}{1.6022 \times 10^{-19} \cancel{C}} \right) (100) = 79.39\% \simeq 79\% \tag{1.1.3.3.6}$$

? Exercise 1.1.3.3.2

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?

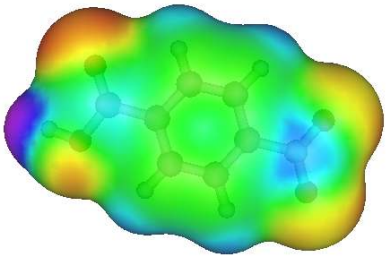
Answer: 55.5%



Dipole Intermolecular Force: https://youtu.be/ACq_95SIBck

Electrostatic Potential Maps

Electrostatic potential maps convey information about the charge distribution of a molecule because of the properties of the nucleus and nature of electrostatic potential energy. A region of higher than average electrostatic potential energy indicates the presence of a stronger positive charge or a weaker negative charger. Given the positive charge of the nuclei, the higher potential energy value indicates the absence of negative charges (less screening of the nuclei), which would mean that there are fewer electrons in this region. The converse is also true with a low electrostatic potential indicateing an abundance of electrons. This property of electrostatic potentials can be extrapolated to molecules as well.



Note: Constructing a Electrostatic Potential Map

The first step involved in creating an electrostatic potential map is collecting a very specific type of data: electrostatic potential energy. An advanced computer program calculates the electrostatic potential energy at a set distance from the nuclei of the molecule. Electrostatic potential energy is fundamentally a measure of the strength of the nearby charges, nuclei and electrons, at a particular position. To accurately analyze the charge distribution of a molecule, a very large quantity of electrostatic potential energy values must be calculated. The best way to convey this data is to visually represent it, as in an electrostatic potential map. A computer program then imposes the calculated data onto an electron density model of the molecule. To make the electrostatic potential energy data easy to interpret, a color spectrum, with red as the lowest electrostatic potential energy value and blue as the highest, is employed to convey the varying intensities of the electrostatic potential energy values.

The most important thing to consider when analyzing an electrostatic potential map is the charge distribution. The relative distributions of electrons will allow you to deduce everything you need to know from these maps. Recall the relationship between electrostatic potential and charge distribution. Areas of low potential, red, are characterized by an abundance of electrons. Areas of high potential, blue, are characterized by a relative absence of electrons. Oxygen has a higher electronegativity value than sulfur (Table A2), hence. oxygen atoms would have a higher electron density around them than sulfur atoms. Thus the spherical region that corresponds to an oxygen atom would have a red portion on it. Now note that there are two oxygen atoms in sulfur dioxide (Figure **1.1.3.3.7**). There are two sphere shaped objects that have red regions. These areas correspond to the location of the oxygen atoms. The blue tainted sphere at the top corresponds to the location of the sulfur atom.

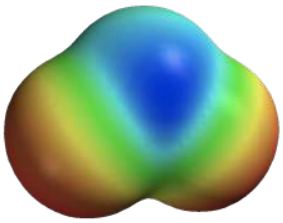


Figure **1.1.3.3.7**. The electrostatic diagram of Sulfur Dioxide (SO_2). Which parts of this diagram correlate to the respective atomic components? Red indicates the lowest electrostatic potential energy, and blue indicates the highest electrostatic potential energy. Intermediary colors represent intermediary electrostatic potentials.

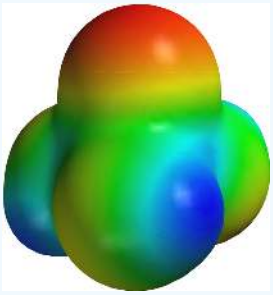
Note

A high electrostatic potential indicates the relative **absence** of electrons and a low electrostatic potential indicates an **abundance** of electrons

Electrostatic potential maps can also be used to determine the nature of the molecules chemical bond. Consider SO_2 in Figure **1.1.3.3.7**, there is a great deal of intermediary potential energy, the non red or blue regions, in this diagram. This indicates that the electronegativity difference is not very great. In a molecule with a great electronegativity difference, charge is very polarized, and there are significant differences in electron density in different regions of the molecule. This great electronegativity difference leads to regions that are almost entirely red and almost entirely blue. Greater regions of intermediary potential, yellow and green, and smaller or no regions of extreme potential, red and blue, are key indicators of a smaller electronegativity difference. Note that the electronegativity difference is a key determinant in the nature of a chemical bond.

Example 1.1.3.3.3

The following electrostatic potential map of phosphoric acid $\ce{H3PO4}$. What regions correspond to atoms of oxygen, hydrogen, and phosphorous respectively?



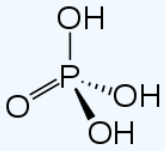
Solution

You do not need to know the molecular structure to answer this question. You do need to know the relative electronegative values of these atoms (Table A4).

- Oxygen has the greatest electronegative value,
- Phosphorous the second most, and
- Hydrogen has the smallest electronegative value.

Simply by knowing this, you can deduce that oxygen would be affiliated with the red region or redish regions of the diagram, and hydrogen would be affiliated with the blue region. Phosphorous would fall in between these two extremes, in the green region.

Here is the molecular diagram of phosphoric acid:



Summary

- Bond polarity and ionic character increase with an increasing difference in electronegativity.

Dipole moment

Label '10.3.2' multiply defined

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.

1.1.3.3: Polar Covalent Bonds and Electrostatic Maps is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

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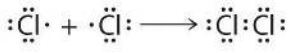
1.1.3.4: Writing Lewis Structures

Learning Objectives

- To use Lewis dot symbols to explain the stoichiometry of a compound

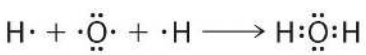
Using Lewis Dot Symbols to Describe Covalent Bonding

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.

Note

The central atom is usually the least electronegative element in the molecule or ion; hydrogen and the halogens are usually terminal.

The H_2O Molecule

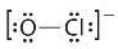
1. Because H atoms are almost always terminal, the arrangement within the molecule must be HOH.
2. Each H atom (group 1) has 1 valence electron, and the O atom (group 16) has 6 valence electrons, for a total of 8 valence electrons.
3. Placing one bonding pair of electrons between the O atom and each 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.

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:



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.

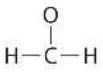
The CH_2O Molecule

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:



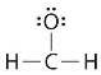
2. Each hydrogen atom (group 1) has one valence electron, carbon (group 14) has 4 valence electrons, and oxygen (group 16) has 6 valence electrons, for a total of [(2)(1) + 4 + 6] = 12 valence electrons.

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.

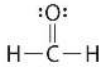
4. Adding all 6 remaining electrons to oxygen (as three lone pairs) gives the following:



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:



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 1.1.3.4.1

Write the Lewis electron structure for each species.

1. NCl_3
2. S_2^{2-}
3. NOCl

Given: chemical species

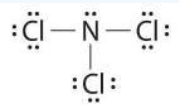
Asked for: Lewis electron structures

Strategy:

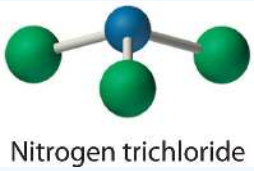
Use the six-step procedure to write the Lewis electron structure for each species.

Solution:

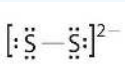
1. Nitrogen is less electronegative than chlorine, and halogen atoms are usually terminal, so nitrogen is the central atom. The nitrogen atom (group 15) has 5 valence electrons and each chlorine atom (group 17) has 7 valence electrons, for a total of 26 valence electrons. Using 2 electrons for each N–Cl 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:

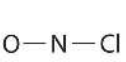
   Nitrogen trichloride is an unstable oily liquid once used to bleach flour; this use is now prohibited in the United States.

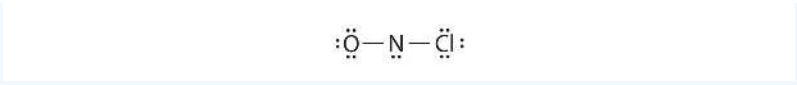
2. In a diatomic molecule or ion, we do not need to worry about a central atom. Each sulfur atom (group 16) contains 6 valence electrons, and we need to add 2 electrons for the −2 charge, giving a total of 14 valence electrons. Using 2 electrons for the S–S bond, we arrange the remaining 12 electrons as three lone pairs on each sulfur, giving each S atom an octet of electrons:

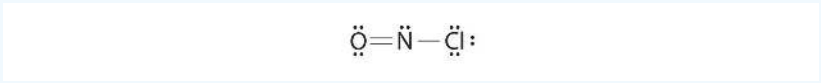
3. Because nitrogen is less electronegative than oxygen or chlorine, it is the central atom. The N atom (group 15) has 5 valence electrons, the O atom (group 16) has 6 valence electrons, and the Cl atom (group 17) has 7 valence electrons, giving a total of 18 valence electrons. Placing one bonding pair of electrons between each pair of bonded atoms uses 4 electrons and gives the following:

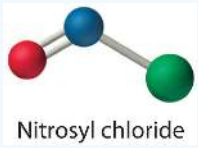
   Adding three lone pairs each to oxygen and to chlorine uses 12 more electrons, leaving 2 electrons to place as a lone pair on nitrogen:



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:



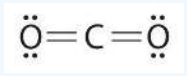
All atoms now have octet configurations. This is the Lewis electron structure of nitrosyl chloride, a highly corrosive, reddish-orange gas.



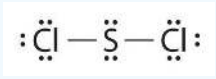
? Exercise 1.1.3.4.1

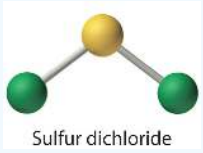
Write Lewis electron structures for CO_2 and SCl_2, a vile-smelling, unstable red liquid that is used in the manufacture of rubber.

Answer

1. 



2. 

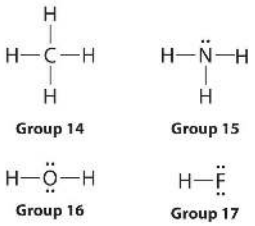




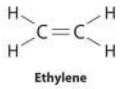
Lewis Structure of Molecules: https://youtu.be/xWiFCqA9Ur0

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:



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.



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.

> **Note**
>
> 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 1.1.3.4.3). Nonetheless, the phosphorus atoms in all three forms obey the octet rule and form three bonds per phosphorus atom.

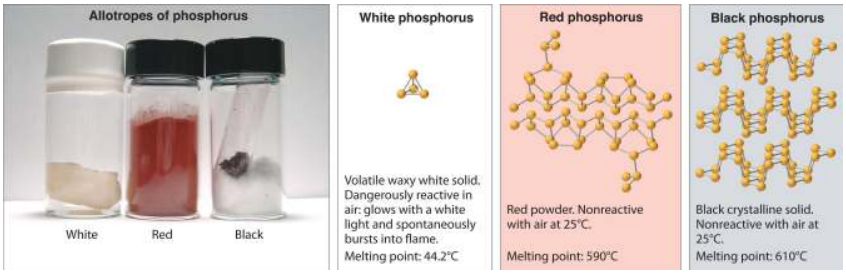


Figure 1.1.3.4.3*: The Three Allotropes of Phosphorus: White, Red, and Black. ll three forms contain only phosphorus atoms, but they differ in the arrangement and connectivity of their atoms. White phosphorus contains P_4 tetrahedra, red phosphorus is a network of linked P_8 and P_9 units, and black phosphorus forms sheets of six-membered rings. As a result, their physical and chemical properties differ dramatically.*

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.

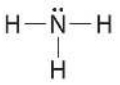
To calculate formal charges, we assign electrons in the molecule to individual atoms according to these rules:

- 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:

$$\underset{(atom\ in\ Lewis\ structure)}{formal\ charge} = \underset{(free\ atom)}{valence\ e^-} - \left(non-bonding\ e^- + \frac{bonding\ e^-}{2}\right) \text{ (atom in Lewis structure)}$$

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 8.5.2, we obtain

$$\underset{formal\ charge\ (N)}{} = 5\ valence\ e^- - \left(2\ non-bonding\ e^- + \frac{6\ bonding\ e^-}{2}\right) = 0 \tag{1.1.3.4.1}$$

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 8.5.2 to calculate the formal charge on hydrogen, we obtain

$$\underset{formal\ charge\ (H)}{} = 1\ valence\ e^- - \left(0\ non-bonding\ e^- + \frac{2\ bonding\ e^-}{2}\right) = 0 \tag{1.1.3.4.2}$$

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.

Note

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.



Lewis Structure of Charged Molecules: https://youtu.be/pTkziPtvMYU

Example 1.1.3.4.2

Calculate the formal charges on each atom in the NH_4^+ ion.

Given: chemical species

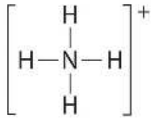
Asked for: formal charges

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 8.5.2 to calculate the formal charge on each atom.

Solution:

The Lewis electron structure for the NH_4^+ ion is as follows:



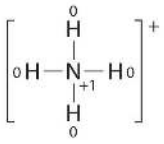
The nitrogen atom shares four bonding pairs of electrons, and a neutral nitrogen atom has five valence electrons. Using Equation 8.5.1, the formal charge on the nitrogen atom is therefore

$$\textit{formal charge}\,(N) = 5 - \left(0 + \frac{8}{2}\right) = 0 \tag{1.1.3.4.3}$$

Each hydrogen atom in has one bonding pair. The formal charge on each hydrogen atom is therefore

$$\textit{formal charge}\,(H) = 1 - \left(0 + \frac{2}{2}\right) = 0 \tag{1.1.3.4.4}$$

The formal charges on the atoms in the NH_4^+ ion are thus

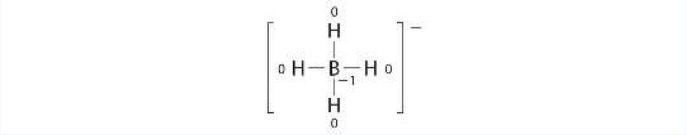


Adding together the formal charges on the atoms should give us the total charge on the molecule or ion. In this case, the sum of the formal charges is 0 + 1 + 0 + 0 + 0 = +1.

Exercise 1.1.3.4.2

Write the formal charges on all atoms in BH_4^-.

Answer



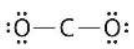
If an atom in a molecule or ion has the number of bonds that is typical for that atom (e.g., four bonds for carbon), its formal charge is zero.

Using Formal Charges to Distinguish Viable Lewis Structures

As an example of how formal charges can be used to determine the most stable Lewis structure for a substance, we can compare two possible structures for CO_2. Both structures conform to the rules for Lewis electron structures.

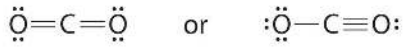
CO_2

1. C is less electronegative than O, so it is the central atom.
2. C has 4 valence electrons and each O has 6 valence electrons, for a total of 16 valence electrons.
3. Placing one electron pair between the C and each O gives O–C–O, with 12 electrons left over.
4. Dividing the remaining electrons between the O atoms gives three lone pairs on each atom:

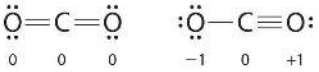


This structure has an octet of electrons around each O atom but only 4 electrons around the C atom.

5. No electrons are left for the central atom.
6. To give the carbon atom an octet of electrons, we can convert two of the lone pairs on the oxygen atoms to bonding electron pairs. There are, however, two ways to do this. We can either take one electron pair from each oxygen to form a symmetrical structure or take both electron pairs from a single oxygen atom to give an asymmetrical structure:



Both Lewis electron structures give all three atoms an octet. How do we decide between these two possibilities? The formal charges for the two Lewis electron structures of CO_2 are as follows:



Both Lewis structures have a net formal charge of zero, but the structure on the right has a +1 charge on the more electronegative atom (O). Thus the symmetrical Lewis structure on the left is predicted to be more stable, and it is, in fact, the structure observed experimentally. Remember, though, that formal charges do *not* represent the actual charges on atoms in a molecule or ion. They are used simply as a bookkeeping method for predicting the most stable Lewis structure for a compound.

Note

The Lewis structure with the set of formal charges closest to zero is usually the most stable.

Example 1.1.3.4.3: The Thiocyanate Ion

The thiocyanate ion (SCN^-), which is used in printing and as a corrosion inhibitor against acidic gases, has at least two possible Lewis electron structures. Draw two possible structures, assign formal charges on all atoms in both, and decide which

is the preferred arrangement of electrons.

Given: chemical species

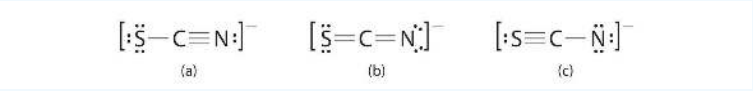
Asked for: Lewis electron structures, formal charges, and preferred arrangement

Strategy:

A. Use the step-by-step procedure to write two plausible Lewis electron structures for SCN^-.
B. Calculate the formal charge on each atom using Equation 8.5.1.
C. Predict which structure is preferred based on the formal charge on each atom and its electronegativity relative to the other atoms present.

Solution:

A Possible Lewis structures for the SCN^- ion are as follows:



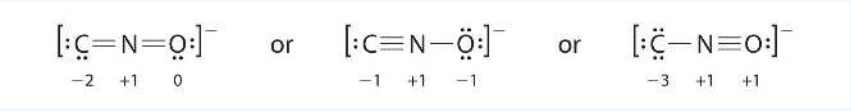
B We must calculate the formal charges on each atom to identify the more stable structure. If we begin with carbon, we notice that the carbon atom in each of these structures shares four bonding pairs, the number of bonds typical for carbon, so it has a formal charge of zero. Continuing with sulfur, we observe that in (a) the sulfur atom shares one bonding pair and has three lone pairs and has a total of six valence electrons. The formal charge on the sulfur atom is therefore $6-\left(6+\frac{2}{2}\right)=-1.5-\left(4+\frac{4}{2}\right)=-1$ In (c), nitrogen has a formal charge of −2.

C Which structure is preferred? Structure (b) is preferred because the negative charge is on the more electronegative atom (N), and it has lower formal charges on each atom as compared to structure (c): 0, −1 versus +1, −2.

? Exercise 1.1.3.4.3: The Fulminate Ion

Salts containing the fulminate ion (CNO^-) are used in explosive detonators. Draw three Lewis electron structures for CNO^- and use formal charges to predict which is more stable. (Note: N is the central atom.)

Answer



The second structure is predicted to be more stable.

Summary

- 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. In Lewis electron structures, we encounter **bonding pairs**, which are shared by two atoms, and **lone pairs**, which are not shared between atoms. If both electrons in a covalent bond come from the same atom, the bond is called a **coordinate covalent bond**. Lewis structures are an attempt to rationalize why certain stoichiometries are commonly observed for the elements of particular families. Neutral compounds of group 14 elements typically contain four bonds around each atom (a double bond counts as two, a triple bond as three), whereas neutral compounds of group 15 elements typically contain three bonds. In cases where it is possible to write more than one Lewis electron structure with octets around all the nonhydrogen atoms of a compound, the **formal charge** on each atom in alternative structures must be considered to decide which of the valid structures can be excluded and which is the most reasonable. The formal charge is the difference between the number of valence electrons of the free atom and the number of electrons assigned to it in the compound, where bonding electrons are divided equally between the bonded atoms. The Lewis structure with the lowest formal charges on the atoms is almost always the most stable one.

Contributors and Attributions

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1.1.3.5: Resonance

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 a single polyatomic species including fractional bonds and fractional charges. Resonance structure are capable of describing delocalized electrons that cannot be expressed by a single Lewis formula with an integer number of covalent bonds.

When 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°.

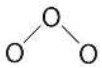
Ozone (O_3)

1. We know that ozone has a V-shaped structure, so one O atom is central:



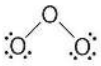
2. Each O atom has 6 valence electrons, for a total of 18 valence electrons.

3. Assigning one bonding pair of electrons to each oxygen–oxygen bond gives



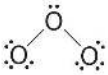
with 14 electrons left over.

4. If we place three lone pairs of electrons on each terminal oxygen, we obtain

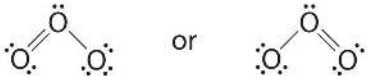


and have 2 electrons left over.

5. At this point, both terminal oxygen atoms have octets of electrons. We therefore place the last 2 electrons on the central atom:

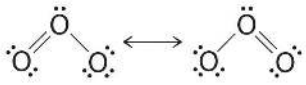


6. The central oxygen has only 6 electrons. We must convert one lone pair on a terminal oxygen atom to a bonding pair of electrons —but which one? Depending on which one we choose, we obtain either



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:



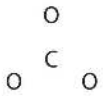
The double-headed arrow indicates that the actual electronic structure is an *average* of those shown, not that the molecule oscillates between the two structures.

> **Note**
>
> 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.

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:

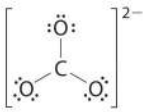


2. Carbon has 4 valence electrons, each oxygen has 6 valence electrons, and there are 2 more for the −2 charge. This gives 4 + (3 × 6) + 2 = 24 valence electrons.

3. Six electrons are used to form three bonding pairs between the oxygen atoms and the carbon:

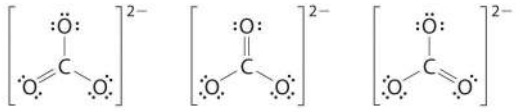


4. We divide the remaining 18 electrons equally among the three oxygen atoms by placing three lone pairs on each and indicating the −2 charge:

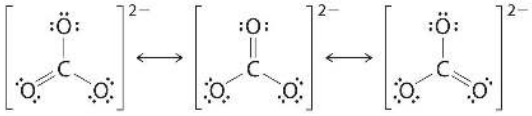


5. No electrons are left for the central atom.

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:

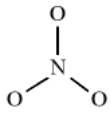


The actual structure is an average of these three resonance structures.

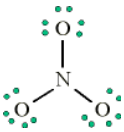
The Nitrate (NO_3^-) ion

1. Count up the valence electrons: (1*5) + (3*6) + 1(ion) = **24** electrons

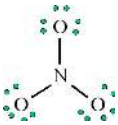
2. Draw the bond connectivities:



3. Add octet electrons to the atoms bonded to the center atom:

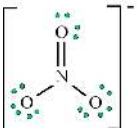


4. Place any leftover electrons (24-24 = **0**) on the center atom:



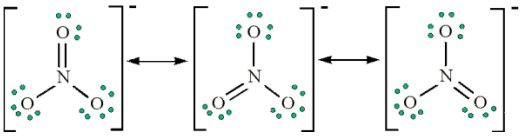
5. Does the central atom have an octet?

- **NO**, it has 6 electrons
- Add a multiple bond (first try a double bond) to see if the central atom can achieve an octet:



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

Example 1.1.3.5.1: 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

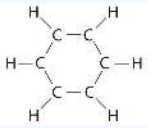
Asked for: resonance structures

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.

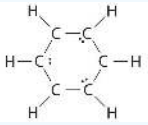
Solution:

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:



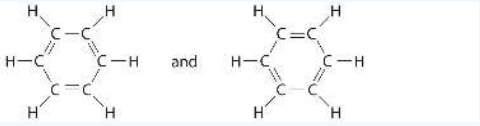
Each carbon atom in this structure has only 6 electrons and has a formal charge of +1, but we have used only 24 of the 30 valence electrons.

B If the 6 remaining electrons are uniformly distributed pairwise on alternate carbon atoms, we obtain the following:

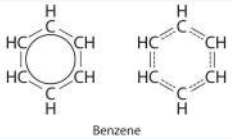


Three carbon atoms now have an octet configuration and a formal charge of −1, while three carbon atoms have only 6 electrons and a formal charge of +1. We can convert each lone pair to a bonding electron pair, which gives each atom an octet of electrons and a formal charge of 0, by making three C=C double 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 1.1.3.5.1: Nitrate Ion

The sodium salt of nitrite is used to relieve muscle spasms. Draw two resonance structures for the nitrite ion (NO_2^-).

Answer



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.



Resonance Structures: https://youtu.be/aSP0D72MKe4

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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1.1.3.6: 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

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 (NO ,refer to figure one). 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 nitrogen monoxide. Nitrogen monoxide has 11 valence electrons. If you need more information about formal charges, see Lewis Structures. If we were to imagine nitrogen monoxide had ten valence electrons we would come up with the Lewis Structure (Figure **1.1.3.6.1**):

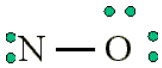


Figure **1.1.3.6.1**: This is if Nitrogen monoxide has only ten valence electrons, which it does not.

Let's look at the formal charges of Figure **1.1.3.6.2** based on this Lewis structure. Nitrogen normally has five valence electrons. In Figure **1.1.3.6.1**, 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 **1.1.3.6.1**, 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 nitrogen monoxide (Figure **1.1.3.6.2**):

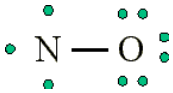


Figure **1.1.3.6.2**: The proper Lewis structure for NO molecule

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, odd Number of Valence Electrons will result in the molecule being paramagnetic.

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 was 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 **1.1.3.6.3**):

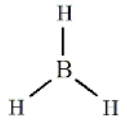


Figure **1.1.3.6.3**

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 **1.1.3.6.4**).

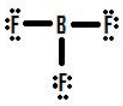


Figure **1.1.3.6.4**

If you look Figure **1.1.3.6.4**, 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 **1.1.3.6.5**):

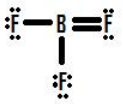


Figure **1.1.3.6.5**

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 **1.1.3.6.5**, 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 ($\chi = 4.0$). 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 **1.1.3.6.6**:

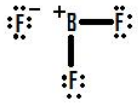


Figure **1.1.3.6.6**

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 **1.1.3.6.4**), the one with the double bond (Figure **1.1.3.6.5**), and the one with the ionic bond (Figure **1.1.3.6.6**). The most contributing structure is probably the incomplete octet structure (due to Figure **1.1.3.6.5** being basically impossible and Figure **1.1.3.6.6** 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 .

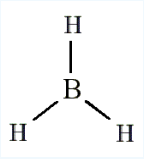
Example 1.1.3.6.1: NF_3

Draw the Lewis structure for boron trifluoride (BF_3).

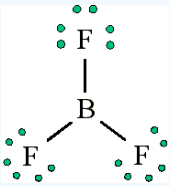
Solution

1. Add electrons (3*7) + 3 = **24**

2. Draw connectivities:



3. Add octets to outer atoms:

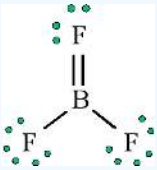


4. Add extra electrons (24-24=0) to central atom:



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:

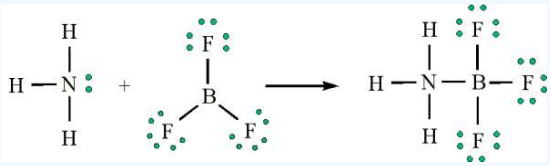


6. The central Boron now has an octet (there would be three resonance Lewis structures)

However...

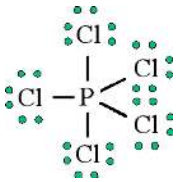
- In this structure with a double bond the fluorine atom is sharing extra electrons with the boron.
- The fluorine would have a '+' partial charge, and the boron a '-' partial charge, this is inconsistent with the electronegativities of fluorine and boron.
- Thus, ***the structure of BF_3, with single 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:



Exception 3: Expanded Valence Shells

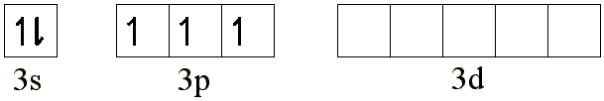
More common than incomplete octets are expanded octets where the central atom in a Lewis structure has more than eight electrons in its valence shell. In expanded octets, the central atom can have ten electrons, or even twelve. *Molecules with expanded octets involve highly electronegative terminal atoms, 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:



Note

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 1.1.3.6.2: 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:

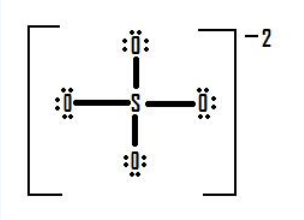


Figure 1.1.3.6.12

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:

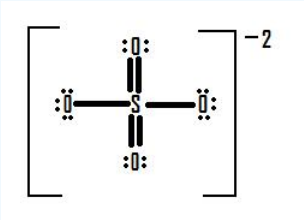


Figure 1.1.3.6.13

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 1.1.3.6.12, as opposed to +2 and -1 (difference of 3) in Figure 1.1.3.6.12) 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.

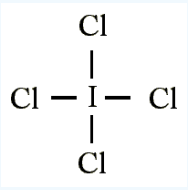
Example 1.1.3.6.3: The ICl_4^- Ion

Draw the Lewis structure for ICl_4^- ion.

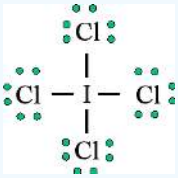
Solution

1. Count up the valence electrons: 7+(4*7)+1 = **36** electrons

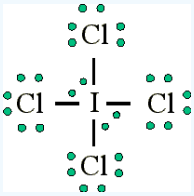
2. Draw the connectivities:



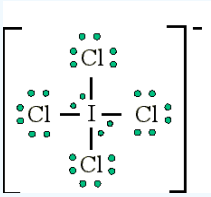
3. Add octet of electrons to outer atoms:



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.



Expanded Valence Shell Bonding: https://youtu.be/Y4fBdOJBSHI

Outside links

- http://www.saskschools.ca/curr_content/chem20/covmolec/exceptns.html
- student.ccbcmd.edu/~cyau1/121...ctetSp2006.pdf
- http://www.youtube.com/watch?v=KEQw9uQ8fUU
- www.rice.edu/~jenky/sports/antiox.html

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.

Contributors and Attributions

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1.1.3.7: The Shapes of Molecules

The Learning Objectives of this Module:

1. To use the VSEPR model to predict molecular geometries.
2. 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.

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.

We can use the VSEPR model to predict the geometry of most polyatomic molecules and ions by focusing on only the number of electron pairs around the *central atom*, ignoring all other valence electrons present. According to this model, valence electrons in the Lewis structure form *groups*, which may consist of a single bond, a double bond, a triple bond, a lone pair of electrons, or even a single unpaired electron, which in the VSEPR model is counted as a lone pair. Because electrons repel each other electrostatically, the most stable arrangement of electron groups (i.e., the one with the lowest energy) is the one that minimizes repulsions. Groups are positioned around the central atom in a way that produces the molecular structure with the lowest energy, as illustrated in Figure 9.1 and Figure 9.2.

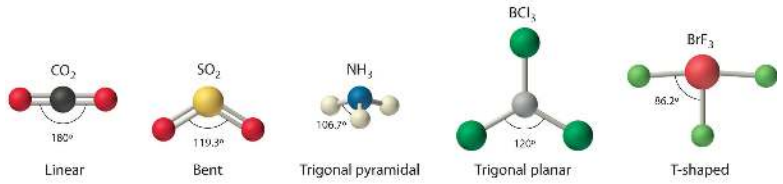


Figure 9.1 Common Structures for Molecules and Polyatomic Ions That Consist of a Central Atom Bonded to Two or Three Other Atoms

The VSEPR model explains these differences in molecular geometry.

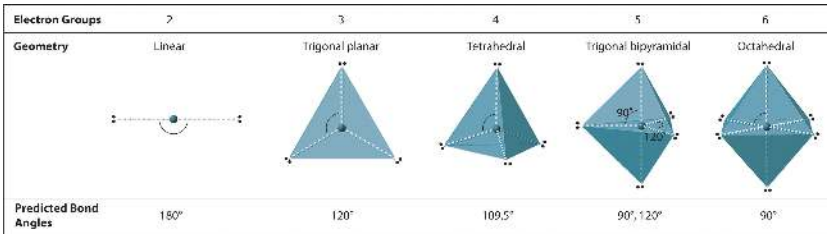


Figure 9.2 *Geometries for Species with Two to Six Electron Groups. Groups are placed around the central atom in a way that produces a molecular structure with the lowest energy. That is, the one that minimizes repulsions.*

In the VSEPR model, the molecule or polyatomic ion is 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. This 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 9.2 and Figure 9.3, which summarize the common molecular geometries and idealized bond angles of molecules and ions with two to six electron groups.

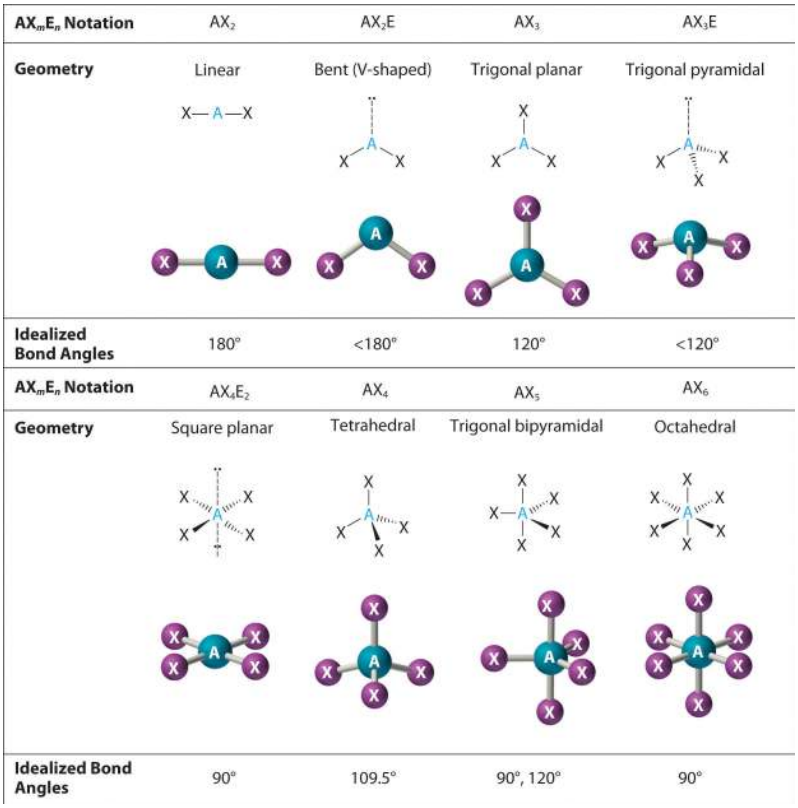


Figure 9.3 Common Molecular Geometries for Species with Two to Six Electron Groups. Lone pairs are shown using a dashed line.

Two Electron Groups

Our first example is a molecule with two bonded atoms and no lone pairs of electrons, BeH_2.

AX_2: BeH_2

1. The central atom, beryllium, contributes two valence electrons, and each hydrogen atom contributes one. The Lewis electron structure is

H:Be:H or H—Be—H

Lewis structure

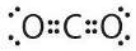
2. There are two electron groups around the central atom. We see from Figure 9.2 that the arrangement that minimizes repulsions places the groups 180° apart.

3. Both groups around the central atom are bonding pairs (BP). Thus BeH_2 is designated as AX_2.

4. From Figure 9.3 we see that with two bonding pairs, the molecular geometry that minimizes repulsions in BeH_2 is *linear*.

AX_2: CO_2

1. The central atom, carbon, contributes four valence electrons, and each oxygen atom contributes six. The Lewis electron structure is



2. The carbon atom forms two double bonds. Each double bond is a group, so there are two electron groups around the central atom. Like BeH_2, the arrangement that minimizes repulsions places the groups 180° apart.

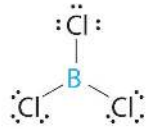
3. Once again, both groups around the central atom are bonding pairs (BP), so CO_2 is designated as AX_2.

4. VSEPR only recognizes groups around the *central* atom. Thus the lone pairs on the oxygen atoms do not influence the molecular geometry. With two bonding pairs on the central atom and no lone pairs, the molecular geometry of CO_2 is linear (Figure 9.3). The structure of CO_2 is shown in Figure 9.1.

Three Electron Groups

AX_3: BCl_3

1. The central atom, boron, contributes three valence electrons, and each chlorine atom contributes seven valence electrons. The Lewis electron structure is



Lewis structure

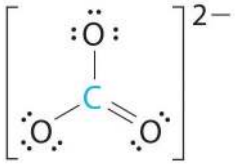
2. There are three electron groups around the central atom. To minimize repulsions, the groups are placed 120° apart (Figure 9.2).

3. All electron groups are bonding pairs (BP), so the structure is designated as AX_3.

4. From Figure 9.3 we see that with three bonding pairs around the central atom, the molecular geometry of BCl_3 is *trigonal planar*, as shown in Figure 9.1.

AX_3: CO_3^{2-}

1. The central atom, carbon, has four valence electrons, and each oxygen atom has six valence electrons. As you learned previously, the Lewis electron structure of one of three resonance forms is represented as

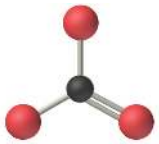


Lewis structure

2. The structure of CO_3^{2-} is a resonance hybrid. It has three identical bonds, each with a bond order of $1\frac{1}{3}$. We minimize repulsions by placing the three groups 120° apart (Figure 9.2).

3. All electron groups are bonding pairs (BP). With three bonding groups around the central atom, the structure is designated as AX_3.

4. We see from Figure 9.3 that the molecular geometry of CO_3^{2-} is trigonal planar.

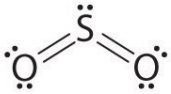


Molecular geometry
(trigonal planar)

In our next example we encounter the effects of lone pairs and multiple bonds on molecular geometry for the first time.

AX_2E: SO_2

1. The central atom, sulfur, has 6 valence electrons, as does each oxygen atom. With 18 valence electrons, the Lewis electron structure is shown below.



2. There are three electron groups around the central atom, two double bonds and one lone pair. We initially place the groups in a trigonal planar arrangement to minimize repulsions (Figure 9.2).

3. There are two bonding pairs and one lone pair, so the structure is designated as AX_2E. This designation has a total of three electron pairs, two X and one E. Because a lone pair is not shared by two nuclei, it occupies more space near the central atom than a bonding pair (Figure 9.4). 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 (Figure 9.1 and Figure 9.3).

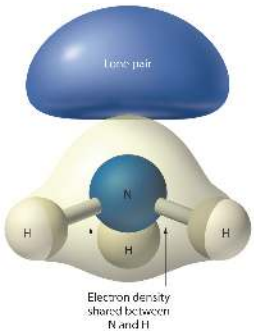
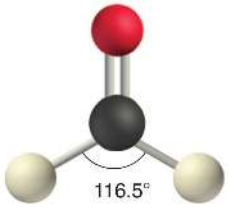


Figure 9.4: The Difference in the Space Occupied by a Lone Pair of Electrons and by a Bonding Pair

As with SO_2, this composite model of electron distribution and negative electrostatic potential in ammonia shows that a lone pair of electrons occupies a larger region of space around the nitrogen atom than does a bonding pair of electrons that is shared with a hydrogen atom.

Like lone pairs of electrons, multiple bonds occupy more space around the central atom than a single bond, which can cause other bond angles to be somewhat smaller than expected. This is because a multiple bond has a higher electron density than a single bond, so its electrons occupy more space than those of a single bond. For example, in a molecule such as CH_2O (AX_3), whose structure is shown below, the double bond repels the single bonds more strongly than the single bonds repel each other. This causes a deviation from ideal geometry (an H–C–H bond angle of 116.5° rather than 120°).



Four Electron Groups

One of the limitations of Lewis structures is that they depict molecules and ions in only two dimensions. With four electron groups, we must learn to show molecules and ions in three dimensions.

AX_4: CH_4

1. The central atom, carbon, contributes four valence electrons, and each hydrogen atom has one valence electron, so the full Lewis electron structure is

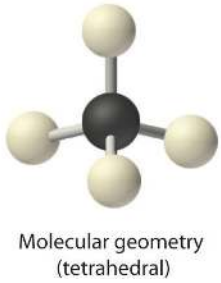


Lewis structure

2. There are four electron groups around the central atom. As shown in Figure 9.2, 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.

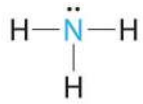
4. With four bonding pairs, the molecular geometry of methane is *tetrahedral* (Figure 9.3).



Molecular geometry
(tetrahedral)

AX_3E: NH_3

1. In ammonia, the central atom, nitrogen, has five valence electrons and each hydrogen donates one valence electron, producing the Lewis electron structure



Lewis structure

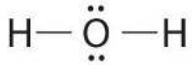
2. There are four electron groups around nitrogen, three bonding pairs and one lone pair. Repulsions are minimized by directing each hydrogen atom and the lone pair to the corners of a tetrahedron.

3. With three bonding pairs and one lone pair, the structure is designated as AX_3E. This designation has a total of four electron pairs, three X and one E. We expect the LP–BP interactions to cause the bonding pair angles to deviate significantly from the angles of a perfect tetrahedron.

4. There are three nuclei and one lone pair, so the molecular geometry is *trigonal pyramidal*. In essence, this is a tetrahedron with a vertex missing (Figure 9.3). However, the H–N–H bond angles are less than the ideal angle of 109.5° because of LP–BP repulsions (Figure 9.3 and Figure 9.4).

AX_2E_2: H_2O

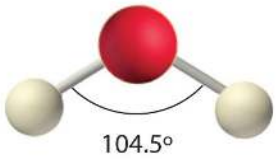
1. Oxygen has six valence electrons and each hydrogen has one valence electron, producing the Lewis electron structure



2. There are four groups around the central oxygen atom, two bonding pairs and two lone pairs. Repulsions are minimized by directing the bonding pairs and the lone pairs to the corners of a tetrahedron Figure 9.2.

3. With two bonding pairs and two lone pairs, the structure is designated as AX_2E_2 with a total of four electron pairs. Due to LP–LP, LP–BP, and BP–BP interactions, we expect a significant deviation from idealized tetrahedral angles.

4. With two hydrogen atoms and two lone pairs of electrons, the structure has significant lone pair interactions. There are two nuclei about the central atom, so the molecular shape is *bent*, or *V shaped*, with an H–O–H angle that is even less than the H–N–H angles in NH_3, as we would expect because of the presence of two lone pairs of electrons on the central atom rather than one.. This molecular shape is essentially a tetrahedron with two missing vertices.

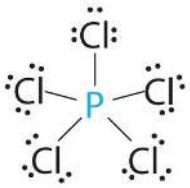


Five Electron Groups

In previous examples it did not matter where we placed the electron groups because all positions were equivalent. In some cases, however, the positions are not equivalent. We encounter this situation for the first time with five electron groups.

AX_5: PCl_5

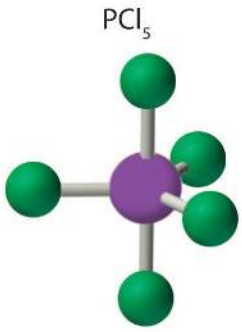
1. Phosphorus has five valence electrons and each chlorine has seven valence electrons, so the Lewis electron structure of PCl_5 is



2. There are five bonding groups around phosphorus, the central atom. The structure that minimizes repulsions is a *trigonal bipyramid*, which consists of two trigonal pyramids that share a base (Figure 9.2):

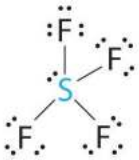
3. All electron groups are bonding pairs, so the structure is designated as AX_5. There are no lone pair interactions.

4. The molecular geometry of PCl_5 is *trigonal bipyramidal*, as shown in Figure 9.3. The molecule has three atoms in a plane in *equatorial* positions and two atoms above and below the plane in *axial* positions. The three equatorial positions are separated by 120° from one another, and the two axial positions are at 90° to the equatorial plane. The axial and equatorial positions are not chemically equivalent, as we will see in our next example.



AX_4E: SF_4

1. The sulfur atom has six valence electrons and each fluorine has seven valence electrons, so the Lewis electron structure is



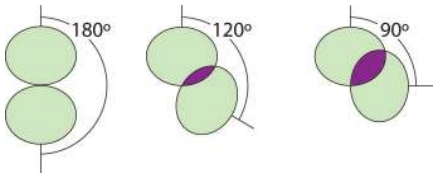
Lewis structure

With an expanded valence, this species is an exception to the octet rule.

2. There are five groups around sulfur, four bonding pairs and one lone pair. With five electron groups, the lowest energy arrangement is a trigonal bipyramid, as shown in Figure 9.2.

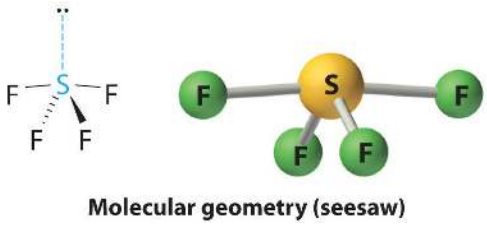
3. We designate SF_4 as AX_4E; it has a total of five electron pairs. However, because the axial and equatorial positions are not chemically equivalent, where do we place the lone pair? If we place the lone pair in the equatorial position, we have three LP–BP repulsions at 90°. If we place it in the axial position, we have two 90° LP–BP repulsions at 90°. With fewer 90° LP–BP repulsions, we can predict that the structure with the lone pair of electrons in the equatorial position is more stable than the one with the lone pair in the axial position. We also expect a deviation from ideal geometry because a lone pair of electrons occupies more space than a bonding pair.

Figure 9.5 Illustration of the Area Shared by Two Electron Pairs versus the Angle between Them



At 90°, the two electron pairs share a relatively large region of space, which leads to strong repulsive electron–electron interactions.

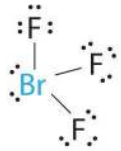
4. With four nuclei and one lone pair of electrons, the molecular structure is based on a trigonal bipyramid with a missing equatorial vertex; it is described as a *seesaw*. The F_{axial}–S–F_{axial} angle is 173° rather than 180° because of the lone pair of electrons in the equatorial plane.



Molecular geometry (seesaw)

AX_3E_2: BrF_3

1. The bromine atom has seven valence electrons, and each fluorine has seven valence electrons, so the Lewis electron structure is

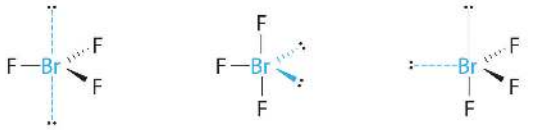


Lewis structure

Once again, we have a compound that is an exception to the octet rule.

2. There are five groups around the central atom, three bonding pairs and two lone pairs. We again direct the groups toward the vertices of a trigonal bipyramid.

3. With three bonding pairs and two lone pairs, the structural designation is AX_3E_2 with a total of five electron pairs. Because the axial and equatorial positions are not equivalent, we must decide how to arrange the groups to minimize repulsions. If we place both lone pairs in the axial positions, we have six LP–BP repulsions at 90°. If both are in the equatorial positions, we have four LP–BP repulsions at 90°. If one lone pair is axial and the other equatorial, we have one LP–LP repulsion at 90° and three LP–BP repulsions at 90°:



	Lone pairs axial (a)	Lone pairs equatorial (b)	Lone pairs axial and equatorial (c)
Interactions			
90° LP–LP	0	0	1
90° LP–BP	6	4	3

Structure (c) can be eliminated because it has a LP–LP interaction at 90°. Structure (b), with fewer LP–BP repulsions at 90° than (a), is lower in energy. However, we predict a deviation in bond angles because of the presence of the two lone pairs of electrons.

4. The three nuclei in BrF_3 determine its molecular structure, which is described as *T shaped*. This is essentially a trigonal bipyramid that is missing two equatorial vertices. The F_{axial}–Br–F_{axial} angle is 172°, less than 180° because of LP–BP repulsions (Figure 9.1).

Note
Because lone pairs occupy more space around the central atom than bonding pairs, electrostatic repulsions are more important for lone pairs than for bonding pairs.

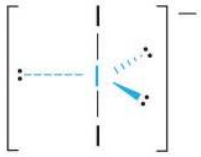
AX_2E_3: I_3^-

1. Each iodine atom contributes seven electrons and the negative charge one, so the Lewis electron structure is



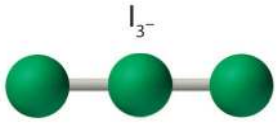
2. There are five electron groups about the central atom in I_3^-, two bonding pairs and three lone pairs. To minimize repulsions, the groups are directed to the corners of a trigonal bipyramid.

3. With two bonding pairs and three lone pairs, I_3^- has a total of five electron pairs and is designated as AX_2E_3. We must now decide how to arrange the lone pairs of electrons in a trigonal bipyramid in a way that minimizes repulsions. Placing them in the axial positions eliminates 90° LP–LP repulsions and minimizes the number of 90° LP–BP repulsions.



The three lone pairs of electrons have equivalent interactions with the three iodine atoms, so we do not expect any deviations in bonding angles.

4. With three nuclei and three lone pairs of electrons, the molecular geometry of I_3^- is linear. This can be described as a trigonal bipyramid with three equatorial vertices missing. The ion has an I–I–I angle of 180°, as expected.

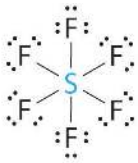


Six Electron Groups

Six electron groups form an *octahedron*, a polyhedron made of identical equilateral triangles and six identical vertices (Figure 9.2.)

AX_6: SF_6

1. The central atom, sulfur, contributes six valence electrons, and each fluorine atom has seven valence electrons, so the Lewis electron structure is



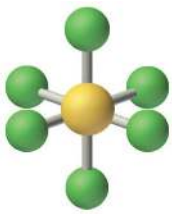
Lewis structure

With an expanded valence, that 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 9.2 that the geometry that minimizes repulsions is *octahedral*.

3. With only bonding pairs, SF_6 is designated as AX_6. All positions are chemically equivalent, so all electronic interactions are equivalent.

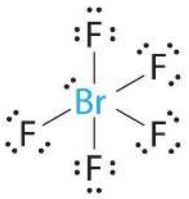
4. There are six nuclei, so the molecular geometry of SF_6 is octahedral.



Molecular geometry
(octahedral)

AX_5E: BrF_5

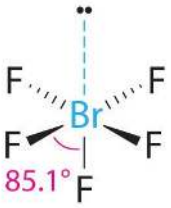
1. The central atom, bromine, has seven valence electrons, as does each fluorine, so the Lewis electron structure is



Lewis structure

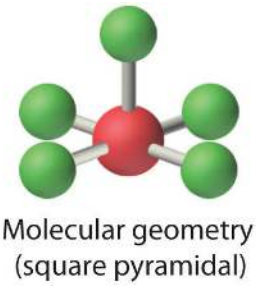
With its expanded valence, this species is an exception to the octet rule.

2. There are six electron groups around the Br, five bonding pairs and one lone pair. Placing five F atoms around Br while minimizing BP–BP and LP–BP repulsions gives the following structure:



3. With five bonding pairs and one lone pair, BrF_5 is designated as AX_5E; it has a total of six electron pairs. The BrF_5 structure has four fluorine atoms in a plane in an equatorial position and one fluorine atom and the lone pair of electrons in the axial positions. We expect all F_{axial}–Br–$F_{equatorial}$ angles to be less than 90° because of the lone pair of electrons, which occupies more space than the bonding electron pairs.

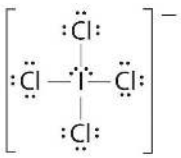
4. With five nuclei surrounding the central atom, the molecular structure is based on an octahedron with a vertex missing. This molecular structure is *square pyramidal*. The F_{axial}–B–$F_{equatorial}$ angles are 85.1°, less than 90° because of LP–BP repulsions.



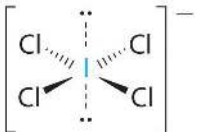
Molecular geometry
(square pyramidal)

AX_4E_2: ICl_4^-

1. The central atom, iodine, contributes seven electrons. Each chlorine contributes seven, and there is a single negative charge. The Lewis electron structure is

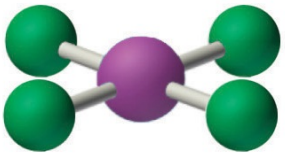


2. There are six electron groups around the central atom, four bonding pairs and two lone pairs. The structure that minimizes LP–LP, LP–BP, and BP–BP repulsions is



3. ICl_4^- is designated as AX_4E_2 and has a total of six electron pairs. Although there are lone pairs of electrons, with four bonding electron pairs in the equatorial plane and the lone pairs of electrons in the axial positions, all LP–BP repulsions are the same. Therefore, we do not expect any deviation in the Cl–I–Cl bond angles.

4. With five nuclei, the ICl4− ion forms a molecular structure that is *square planar*, an octahedron with two opposite vertices missing.



The relationship between the number of electron groups around a central atom, the number of lone pairs of electrons, and the molecular geometry is summarized in Figure 9.6.

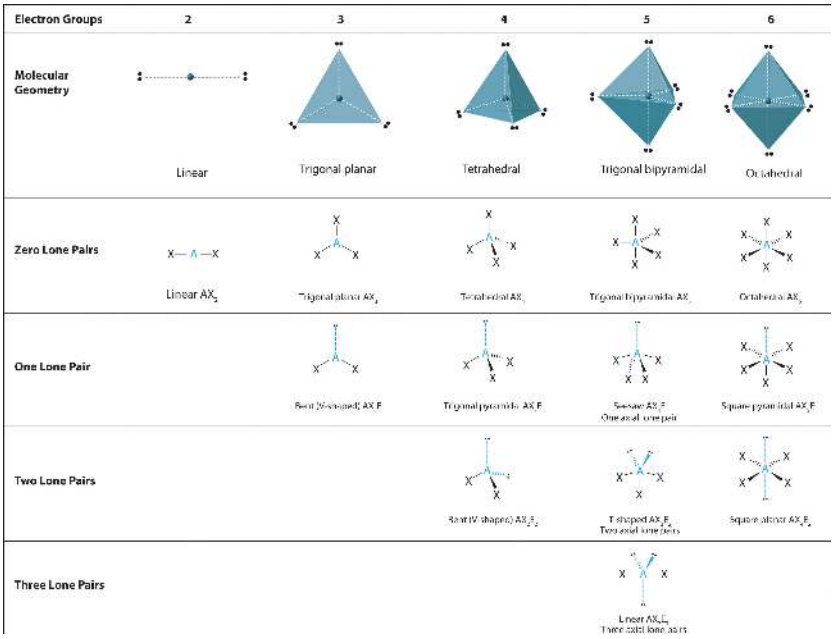


Figure 9.6 Overview of Molecular Geometries

Example 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_30^+ (hydronium ion)

Given: two chemical species

Asked for: molecular geometry

Strategy:

A. Draw the Lewis electron structure of the molecule or polyatomic ion.

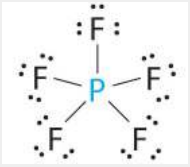
B. Determine the electron group arrangement around the central atom that minimizes repulsions.

C. Assign an AX_mE_n designation; then identify the LP–LP, LP–BP, or BP–BP interactions and predict deviations in bond angles.

D. Describe the molecular geometry.

Solution:

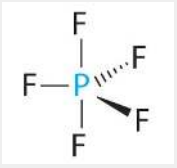
1. **A** The central atom, P, has five valence electrons and each fluorine has seven valence electrons, so the Lewis structure of PF_5 is



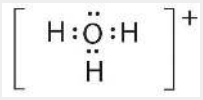
B There are five bonding groups about phosphorus. The structure that minimizes repulsions is a trigonal bipyramid (Figure 9.6).

C All electron groups are bonding pairs, so PF_5 is designated as AX_5. Notice that this gives a total of five electron pairs. With no lone pair repulsions, we do not expect any bond angles to deviate from the ideal.

D The PF_5 molecule has five nuclei and no lone pairs of electrons, so its molecular geometry is trigonal bipyramidal.



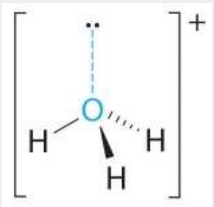
2. **A** The central atom, O, has six valence electrons, and each H atom contributes one valence electron. Subtracting one electron for the positive charge gives a total of eight valence electrons, so the Lewis electron structure is



B There are four electron groups around oxygen, three bonding pairs and one lone pair. Like NH_3, repulsions are minimized by directing each hydrogen atom and the lone pair to the corners of a tetrahedron.

C With three bonding pairs and one lone pair, the structure is designated as AX_3E and has a total of four electron pairs (three X and one E). We expect the LP–BP interactions to cause the bonding pair angles to deviate significantly from the angles of a perfect tetrahedron.

D There are three nuclei and one lone pair, so the molecular geometry is *trigonal pyramidal*, in essence a tetrahedron missing a vertex. However, the H–O–H bond angles are less than the ideal angle of 109.5° because of LP–BP repulsions:



Exercise

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

b. octahedral

c. linear

Example 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 1.

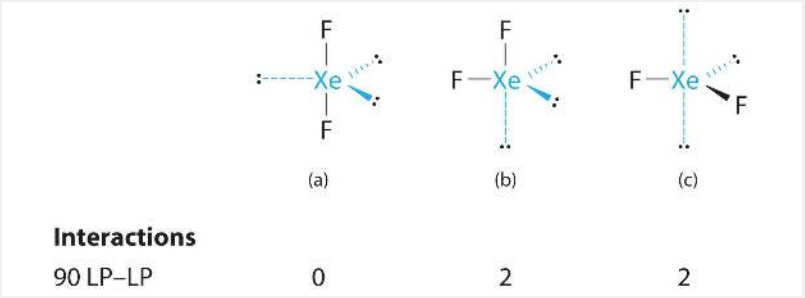
Solution:

1. **A** Xenon contributes eight electrons and each fluorine seven valence electrons, so the Lewis electron structure is



B There are five electron groups around the central atom, two bonding pairs and three lone pairs. Repulsions are minimized by placing the groups in the corners of a trigonal bipyramid.

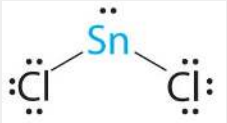
C From B, XeF_2 is designated as AX_2E_3 and has a total of five electron pairs (two X and three E). With three lone pairs about the central atom, we can arrange the two F atoms in three possible ways: both F atoms can be axial, one can be axial and one equatorial, or both can be equatorial:



The structure with the lowest energy is the one that minimizes LP–LP repulsions. Both (b) and (c) have two 90° LP–LP interactions, whereas structure (a) has none. Thus both F atoms are in the axial positions, like the two iodine atoms around the central iodine in I_3^-. All LP–BP interactions are equivalent, so we do not expect a deviation from an ideal 180° in the F–Xe–F bond angle.

D With two nuclei about the central atom, the molecular geometry of XeF_2 is linear. It is a trigonal bipyramid with three missing equatorial vertices.

2. **A** The tin atom donates 4 valence electrons and each chlorine atom donates 7 valence electrons. With 18 valence electrons, the Lewis electron structure is



B There are three electron groups around the central atom, two bonding groups and one lone pair of electrons. To minimize repulsions the three groups are initially placed at 120° angles from each other.

C From B we designate $SnCl_2$ as AX_2E. It has a total of three electron pairs, two X and one E. Because the lone pair of electrons occupies more space than the bonding pairs, we expect a decrease in the Cl–Sn–Cl bond angle due to increased LP–BP repulsions.

D With two nuclei around the central atom and one lone pair of electrons, the molecular geometry of $SnCl_2$ is bent, like SO_2, but with a Cl–Sn–Cl bond angle of 95°. The molecular geometry can be described as a trigonal planar arrangement with one vertex missing.

Exercise 2

Predict the molecular geometry of each molecule.

a. SO_3

b. XeF_4

Answers:

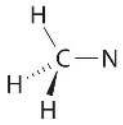
a. trigonal planar

b. square planar

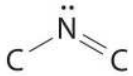
Molecules with No Single Central Atom

The VSEPR model can be used to predict the structure of somewhat more complex molecules with no single central atom by treating them as linked AX_mE_n fragments. We will demonstrate with methyl isocyanate (CH_3–N=C=O), a volatile and highly toxic molecule that is used to produce the pesticide Sevin. In 1984, large quantities of Sevin were accidentally released in Bhopal, India, when water leaked into storage tanks. The resulting highly exothermic reaction caused a rapid increase in pressure that ruptured the tanks, releasing large amounts of methyl isocyanate that killed approximately 3800 people and wholly or partially disabled about 50,000 others. In addition, there was significant damage to livestock and crops.

We can treat methyl isocyanate as linked AX_mE_n fragments beginning with the carbon atom at the left, which is connected to three H atoms and one N atom by single bonds. The four bonds around carbon mean that it must be surrounded by four bonding electron pairs in a configuration similar to AX_4. We can therefore predict the CH_3–N portion of the molecule to be roughly tetrahedral, similar to methane:

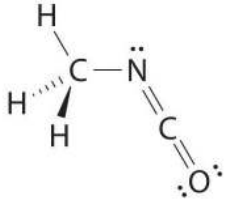


The nitrogen atom is connected to one carbon by a single bond and to the other carbon by a double bond, producing a total of three bonds, C–N=C. For nitrogen to have an octet of electrons, it must also have a lone pair:



Because multiple bonds are not shown in the VSEPR model, the nitrogen is effectively surrounded by three electron pairs. Thus according to the VSEPR model, the C–N=C fragment should be bent with an angle less than 120°.

The carbon in the –N=C=O fragment is doubly bonded to both nitrogen and oxygen, which in the VSEPR model gives carbon a total of two electron pairs. The N=C=O angle should therefore be 180°, or linear. The three fragments combine to give the following structure:



We predict that all four nonhydrogen atoms lie in a single plane, with a C–N–C angle of approximately 120°. The experimentally determined structure of methyl isocyanate confirms our prediction (Figure 9.7).

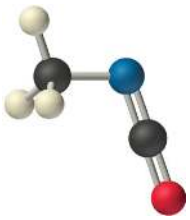


Figure 9.7: *The Experimentally Determined Structure of Methyl Isocyanate*

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 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 9.3 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

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°.

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 (part (a) in Figure 9.8). 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 (part (b) in Figure 9.8); 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.

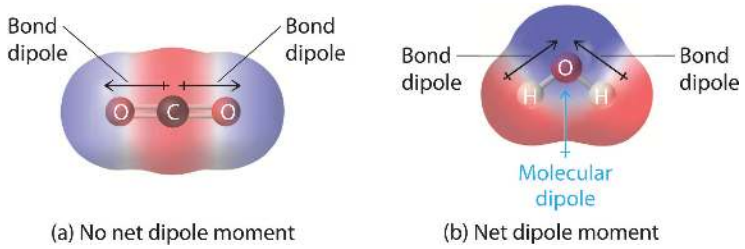


Figure 9.8 How Individual Bond Dipole Moments Are Added Together to Give an Overall Molecular Dipole Moment for Two Triatomic Molecules with Different Structures. (a) In CO_2, the C–O bond dipoles are equal in magnitude but oriented in opposite

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 9.9. 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.

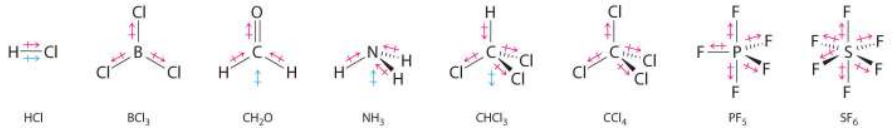


Figure 9.9: Molecules with Polar Bonds. Individual bond dipole moments are indicated in red. Due to their different three-dimensional structures, some molecules with polar bonds have a net dipole moment (HCl, CH_2O, NH_3, and $CHCl_3$), indicated in blue, whereas others do not because the bond dipole moments cancel (BCl_3, CCl_4, PF_5, and SF_6).

Note
Molecules with asymmetrical charge distributions have a net dipole moment.

Example 4

Which molecule(s) has a net dipole moment?

a. H_2S
b. NHF_2
c. BF_3

Given: three chemical compounds

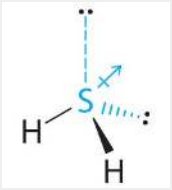
Asked for: net dipole moment

Strategy:

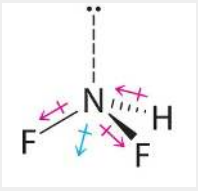
For each three-dimensional molecular geometry, predict whether the bond dipoles cancel. If they do not, then the molecule has a net dipole moment.

Solution:

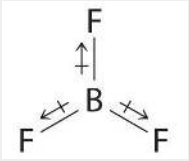
1. The total number of electrons around the central atom, S, is eight, which gives four electron pairs. Two of these electron pairs are bonding pairs and two are lone pairs, so the molecular geometry of H_2S is bent (Figure 9.6). The bond dipoles cannot cancel one another, so the molecule has a net dipole 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

Which molecule(s) has a net dipole moment?

1. CH_3Cl
2. SO_3
3. XeO_3

Answer: CH_3Cl; XeO_3

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**. A combination of VSEPR and a bonding model, such as Lewis electron structures, however, 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.

Key Takeaway

- 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.

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?

- 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.
- 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?
- 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.
- How is molecular geometry related to the presence or absence of a molecular dipole moment?
- How are molecular geometry and dipole moments related to physical properties such as melting point and boiling point?
- 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.
- When a chemist says that a molecule is *polar*, what does this mean? What are the general physical properties of polar molecules?
- 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

- 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?
- Which has the smallest bond angle around the central atom—H_2S, H_2Se, or H_2Te? the largest? Justify your answers.
- 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?

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.

Answers

1.
2.
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.
14.
15.
16.
17.

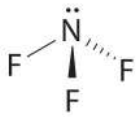
Numerical Problems

1. 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

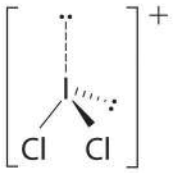
2. Give the number of electron groups around the central atom and the molecular geometry for each species. Classify the electron groups in each species as bonding pairs or lone pairs.
    1. ICl_3
    2. CCl_3^+
    3. H_2Te
    4. XeF_4
    5. NH_4^+
3. Give the number of electron groups around the 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^+
4. 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
5. 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.
6. Predict the molecular geometry of each of the following.
    1. ICl_3
    2. AsF_5
    3. NO_2^-
    4. $TeCl_4$
7. 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
8. 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
9. Of the molecules $Cl_2C{=}Cl_2$, IF_3, and SF_6, which has a net dipole moment? Explain your reasoning.
10. Of the molecules SO_3, XeF_4, and $H_2C{=}Cl_2$, which has a net dipole moment? Explain your reasoning.

Answers

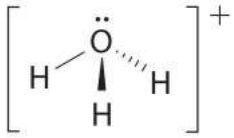
1. 1. trigonal planar (all electron groups are bonding pairs)
   2. tetrahedral (one lone pair on P)
   3. trigonal bipyramidal (three lone pairs on Xe)
   4. tetrahedral (all electron groups on Al are bonding pairs)
   5. tetrahedral (all electron groups on C are bonding pairs)
2.
3. 1. four electron groups, linear molecular geometry
   2. four electron groups, pyramidal molecular geometry

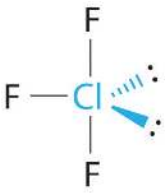
      

   3. four electron groups, bent molecular geometry

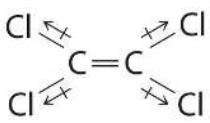
      

   4. two electron groups, linear molecular geometry
   5. four electron groups, pyramidal molecular geometry

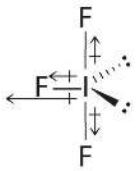
      

4.
5. 

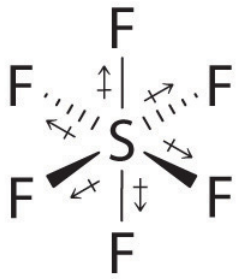
   The idealized geometry is T shaped, but the two lone pairs of electrons on Cl will distort the structure, making the F–Cl–F angle *less* than 180°.
6.
7.
8.
9. $Cl_2C=CCl_2$: Although the C–Cl bonds are rather polar, the individual bond dipoles cancel one another in this symmetrical structure, and $Cl_2C=CCl_2$ 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.



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1.1.3.8: Bond Order and Bond Lengths

Bond order is the number of chemical bonds between a pair of atoms and indicates the stability of a bond. For example, in diatomic nitrogen, N≡N, the bond order is 3; in acetylene, H−C≡C−H, the carbon-carbon bond order is also 3, and the C−H bond order is 1. Bond order and bond length indicate the type and strength of covalent bonds between atoms. Bond order and length are inversely proportional to each other: when bond order is increased, bond length is decreased.

Introduction

Chemistry deals with the way in which subatomic particles bond together to form atoms. Chemistry also focuses on the way in which atoms bond together to form molecules. In the atomic structure, electrons surround the atomic nucleus in regions called orbitals. Each orbital shell can hold a certain number of electrons. When the nearest orbital shell is full, new electrons start to gather in the next orbital shell out from the nucleus, and continue until that shell is also full. The collection of electrons continues in ever widening orbital shells as larger atoms have more electrons than smaller atoms. When two atoms bond to form a molecule, their electrons bond them together by mixing into openings in each others' orbital shells. As with the collection of electrons by the atom, the formation of bonds by the molecule starts at the nearest available orbital shell opening and expand outward.

Bond Order

Bond order is the number of bonding pairs of electrons between two atoms. In a covalent bond between two atoms, a single bond has a bond order of one, a double bond has a bond order of two, a triple bond has a bond order of three, and so on. To determine the bond order between two covalently bonded atoms, follow these steps:

1. Draw the Lewis structure.
2. Determine the type of bonds between the two atoms.
    - 0: No bond
    - 1: Single bond
    - 2: double bond
    - 3: triple bond

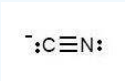
If the bond order is zero, the molecule cannot form. The higher bond orders indicate greater stability for the new molecule. In molecules that have resonance bonding, the bond order does not need to be an integer.

Example 1.1.3.8.1: CN^-

Determine the bond order for cyanide, CN^-.

Solution

1) Draw the Lewis structure.



2) Determine the type of bond between the two atoms.

Because there are 3 dashes, the bond is a triple bond. A triple bond corresponds to a bond order of 3.

Example 1.1.3.8.2: H_2

Determine the bond order for hydrogen gas, H_2.

Solution

1) Draw the Lewis structure.



2) Determine the type of bond between the two atoms.

There is only one pair of shared electrons (or dash), indicating is a single bond, with a bond order of 1.

Polyatomic molecules

If there are more than two atoms in the molecule, follow these steps to determine the bond order:

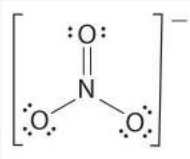
1. Draw the Lewis structure.
2. Count the total number of bonds.
3. Count the number of bond groups between individual atoms.
4. Divide the number of bonds between atoms by the total number of bond groups in the molecule.

Example 1.1.3.8.3: NO_3^-

Determine the bond order for nitrate, NO_3^-.

Solution

1) Draw the Lewis structure.



2) Count the total number of bonds.

4

The total number of bonds is 4.

3) Count the number of bond groups between individual atoms.

3

The number of bond groups between individual atoms is 3.

4) Divide the number of bonds between individual atoms by the total number of bonds.

$$\frac{4}{3} = 1.33 \qquad (1.1.3.8.1)$$

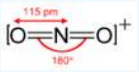
The bond order is 1.33

Example 1.1.3.8.4: NO_2^+

Determine the bond order for nitronium ion: NO_2^+.

Solution

1) Draw the Lewis Structure.



2) Count the total number of bonds.

4

The total number of bonds is 4.

3) Count the number of bond groups between individual atoms.

2

The number of bond groups between atoms is 2.

4) Divide the bond groups between individual atoms by the total number of bonds.

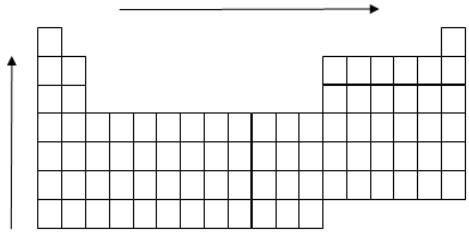
$$\frac{4}{2} = 2 \tag{1.1.3.8.2}$$

The bond order is 2.

A high bond order indicates more attraction between electrons. A higher bond order also means that the atoms are held together more tightly. With a lower bond order, there is less attraction between electrons and this causes the atoms to be held together more loosely. Bond order also indicates the stability of the bond. The higher the bond order, the more electrons holding the atoms together, and therefore the greater the stability.

Trends in the Periodic Table

Bond order increases across a period and decreases down a group.



Bond Length

Bond length is defined as the distance between the centers of two covalently bonded atoms. The length of the bond is determined by the number of bonded electrons (the bond order). The higher the bond order, the stronger the pull between the two atoms and the shorter the bond length. Generally, the length of the bond between two atoms is approximately the sum of the covalent radii of the two atoms. Bond length is reported in picometers. Therefore, bond length increases in the following order: triple bond < double bond < single bond.

To find the bond length, follow these steps:

1. Draw the Lewis structure.
2. Look up the chart below for the radii for the corresponding bond.
3. Find the sum of the two radii.

✔ 4

Determine the carbon-to-chlorine bond length in CCl_4.

Solution

Using Table A3, a C single bond has a length of 75 picometers and that a Cl single bond has a length of 99 picometers. When added together, the bond length of a C-Cl bond is approximately 174 picometers.

✔ 2

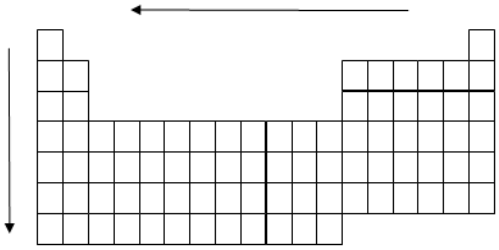
Determine the carbon-oxygen bond length in CO_2.

Solution

Using Table A3, we see that a C double bond has a length of 67 picometers and that an O double bond has a length of 57 picometers. When added together, the bond length of a C=O bond is approximately 124 picometers.

Trends in the Periodic Table

Because the bond length is proportional to the atomic radius, the bond length trends in the periodic table follow the same trends as atomic radii: bond length decreases across a period and increases down a group.



Problems

1. What is the bond order of O_2?
2. What is the bond order of NO_3^-?
3. What is the carbon-nitrogen bond length in HCN?
4. Is the carbon-to-oxygen bond length greater in CO_2 or CO?
5. What is the nitrogen-fluoride bond length in NF_3?

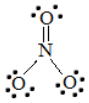
Solutions

1. First, write the Lewis structure for O_2.



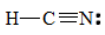
There is a double bond between the two oxygen atoms; therefore, the bond order of the molecule is 2.

2. The Lewis structure for NO_3^- is given below:



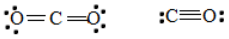
To find the bond order of this molecule, take the average of the bond orders. N=O has a bond order of two, and both N-O bonds have a bond order of one. Adding these together and dividing by the number of bonds (3) reveals that the bond order of nitrate is 1.33.

3. To find the carbon-nitrogen bond length in HCN, draw the Lewis structure of HCN.



The bond between carbon and nitrogen is a triple bond, and a triple bond between carbon and nitrogen has a bond length of approximately 60 + 54 =114 pm.

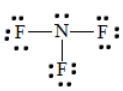
4. From the Lewis structures for CO_2 and CO, there is a double bond between the carbon and oxygen in CO_2 and a triple bond between the carbon and oxygen in CO.



Referring to the table above, a double bond between carbon and oxygen has a bond length of approximately 67 + 57 = 124 pm and a triple bond between carbon and oxygen has a bond length of approximately 60 + 53 =113 pm. Therefore, the bond length is greater in CO_2.

Another method makes use of the fact that the more electron bonds between the atoms, the tighter the electrons are pulling the atoms together. Therefore, the bond length is greater in CO_2.

5. To find the nitrogen-to-fluorine bond length in NF_3, draw the Lewis structure.



The bond between fluorine and nitrogen is a single bond. From the table above, a single bond between fluorine and nitrogen has a bond length of approximately 64 + 71 =135 pm.

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4. Pekka Pyykkö and Michiko Atsumi, Chem. Eur. J. Molecular Double-Bond Covalent Radii for Elements Li–E112 2009

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1.1.3.9: Bond Energies

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.

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 **1.1.3.9.1** lists the average values for some commonly encountered bonds. Although the values shown vary widely, we can observe four trends:

Table **1.1.3.9.1**: 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.

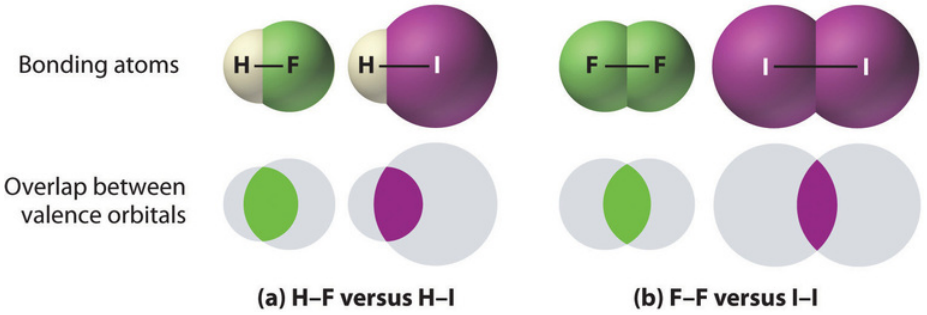


Figure **1.1.3.9.1**: The Strength of Covalent Bonds Depends on the Overlap between the Valence Orbitals of the Bonded Atoms. The relative sizes of the region of space in which electrons are shared between (a) a hydrogen atom and lighter (smaller) vs. heavier (larger) atoms in the same periodic group; 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**.*

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 **1.1.3.9.2**); that is, the C–H bond energy depends on its molecular environment. Except for diatomic molecules, the bond energies listed in Table **1.1.3.9.1** 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 **1.1.3.9.2**: 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 ($\Delta H_{rxn} < 0$):

$$\Delta H_{rxn} \approx \sum(\text{bond energies of bonds broken}) - \sum(\text{bond energies of bonds formed}) \quad (1.1.3.9.1)$$

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:

$$CH_3(CH_2)_5CH_3\,(l) + 11\,O_2\,(g) \rightarrow 7\,CO_2\,(g) + 8\,H_2O\,(g) \quad (1.1.3.9.2)$$

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)

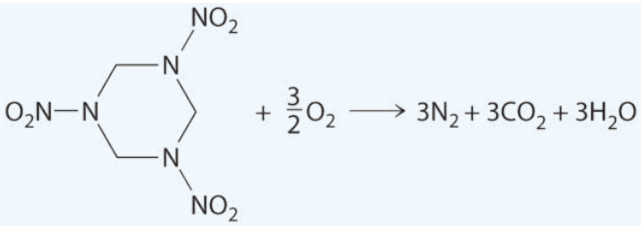
Bonds Broken (kJ/mol)		Bonds Formed (kJ/mol)	
6 C–C	346 × 6 = 2076	14 C=O	799 × 14 = 11,186
16 C–H	411 × 16 = 6576	16 O–H	459 × 16 = 7344
11 O=O	494 × 11 = 5434		**Total** = 18,530
	Total = 14,086		

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° 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° values are unknown. These approximations can be important for predicting whether a reaction is **exothermic** or **endothermic**—and to what degree.

Example 1.1.3.9.1: 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 **1.1.3.9.1** to estimate the ΔH_{rxn} per mole of RDX.



RDX

Given: chemical reaction, structure of reactant, and Table **1.1.3.9.1**.

Asked for: ΔH_{rxn} per mole

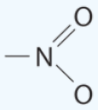
Strategy:

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 **1.1.3.9.1** 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		

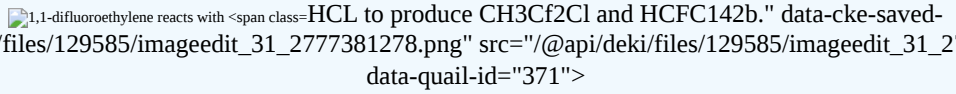
B From Equation **1.1.3.9.1**, we have

$$\begin{aligned}\Delta H_{rxn} &\approx \sum(\text{bond energies of bonds broken}) - \sum(\text{bond energies of bonds formed}) \\ &= 7962\ kJ/mol - 10,374\ kJ/mol \\ &= -2412\ kJ/mol\end{aligned}$$

Thus this reaction is also highly exothermic

Exercise 1.1.3.9.1: Freon

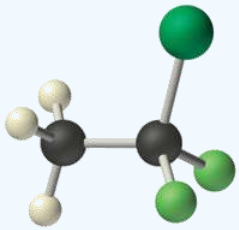
The molecule HCFC-142b is a hydrochlorofluorocarbon that is used in place of chlorofluorocarbons (CFCs) such as the Freons and can be prepared by adding HCl to 1,1-difluoroethylene:



Use tabulated bond energies to calculate ΔH_{rxn}.

Answer

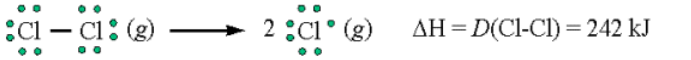
−54 kJ/mol



HCFC-142b

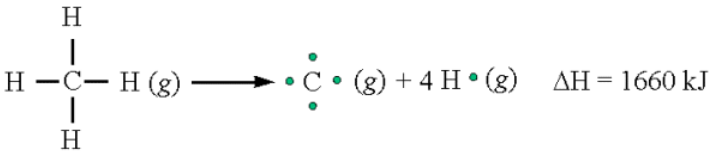
Bond Dissociation Energy

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 **1.1.3.9.4**: 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.



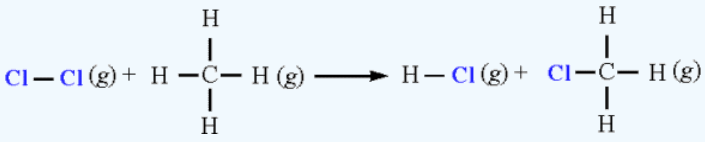
Bond Energies and the Enthalpy of Reactions

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:

$$\Delta H = \sum \text{bond energies of broken bonds} - \sum \text{bond energies of formed bonds} \tag{1.1.3.9.3}$$

Example 1.1.3.9.2: Chlorination of Methane

What is the enthalpy of reaction between 1 mol of chlorine and 1 mol methane?



Solution

We use Equation 1.1.3.9.3, 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

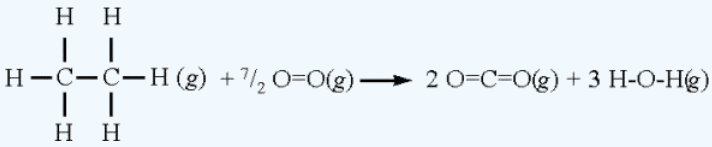
$$\begin{aligned}\Delta H &= [D(Cl-Cl)+D(C-H)]-[D(H-Cl)+D(C-Cl)]\\ &= [242kJ+413kJ]-[431kJ+328kJ]\\ &= -104\,kJ\end{aligned}$$

Thus, the reaction is **exothermic** (because the bonds in the products are stronger than the bonds in the reactants)

Example 1.1.3.9.3: 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 1.1.3.9.3, 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 1.1.3.9.5: 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

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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SECTION OVERVIEW

1.1.4: Bonding II- Additional Aspects

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In this chapter, we begin with a general method for predicting the structures of simple covalent molecules and polyatomic ions; then we discuss the actual distribution of electrons in covalent bonds. We apply two distinct approaches for describing covalent bonds:

1. a localized model to describe bonding in molecules with two or more atoms attached to a central atom and
2. a delocalized model to explain and predict which diatomic species exist and which do not exist.

We conclude by describing more complex molecules and ions with multiple bonds. The tools you acquire in this chapter will enable you to explain why Ca_2 is too unstable to exist in nature and why the unpaired electrons on O_2 are crucial to the existence of life as we know it. You will also discover why carbon, the basic component of all organic compounds, forms four bonds despite having only two unpaired electrons in its valence electron configuration and how the structure of retinal, the key light-sensing component in our eyes, allows us to detect visible light.

Topic hierarchy

1.1.4.1: Bonding Theories

1.1.4.2: Introduction to Valence Bond Theory

1.1.4.3: Hybridization of Atomic Orbitals

1.1.4.4: Multiple Covalent Bonds

1.1.4.5: Molecular Orbital Theory

1.1.4.6: Exercises

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1.1.4.1: Bonding Theories

As we have talked about using Lewis structures to depict the bonding in organic 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?

In this chapter, the **valence bond theory** is introduced to describe bonding in organic 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. In order to explain the bonding in organic molecules, however, we will need to introduce the concept of **hybrid orbitals**.

Valence bond theory is adequate for describing many aspects of organic structure. In some cases, however, chemists need to use a different model, called **molecular orbital (MO) theory**, to talk about covalent bonds in which electrons are shared not just between two atoms, but between several, or even over an entire molecule.

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.

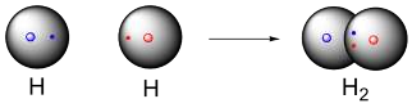


Figure 1.1.4.1.1: Addition of twe hydrogen atoms to form the diatomic hydrogen molecule.

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.

But 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.

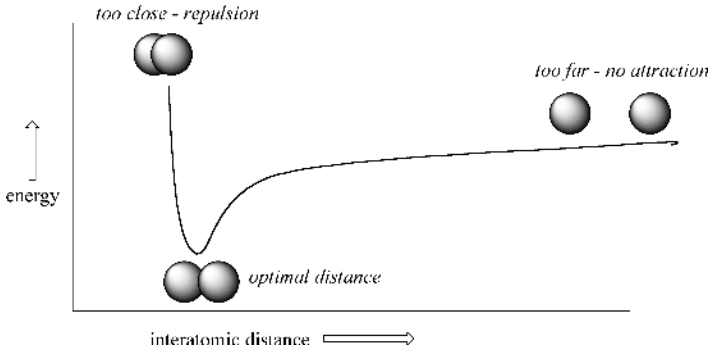


Figure 1.1.4.1.2.: Potential of interaction for the addition of twe hydrogen atoms to form the diatomic hydrogen molecule.

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.

It is not accurate, however, 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.

Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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1.1.4.2: Introduction to Valence Bond Theory

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 H_2O and NH_3, respectively. In fact, structural studies have shown that the H–S–H and H–P–H angles are more than 12° smaller than the corresponding bond angles in H_2O and NH_3. More disturbing, the VSEPR model predicts that the simple group 2 halides (MX_2), which have four valence electrons, should all have linear X–M–X geometries. Instead, many of these species, including SrF_2 and BaF_2, are significantly bent. A more sophisticated treatment of bonding is needed for systems such as these. In this section, we present a quantum mechanical description of bonding, in which bonding electrons are viewed as being localized between the nuclei of the bonded atoms.

Valence Bond Theory: A Localized Bonding Approach

Valence Bond Theory has its roots in Gilbert Newton Lewis's paper *The Atom and The Molecule*. Possibly unaware that Lewis's model existed, Walter Heitler and Fritz London came up with the idea that resonance and wavefunctions contributed to chemical bonds, in which they used dihydrogen as an example. Their theory was equivalent to Lewis's theory, with the difference of quantum mechanics being developed. Nonetheless, Heitler and London's theory proved to be successful, providing Linus Pauling and John C. Slater with an opportunity to assemble a general chemical theory containing all of these ideas. Valence Bond Theory was the result, which included the ideas of resonance, covalent-ionic superposition, atomic orbital overlap, and hybridization to describe chemical bonds.

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. 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 **1.1.4.2.1**).

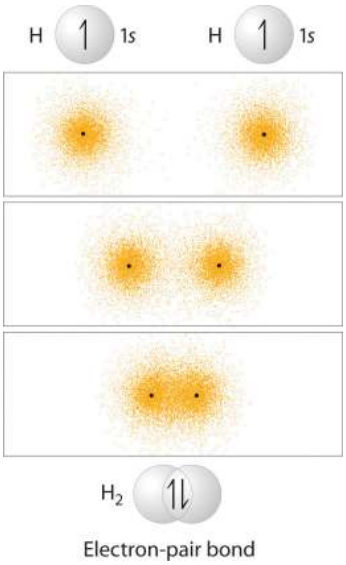


Figure **1.1.4.2.1**: Overlap of Two Singly Occupied Hydrogen 1*s* Atomic Orbitals Produces an H–H Bond in H_2. The formation of H_2 from two hydrogen atoms, each with a single electron in a 1*s* orbital, occurs as the electrons are shared to form an electron-pair bond, as indicated schematically by 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 both 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 **1.1.4.2.2** 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 $n = 2$. Maximum overlap occurs between orbitals with the same spatial orientation and similar energies.

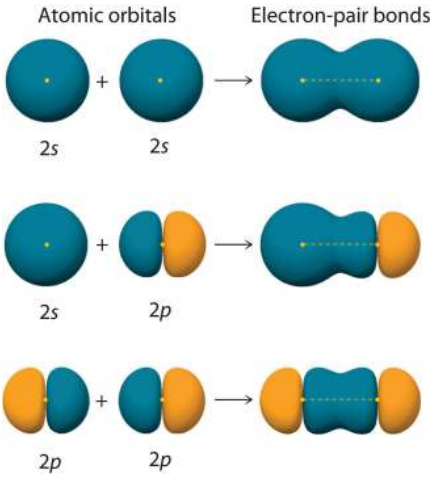


Figure **1.1.4.2.2**: Three Different Ways to Form an Electron-Pair Bond. An electron-pair bond can be formed by the overlap of any of the following combinations of two singly occupied atomic orbitals: two *ns* atomic orbitals (a), an *ns* and an *np* atomic orbital (b), and two *np* atomic orbitals (c) where $n = 2$. The positive lobe is indicated in yellow, and the negative lobe is in blue.

Note

An important aspect of Valence Bond theory is the concept of maximum overlap to form the strongest possible covalent bonds.

Let's examine the bonds in BeH_2, for example. According to the VSEPR model, BeH_2 is a linear compound with four valence electrons and two Be–H bonds. Its bonding can also be described using an atomic orbital approach. Beryllium has a $1s^2 2s^2$ electron configuration, and each H atom has a $1s^1$ electron configuration. Because the Be atom has a filled 2*s* subshell, however, it has no singly occupied orbitals available to overlap with the singly occupied 1*s* orbitals on the H atoms. If a singly occupied 1*s* orbital on hydrogen were to overlap with a filled 2*s* orbital on beryllium, the resulting bonding orbital would contain *three* electrons, but the maximum allowed by quantum mechanics is *two*. How then is beryllium able to bond to two hydrogen atoms? One way would be to add enough energy to excite one of its 2*s* electrons into an empty 2*p* orbital and reverse its spin, in a process called promotion:



In this excited state, the Be atom would have two singly occupied atomic orbitals (the 2*s* and one of the 2*p* orbitals), each of which could overlap with a singly occupied 1*s* orbital of an H atom to form an electron-pair bond. Although this would produce BeH_2, the two Be–H bonds would not be equivalent: the 1*s* orbital of one hydrogen atom would overlap with a Be 2*s* orbital, and the 1*s* orbital of the other hydrogen atom would overlap with an orbital of a different energy, a Be 2*p* orbital. Experimental evidence indicates, however, that the two Be–H bonds have identical energies. To resolve this discrepancy and explain how molecules such as BeH_2 form, scientists developed the concept of hybridization.

Reliability of Valence Bond Theory and Uses

As one can see, Valence Bond Theory can help describe how bonds are formed. However, there are some notable failures when it comes to Valence Bond Theory. One such failure is dioxygen. Valence Bond Theory fails to predict dioxygen's paramagnitism; it predicts that oxygen is diamagnetic. A species is paramagnetic if electrons are not spin paired and diamagnetic if the electrons are spin paired. Since Valence Bond theory begins with the basis that atomic orbitals overlap to create bonds and through that reasoning, one can see that electrons are spin paired when bonds overlap, dioxygen is indeed predicted to be diamagnetic if Valence Bond Theory is used. In reality, that is not the case. Also, sp^2d and sp^3 both have a coordinate number of four. Thus, Valence Bond Theory cannot predict whether the molecule is a square planar or the other shape (3). One must correctly draw the Lewis structure and use VSEPR to determine the shape.

Contributors and Attributions

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1.1.4.3: Hybridization of Atomic Orbitals

Learning Objectives

- To describe the hybridication in the bonding of simple compounds via valence bond theory.

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.

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 **1.1.4.3.0**.

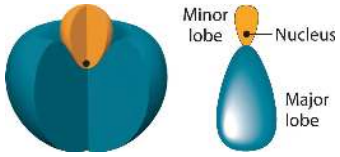


Figure 1.1.4.3.0: The position of the atomic nucleus with respect to an sp hybrid orbital. The nucleus is actually located slightly inside the minor lobe, not at the node separating the major and minor lobes.

Because the difference A − B can also be written as A + (−B), in Figure **1.1.4.3.1** 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 11.3.1, 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.

$$sp = \frac{1}{\sqrt{2}}(2s + 2p_z) \tag{1.1.4.3.1}$$

and

$$sp = \frac{1}{\sqrt{2}}(2s - 2p_z) \tag{1.1.4.3.2}$$

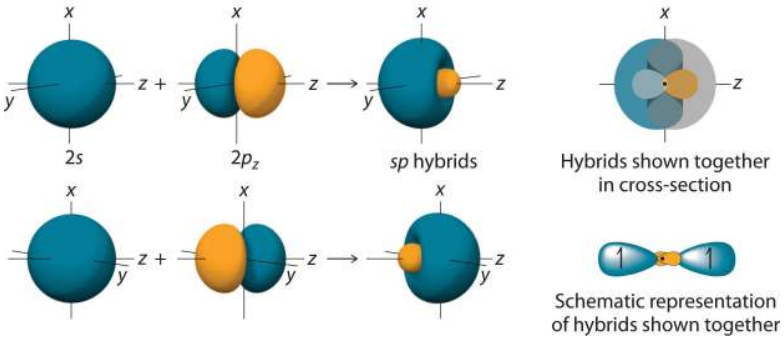


Figure **1.1.4.3.1**: The Formation of *sp* Hybrid Orbitals. Taking the sum and difference of an *ns* and an *np* atomic orbital where *n* = 2 gives two equivalent *sp* hybrid orbitals oriented at 180° to each other.

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:

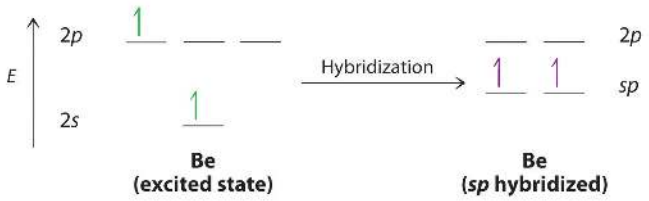


Figure **1.1.4.3.2**, each *sp* orbital on Be has the correct orientation for the major lobes to overlap with the 1*s* atomic orbital of an H atom. The formation of two energetically equivalent Be–H bonds produces a linear $\boldsymbol{BeH_2}$ molecule. Thus valence bond theory does what neither the 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.

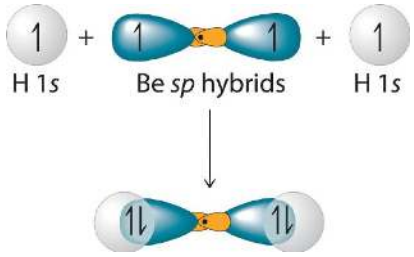


Figure **1.1.4.3.2**: Explanation of the Bonding in BeH_2 Using *sp* Hybrid Orbitals. Each singly occupied *sp* hybrid orbital on beryllium can form an electron-pair bond with the singly occupied 1*s* orbital of a hydrogen atom. Because the two *sp* hybrid orbitals are oriented at a 180° angle, the BeH_2 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 **1.1.4.3.3**). 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.

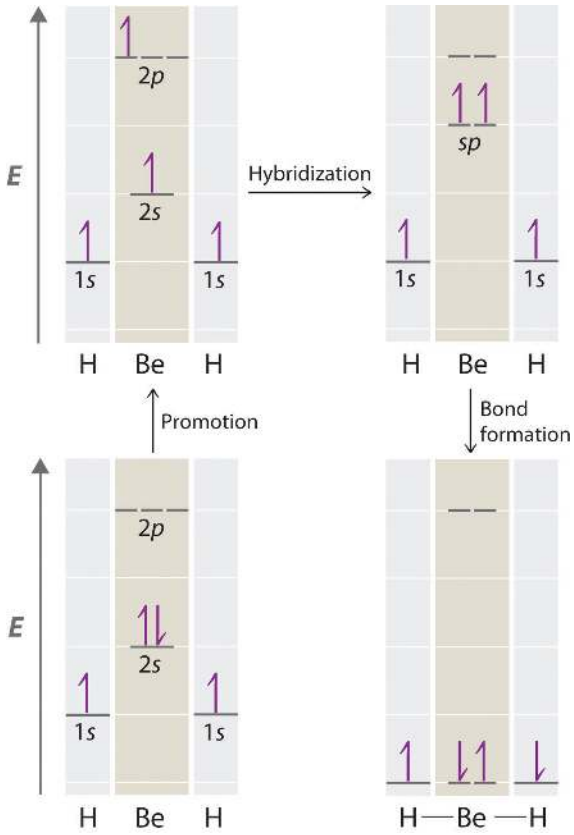


Figure **1.1.4.3.3**: A Hypothetical Stepwise Process for the Formation of BeH_2 from a Gaseous Be Atom and Two Gaseous H Atoms. The promotion of an electron from the 2*s* orbital of beryllium to one of the 2*p* orbitals is energetically uphill. The overall process of forming a BeH_2 molecule from a 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.

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:

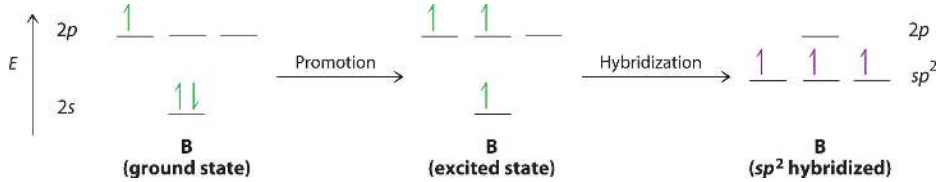


Figure **1.1.4.3.4**). Because the hybrid atomic orbitals are formed from one *s* and two *p* orbitals, boron is said to be sp^2 *hybridized* (pronounced "s-p-two" or "s-p-squared"). The singly occupied sp^2 hybrid atomic orbitals can overlap with the singly occupied orbitals on each of the three F atoms to form a trigonal planar structure with three energetically equivalent B–F bonds.

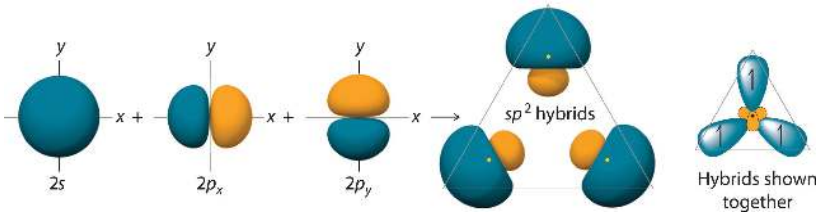
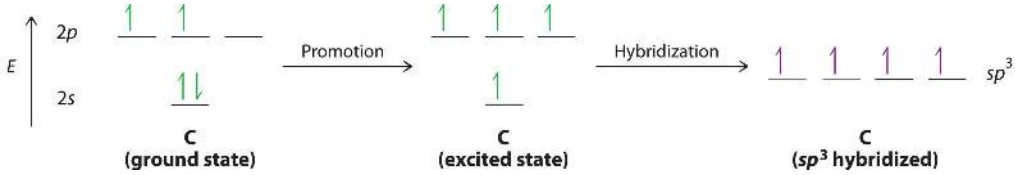


Figure **1.1.4.3.4**: Formation of sp^2 Hybrid Orbitals. Combining one *ns* and two *np* atomic orbitals gives three equivalent sp^2 hybrid orbitals in a trigonal planar arrangement; that is, oriented at 120° to one another.

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:



The large lobes of the hybridized orbitals are oriented toward the vertices of a tetrahedron, with 109.5° angles between them (Figure **1.1.4.3.5**). Like all the hybridized orbitals discussed earlier, the sp^3 hybrid atomic orbitals are predicted to be equal in energy.

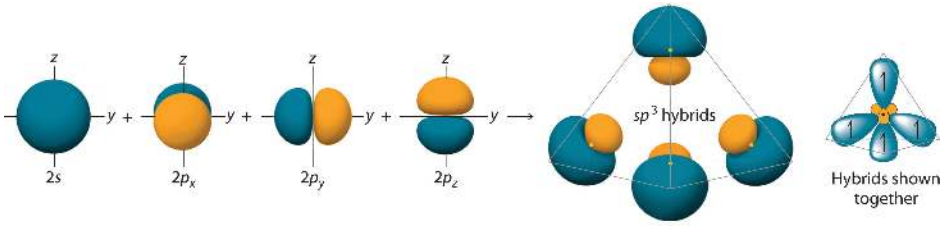


Figure **1.1.4.3.5**: Formation of sp^3 Hybrid Orbitals. Combining one *ns* and three *np* atomic orbitals results in four sp^3 hybrid orbitals oriented at 109.5° to one another in a tetrahedral arrangement.

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 form in only 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 $2s^22p^3$ 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 CH_4 and NH_3, the hybridized orbitals are *not* entirely equivalent in energy, making this bonding model an active area of research.



Valence Bond Method & sp3 Hybridization: https://youtu.be/2hxKLGWQ5EQ

Example 1.1.4.3.1

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 VPSER 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 1.1.4.3.1

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.
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.

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 **1.1.4.3.6**). 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 **1.1.4.3.6**). 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.

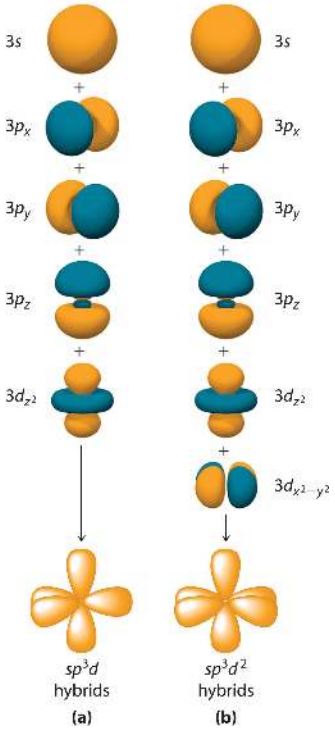


Figure **1.1.4.3.6**: Hybrid Orbitals Involving *d* Orbitals. The formation of a set of (a) five sp^3d hybrid orbitals and (b) six sp^3d^2 hybrid orbitals from *ns*, *np*, and *nd* atomic orbitals where $n = 4$.

Example 1.1.4.3.2

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 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 1.1.4.3.2

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
b. sp^3d with three Br–F bonds and two lone pairs
c. 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 1.1.4.3.3: 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 1.1.4.3.3

What is the hybridization of the boron atom in BF_6^{3-}? Is this ion likely to exist?

Answer sp^3d^2 hybridization; no



Expanded Octet Hybridization: https://youtu.be/1WpxXcKl_Io

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*^{3}*d*^{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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1.1.4.4: Multiple Covalent Bonds

Learning Objectives

- To explain resonance structures using molecular orbitals.

So far in our molecular 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.

Non-singular 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. Thus each carbon forms a set of three σ bonds: two C–H (sp^2 + *s*) and one C–C (sp^2 + sp^2) (part (a) in Figure **1.1.4.4.1**). The sp^2 hybridization can be represented as follows:

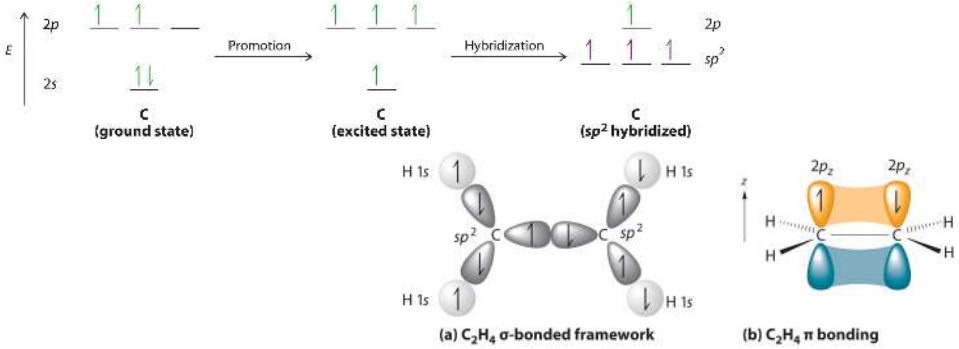


Figure **1.1.4.4.1**: Bonding in Ethylene. (a) The σ-bonded framework is formed by the overlap of two sets of singly occupied carbon sp^2 hybrid orbitals and four singly occupied hydrogen 1*s* orbitals to form electron-pair bonds. This uses 10 of the 12 valence electrons to form a total of five σ bonds (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.)

After hybridization, each carbon still has one unhybridized $2p_z$ orbital that is perpendicular to the hybridized lobes and contains a single electron (part (b) in Figure **1.1.4.4.1**). The two singly occupied $2p_z$ orbitals can overlap to form a π bonding orbital and a π^* antibonding orbital, which produces the energy-level diagram shown in Figure **1.1.4.4.2**. With the formation of a π bonding orbital, electron density increases in the plane between the carbon nuclei. The π^* orbital lies outside the internuclear region and has a nodal plane perpendicular to the internuclear axis. 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.

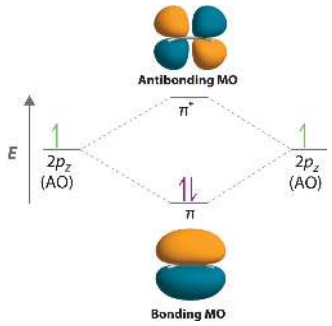


Figure **1.1.4.4.2**: Molecular Orbital Energy-Level Diagram for π Bonding in Ethylene. As in the diatomic molecules discussed previously, the singly occupied $2p_z$ orbitals in ethylene can overlap to form a bonding/antibonding pair of π molecular orbitals. The two electrons remaining are enough to fill only the bonding π orbital. With one σ bond plus one π bond, the carbon–carbon bond order in ethylene is 2.



sp2 Hybridization: https://youtu.be/EepTvePnfBA

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 **1.1.4.4.3**).

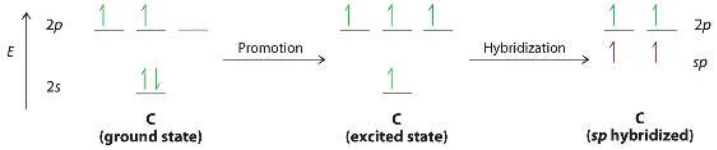


Figure **1.1.4.4.3**). Because each of the unhybridized 2*p* orbitals has a single electron, four electrons are available for π bonding, which is enough to occupy only the bonding molecular orbitals. Acetylene must therefore have a carbon–carbon triple bond, which consists of a C–C σ bond and two mutually 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.

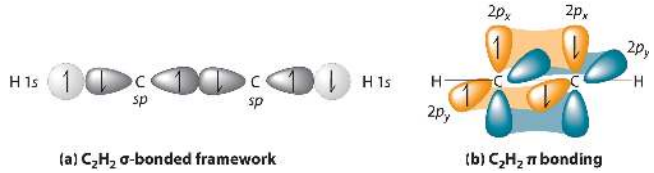


Figure* 1.1.4.4.3*: *Bonding in Acetylene (a) In the formation of the σ-bonded framework, two sets of singly occupied carbon sp hybrid orbitals and two singly occupied hydrogen 1s orbitals overlap. (b) In the formation of two carbon–carbon π bonds in acetylene, two singly occupied unhybridized $2p_{x,y}$ orbitals on each carbon atom overlap. With one σ bond plus two π bonds, the carbon–carbon bond order in acetylene is 3.*

Note

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 1.1.4.4.1

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

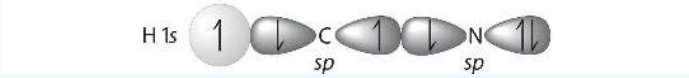
Asked for: bonding description using hybrid atomic orbitals and molecular orbitals

Strategy:

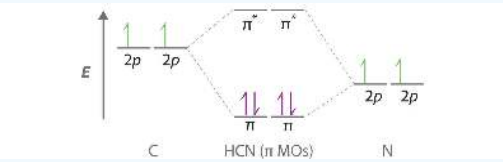
A. From the geometry given, predict the hybridization in HCN. Use the hybrid orbitals to form the σ-bonded framework of the molecule and determine the number of valence electrons that are used for σ bonding.
B. Determine the number of remaining valence electrons. Use any remaining unhybridized *p* orbitals 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

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.



sp Hybridization: https://youtu.be/epQXzG9WDRw

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.

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1.1.4.5: Molecular Orbital Theory

Learning Objectives

- To use molecular orbital theory to predict bond order
- To apply Molecular Orbital Theory to the diatomic homonuclear molecule from the elements in the second period.

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.

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.

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 discussed previously, 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*:

$$\begin{aligned} MO(1) &= AO(atom\ A) + AO(atom B) \\ MO(1) &= AO(atom\ A) - AO(atom B) \end{aligned} \tag{1.1.4.5.1}$$

The molecular orbitals created from Equation 1.1.4.5.1 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.

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 **1.1.4.5.1**). In a sigma (σ) orbital, 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.

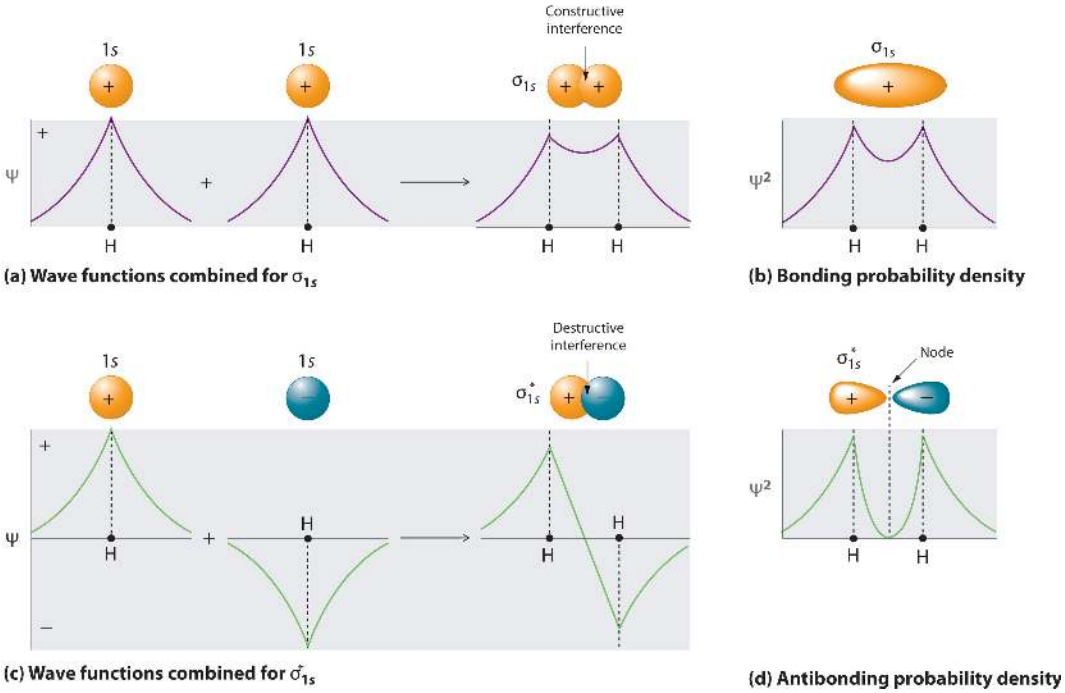


Figure **1.1.4.5.1**: Molecular Orbitals for the H_2 Molecule**.** (a) This diagram shows the formation of a bonding σ_{1s} molecular orbital for H_2 as the sum of the wave functions (Ψ) of two H 1s atomic orbitals. (b) This plot of the square of the wave function (Ψ^2) for the bonding σ_{1s} molecular 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 1s 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.

$$\sigma_{1s} \approx 1s\,(A) + 1s\,(B) \tag{1.1.4.5.2}$$

Conversely, subtracting one atomic orbital from another corresponds to *destructive* interference between two waves, which reduces their intensity and causes a *decrease* in the internuclear electron probability density (part (c) and part (d) in Figure **1.1.4.5.1**). The resulting pattern contains a *node* where the electron density is zero. The molecular orbital corresponding to the difference is called σ^*_{1s} (“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:

$$\sigma^*_{1s} \approx 1s\,(A) - 1s\,(B) \tag{1.1.4.5.3}$$

> *A molecule must have as many molecular orbitals as there are atomic orbitals.*

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.*

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 **1.1.4.5.2**

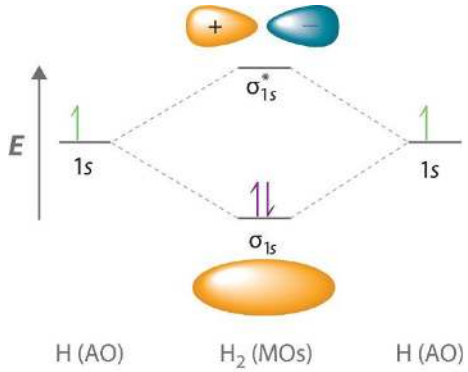


Figure **1.1.4.5.2**: Molecular Orbital Energy-Level Diagram for H_2. The two available electrons (one from each H atom) in this diagram fill the bonding σ_{1s} molecular orbital. Because the energy of the σ_{1s} molecular orbital is lower than that of the two H 1*s* atomic orbitals, the H_2 molecule 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 **1.1.4.5.2**). 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.

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:

$$\text{bond order} = \frac{\text{number of bonding electrons} - \text{number of antibonding electrons}}{2} \tag{1.1.4.5.4}$$

To calculate the bond order of H_2, we see from Figure **1.1.4.5.2** 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

$$\frac{2-0}{2} = 1 \tag{1.1.4.5.5}$$

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 **1.1.4.5.2** 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.

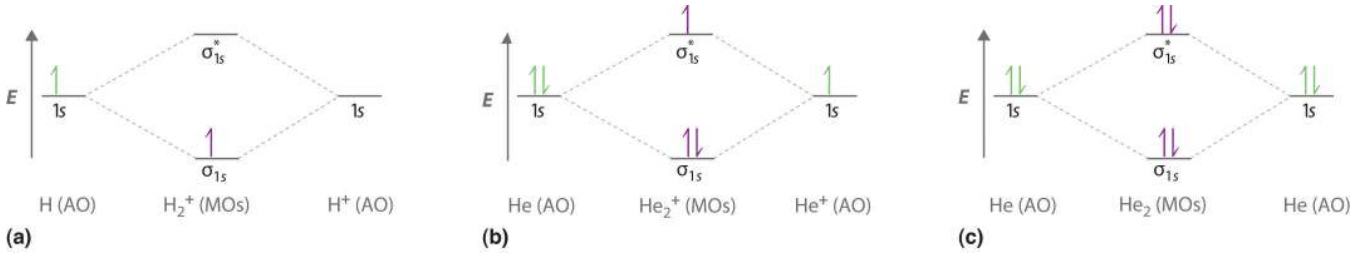


Figure **1.1.4.5.3**: Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1*s* Atomic Orbitals. (a) The H_2^+ ion, (b) the He_2^+ ion, and (c) the He_2 molecule are shown here.

Part (a) in Figure **1.1.4.5.3** 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 (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 **1.1.4.5.1**, these predictions agree with the experimental data.

Part (b) in Figure **1.1.4.5.3** 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 (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 **1.1.4.5.1**).

Table **1.1.4.5.1**: 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. Part (c) in Figure **1.1.4.5.3** 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 $(\sigma_{1s})^2(\sigma^*_{1s})^1$ electron configuration, with a predicted bond order of $(2 - 2) \div 2 = 0$, 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.

Molecular Orbital Theory: https://youtu.be/XgtOG0ezw78

In contrast to Lewis electron structures and the valence bond approach, molecular orbital theory can accommodate systems with an odd number of electrons.

Example 1.1.4.5.1

Use a molecular orbital energy-level diagram, such as those in Figure **1.1.4.5.3**, to predict the bond order in the He_2^{2+} ion. Is this a stable species?

Given: chemical species

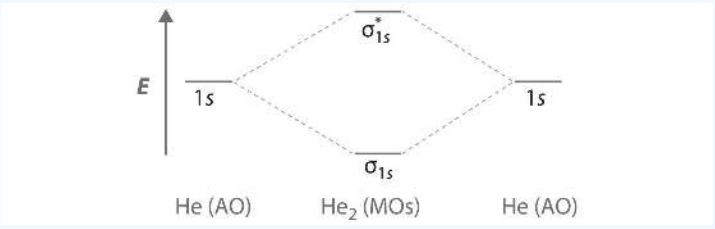
Asked for: molecular orbital energy-level diagram, bond order, and stability

Strategy:

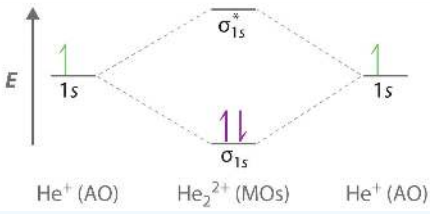
A. Combine the two He valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for the system.
B. Determine the total number of valence electrons in the He_2^{2+} ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.
C. Calculate the bond order and predict whether the species is stable.

Solution:

A Two He 1*s* atomic orbitals combine to give two molecular orbitals: a σ_{1s} bonding orbital at lower energy than the atomic orbitals and a 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:



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 1.1.4.5.1

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 **1.1.4.5.4**, 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 **1.1.4.5.2**. Experimentally, all are found to be stable in the gas phase, and some are even stable in solution.

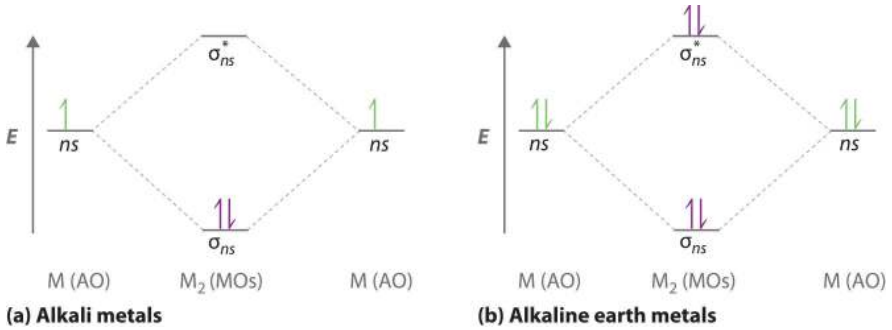


Figure **1.1.4.5.4**: Molecular Orbital Energy-Level Diagrams for Alkali Metal and Alkaline Earth Metal Diatomic (M_2) Molecules. *(a) For alkali metal diatomic molecules, the two valence electrons are enough to fill the σ_{ns} (bonding) level, giving a bond order of 1. (b) For alkaline earth metal diatomic 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 **1.1.4.5.3** As shown in part (b) in Figure **1.1.4.5.4**, 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, $\boldsymbol{Be_2}$ is stable.

Example 1.1.4.5.2

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

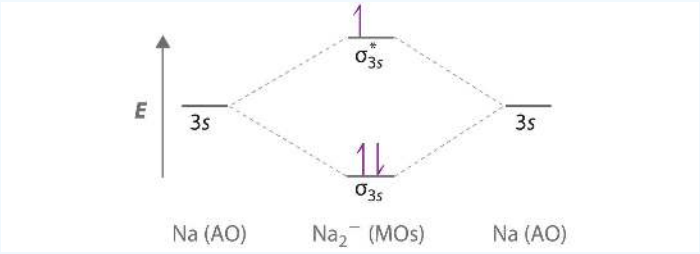
Asked for: molecular orbital energy-level diagram, valence electron configuration, bond order, and stability

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 1.1.4.5.2

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.

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.

$$\sigma_{np_z} = np_z(A) - np_z(B) \tag{1.1.4.5.6}$$

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 **1.1.4.5.5**, 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):

$$\sigma_{np_z} = np_z(A) - np_z(B) \tag{1.1.4.5.7}$$

The other possible combination of the two np_z orbitals is the mathematical sum:

$$\sigma_{np_z} = np_z(A) + np_z(B) \tag{1.1.4.5.8}$$

In this combination, shown in part (b) in Figure **1.1.4.5.5**, 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).

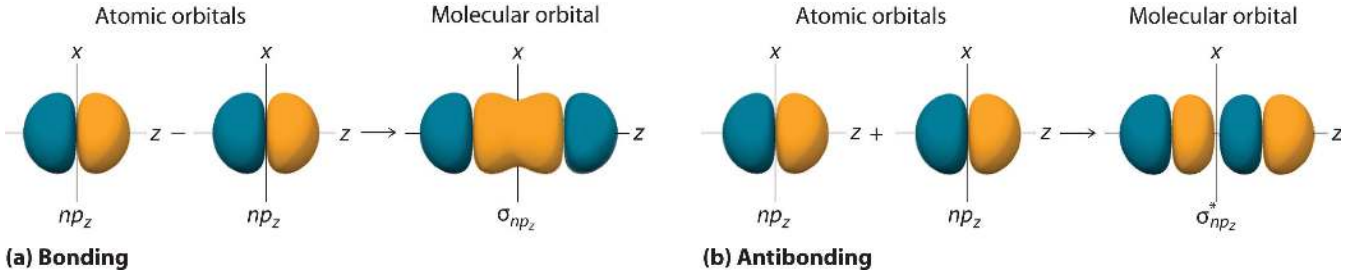


Figure **1.1.4.5.5**: Formation of Molecular Orbitals from np_z Atomic Orbitals on Adjacent Atoms.(a) By convention, in a linear molecule or ion, the *z*-axis always corresponds to the internuclear axis, with +*z* to the right. As a result, the signs of the lobes of the np_z atomic orbitals on the two 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 **1.1.4.5.6**, 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..

$$\pi_{np_z} = np_x(A) + np_x(B) \tag{1.1.4.5.9}$$

$$\pi^*_{np_z} = np_x(A) - np_x(B) \tag{1.1.4.5.10}$$

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.

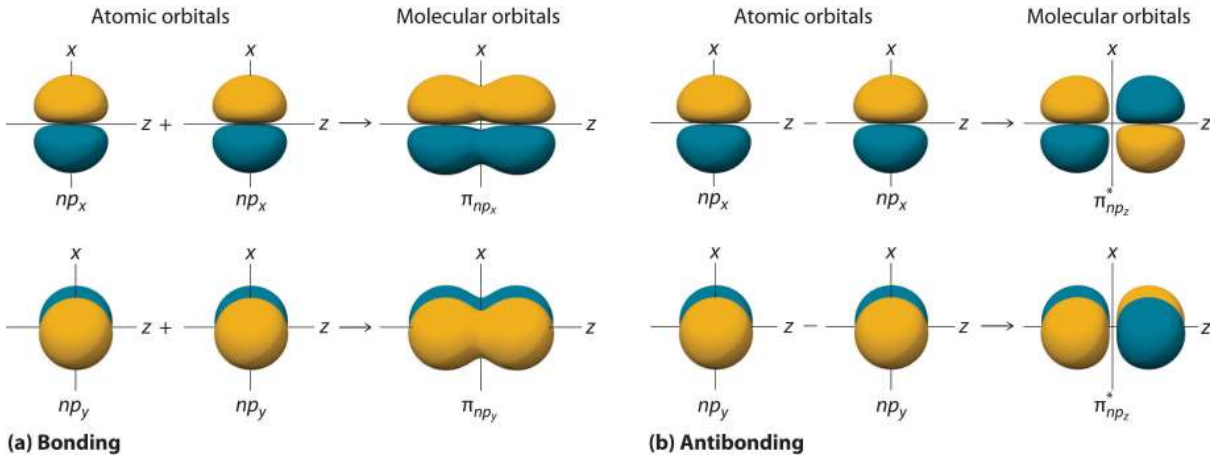


Figure 1.1.4.5.6: Formation of π Molecular Orbitals from np_x and np_y Atomic Orbitals on Adjacent Atoms.(a) Because the signs of the lobes of both the np_x and the np_y atomic orbitals on adjacent atoms are the same, in both cases the mathematical sum corresponds to a π (bonding) molecular orbital. (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 1.1.4.5.7 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.

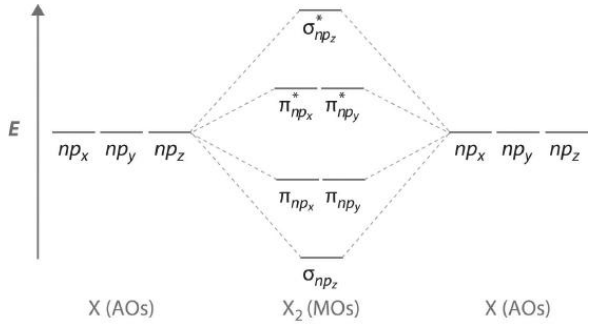


Figure 1.1.4.5.7: The Relative Energies of the σ and π Molecular Orbitals Derived from np_x, np_y, and np_z Orbitals on Identical Adjacent Atoms. Because the two np_z orbitals point directly at each other, their orbital overlap is greater, so the difference in energy between the σ and σ* molecular orbitals 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 1.1.4.5.8, 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.

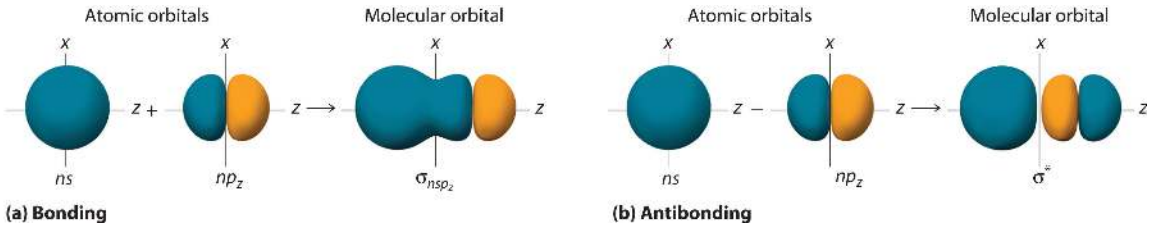


Figure 1.1.4.5.8: Formation of Molecular Orbitals from an ns Atomic Orbital on One Atom and an np_z Atomic Orbital on an Adjacent Atom.(a) The mathematical sum results in a σ (bonding) molecular orbital, with increased probability density between the nuclei. (b) The mathematical difference results in a σ* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis.

Second Row Diatomic Molecules

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. When we draw a molecular orbital diagram for a molecule, there are four key points to remember:

1. The number of molecular orbitals produced is the same as the number of atomic orbitals used to create them (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.

> The number of molecular orbitals is **always** equal to the total number of atomic orbitals we started with.

We illustrate how to use these points by constructing a molecular orbital energy-level diagram for F_2. We use the diagram in part (a) in Figure 1.1.4.5.9; 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) ÷ 2 = 1. Thus F_2 is predicted to have a stable F–F single bond, in agreement with experimental data.

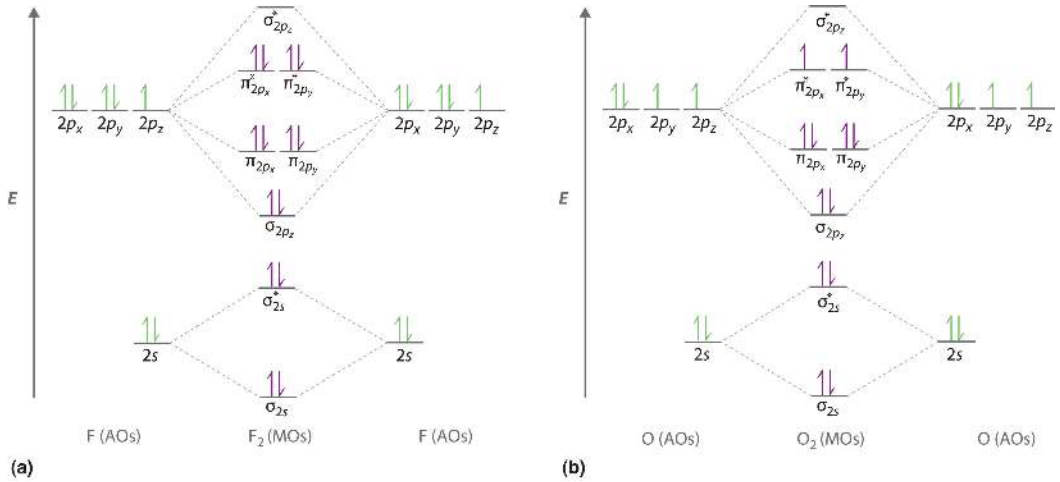


Figure **1.1.4.5.9**: Molecular Orbital Energy-Level Diagrams for Homonuclear Diatomic Molecules.(a) For F_2, with 14 valence electrons (7 from each F atom), all of the energy levels except the highest, $\sigma^*_{2p_z}$ are filled. This diagram shows 8 electrons in bonding orbitals and 6 in antibonding 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 **1.1.4.5.9**. 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 **1.1.4.5.10**, 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 **1.1.4.5.10**: 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 https://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 $\pi^*_{np_x}$ 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 **1.1.4.5.11** Experimentally, it is found that the energy gap between the *ns* and *np* atomic orbitals *increases* as the nuclear charge increases (Figure **1.1.4.5.11**). Thus for example, the σ_{2p_z} molecular orbital is at a lower energy than the $\pi_{2p_{x,y}}$ pair.

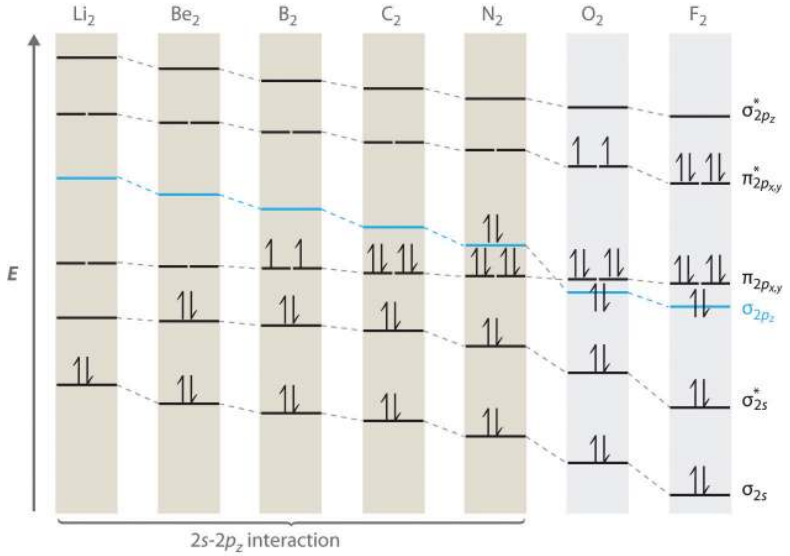


Figure **1.1.4.5.11**: Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements. Unlike earlier diagrams, only the molecular orbital energy levels for the molecules are shown here. For simplicity, the atomic orbital energy levels for the component *atoms* have been 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 1.1.4.5.3

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

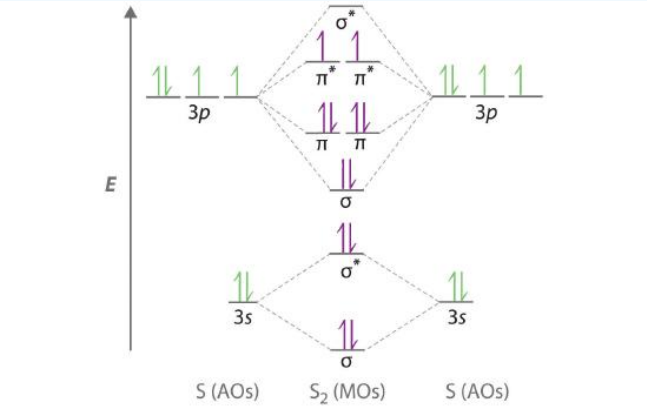
Strategy:

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 **1.1.4.5.9** and Figure **1.1.4.5.11**, we need to know how close in energy the 3*s* and 3*p* atomic orbitals are because their energy separation will determine whether the $\pi_{3p_{x,y}}$ or the σ_{3p_z}> molecular orbital is higher in energy. Because the *ns*–*np* energy gap *increases* as the nuclear charge increases (Figure **1.1.4.5.11**), the σ_{3p_z} molecular orbital will be lower in energy than the $\pi_{3p_{x,y}}$ pair.

B The molecular orbital energy-level diagram is as follows:



Each sulfur atom contributes 6 valence electrons, for a total of 12 valence electrons.

C Ten valence electrons are used to fill the orbitals through π_{3p_x} and π_{3p_y}, leaving 2 electrons to occupy the degenerate $\pi^*_{3p_x}$ 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 $(\sigma_{3s})^2(\sigma^*_{3s})^2(\sigma_{3p_z})^2(\pi_{3p_{x,y}})^4(\pi^*_{3p_{x,y}})^2$ with 2 unpaired electrons. The bond order is (8 − 4) ÷ 2 = 2, so we predict an S=S double bond.

? Exercise 1.1.4.5.3

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

$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p_z})^2(\pi_{2p_{x,y}})^4(\pi^*_{2p_{x,y}})^4$

bond order of 1;

no unpaired electrons

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 **1.1.4.5.12**. 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.

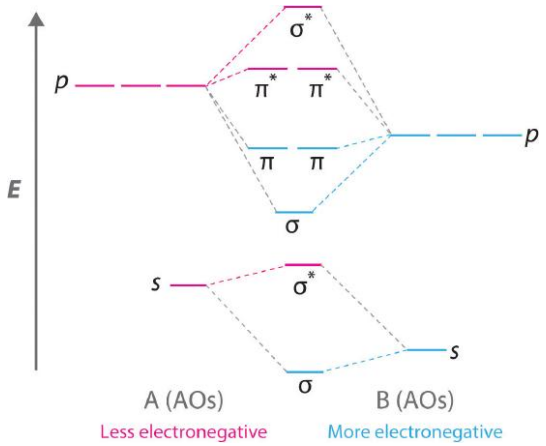


Figure 1.1.4.5.12: Molecular Orbital Energy-Level Diagram for a Heteronuclear Diatomic Molecule AB, Where $\chi_B > \chi_A$. The bonding molecular orbitals are closer in energy to the atomic orbitals of the more electronegative B atom. Consequently, the electrons in the bonding orbitals are not shared 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 **1.1.4.5.13**) shows that the general pattern is similar to that for the O_2 molecule (Figure 1.1.4.5.11). 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.

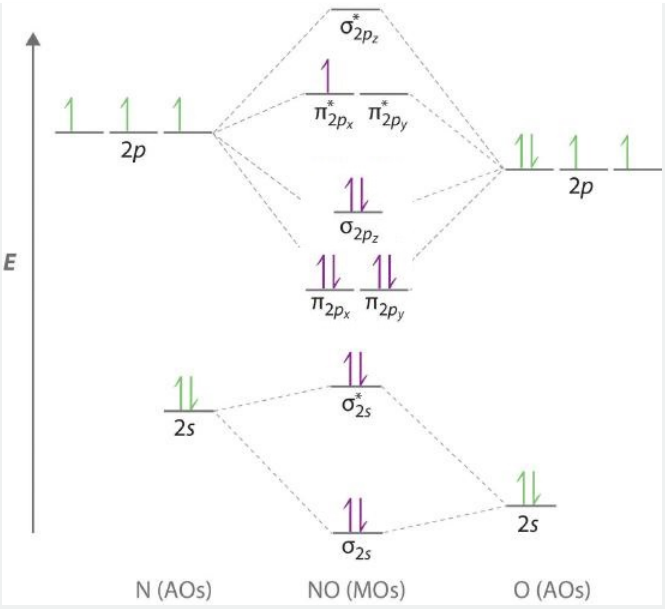


Figure 1.1.4.5.13: Molecular Orbital Energy-Level Diagram for NO. Because NO has 11 valence electrons, it is paramagnetic, with a single electron occupying the $\left(\pi^*_{2p_x}, \pi^*_{2p_y}\right)$ pair of orbitals.

Note that electronic structure studies show the ground state configuration of NO to be $(\sigma_{2s})^2 (\sigma^*_{2s})^2 \left(\pi_{2p_{x,y}}\right)^4 (\sigma_{2p_z})^2 \left(\pi_{2p^*_{x,y}}\right)^2$ 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 1.1.4.5.11).

Molecular orbital theory can also tell us something about the *chemistry* of *NO*. As indicated in the energy-level diagram in Figure 1.1.4.5.13, 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.



Molecular Orbital Bonding for Second Row Elements: https://youtu.be/A_5Xa3sK_YE

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 1.1.4.5.14 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 $H^{\delta+}-\!-Cl^{\delta-}$.

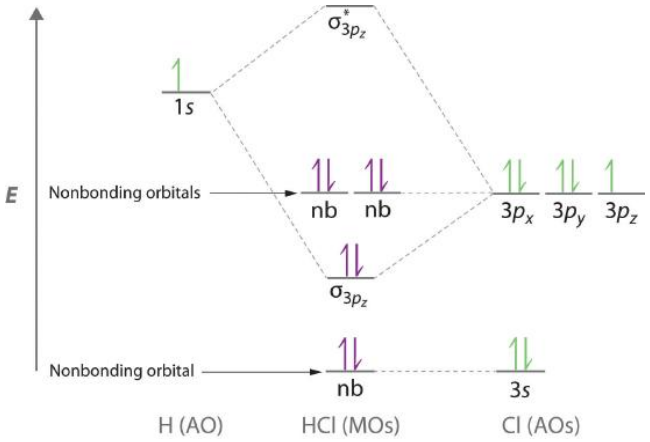


Figure **1.1.4.5.14**: Molecular Orbital Energy-Level Diagram for HCl. The hydrogen 1*s* atomic orbital interacts most strongly with the 3p_z orbital on chlorine, producing a bonding/antibonding pair of molecular orbitals. The other electrons on Cl are best viewed as nonbonding. As a result, only the 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 1.1.4.5.4

Use a "skewed" molecular orbital energy-level diagram like the one in Figure **1.1.4.5.12** 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

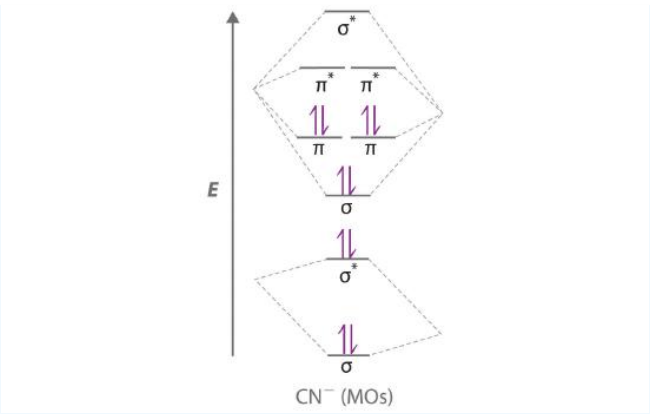
Strategy:

A. Calculate the total number of valence electrons in CN^-. Then place these electrons in a molecular orbital energy-level diagram like Figure **1.1.4.5.12** 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 **1.1.4.5.12** 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 $(8 - 2) \div 2 = 3$, indicating that the CN^- ion has a triple bond, analogous to that in N_2.

? Exercise 1.1.4.5.4

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.

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.

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.

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.

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.

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1.1.4.6: Exercises

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SECTION OVERVIEW

1.2: Bonding

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In this chapter, we begin with a general method for predicting the structures of simple covalent molecules and polyatomic ions; then we discuss the actual distribution of electrons in covalent bonds. We apply two distinct approaches for describing covalent bonds:

1. a localized model to describe bonding in molecules with two or more atoms attached to a central atom and
2. a delocalized model to explain and predict which diatomic species exist and which do not exist.

We conclude by describing more complex molecules and ions with multiple bonds. The tools you acquire in this chapter will enable you to explain why Ca_2 is too unstable to exist in nature and why the unpaired electrons on O_2 are crucial to the existence of life as we know it. You will also discover why carbon, the basic component of all organic compounds, forms four bonds despite having only two unpaired electrons in its valence electron configuration and how the structure of retinal, the key light-sensing component in our eyes, allows us to detect visible light.

Topic hierarchy

1.2.1: Bonding Theories

1.2.2: Introduction to Valence Bond Theory

1.2.3: Hybridization of Atomic Orbitals

1.2.4: Molecular Orbital Theory

1.2.5: Multiple Covalent Bonds

1.2.6: Exercises

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1.2.1: Bonding Theories

As we have talked about using Lewis structures to depict the bonding in organic 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?

In this chapter, the **valence bond theory** is introduced to describe bonding in organic 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. In order to explain the bonding in organic molecules, however, we will need to introduce the concept of **hybrid orbitals**.

Valence bond theory is adequate for describing many aspects of organic structure. In some cases, however, chemists need to use a different model, called **molecular orbital (MO) theory**, to talk about covalent bonds in which electrons are shared not just between two atoms, but between several, or even over an entire molecule.

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.

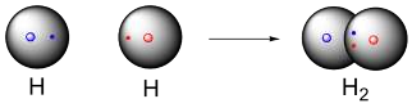


Figure **1.2.1.1**: Addition of twe hydrogen atoms to form the diatomic hydrogen molecule.

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.

But 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.

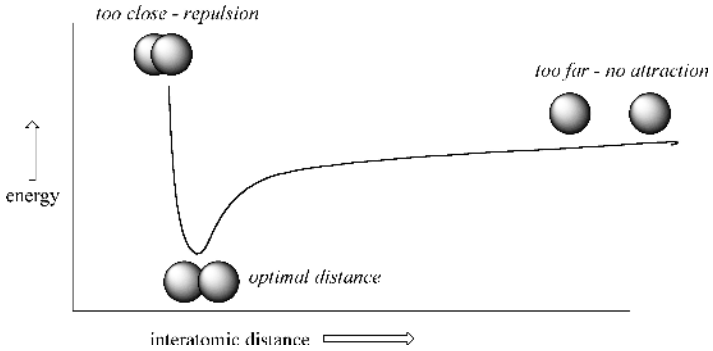


Figure **1.2.1.2**.: Potential of interaction for the addition of twe hydrogen atoms to form the diatomic hydrogen molecule.

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.

It is not accurate, however, 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.

Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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1.2.2: Introduction to Valence Bond Theory

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 H_2O and NH_3, respectively. In fact, structural studies have shown that the H–S–H and H–P–H angles are more than 12° smaller than the corresponding bond angles in H_2O and NH_3. More disturbing, the VSEPR model predicts that the simple group 2 halides (MX_2), which have four valence electrons, should all have linear X–M–X geometries. Instead, many of these species, including SrF_2 and BaF_2, are significantly bent. A more sophisticated treatment of bonding is needed for systems such as these. In this section, we present a quantum mechanical description of bonding, in which bonding electrons are viewed as being localized between the nuclei of the bonded atoms.

Valence Bond Theory: A Localized Bonding Approach

Valence Bond Theory has its roots in Gilbert Newton Lewis's paper *The Atom and The Molecule*. Possibly unaware that Lewis's model existed, Walter Heitler and Fritz London came up with the idea that resonance and wavefunctions contributed to chemical bonds, in which they used dihydrogen as an example. Their theory was equivalent to Lewis's theory, with the difference of quantum mechanics being developed. Nonetheless, Heitler and London's theory proved to be successful, providing Linus Pauling and John C. Slater with an opportunity to assemble a general chemical theory containing all of these ideas. Valence Bond Theory was the result, which included the ideas of resonance, covalent-ionic superposition, atomic orbital overlap, and hybridization to describe chemical bonds.

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. 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 **1.2.2.1**).

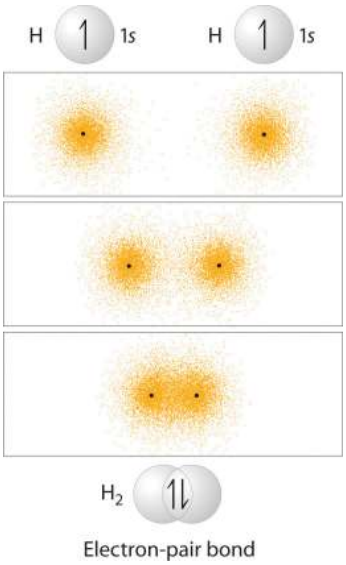


Figure **1.2.2.1**: Overlap of Two Singly Occupied Hydrogen 1*s* Atomic Orbitals Produces an H–H Bond in H_2. The formation of H_2 from two hydrogen atoms, each with a single electron in a 1*s* orbital, occurs as the electrons are shared to form an electron-pair bond, as indicated schematically by the 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 both 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 **1.2.2.2** 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 $n = 2$. Maximum overlap occurs between orbitals with the same spatial orientation and similar energies.

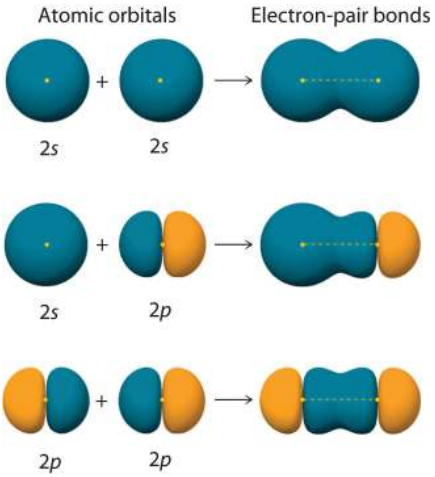


Figure **1.2.2.2**: Three Different Ways to Form an Electron-Pair Bond. An electron-pair bond can be formed by the overlap of any of the following combinations of two singly occupied atomic orbitals: two *ns* atomic orbitals (a), an *ns* and an *np* atomic orbital (b), and two *np* atomic orbitals (c) where $n = 2$. The positive lobe is indicated in yellow, and the negative lobe is in blue.

Note

An important aspect of Valence Bond theory is the concept of maximum overlap to form the strongest possible covalent bonds.

Let's examine the bonds in BeH_2, for example. According to the VSEPR model, BeH_2 is a linear compound with four valence electrons and two Be–H bonds. Its bonding can also be described using an atomic orbital approach. Beryllium has a $1s^2 2s^2$ electron configuration, and each H atom has a $1s^1$ electron configuration. Because the Be atom has a filled 2*s* subshell, however, it has no singly occupied orbitals available to overlap with the singly occupied 1*s* orbitals on the H atoms. If a singly occupied 1*s* orbital on hydrogen were to overlap with a filled 2*s* orbital on beryllium, the resulting bonding orbital would contain *three* electrons, but the maximum allowed by quantum mechanics is *two*. How then is beryllium able to bond to two hydrogen atoms? One way would be to add enough energy to excite one of its 2*s* electrons into an empty 2*p* orbital and reverse its spin, in a process called promotion:



In this excited state, the Be atom would have two singly occupied atomic orbitals (the 2*s* and one of the 2*p* orbitals), each of which could overlap with a singly occupied 1*s* orbital of an H atom to form an electron-pair bond. Although this would produce BeH_2, the two Be–H bonds would not be equivalent: the 1*s* orbital of one hydrogen atom would overlap with a Be 2*s* orbital, and the 1*s* orbital of the other hydrogen atom would overlap with an orbital of a different energy, a Be 2*p* orbital. Experimental evidence indicates, however, that the two Be–H bonds have identical energies. To resolve this discrepancy and explain how molecules such as BeH_2 form, scientists developed the concept of hybridization.

Reliability of Valence Bond Theory and Uses

As one can see, Valence Bond Theory can help describe how bonds are formed. However, there are some notable failures when it comes to Valence Bond Theory. One such failure is dioxygen. Valence Bond Theory fails to predict dioxygen's paramagnitism; it predicts that oxygen is diamagnetic. A species is paramagnetic if electrons are not spin paired and diamagnetic if the electrons are spin paired. Since Valence Bond theory begins with the basis that atomic orbitals overlap to create bonds and through that reasoning, one can see that electrons are spin paired when bonds overlap, dioxygen is indeed predicted to be diamagnetic if Valence Bond Theory is used. In reality, that is not the case. Also, sp^2d and sp^3 both have a coordinate number of four. Thus, Valence Bond Theory cannot predict whether the molecule is a square planar or the other shape (3). One must correctly draw the Lewis structure and use VSEPR to determine the shape.

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1.2.3: Hybridization of Atomic Orbitals

Learning Objectives

- To describe the hybridication in the bonding of simple compounds via valence bond theory.

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.

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 **1.2.3.0**.

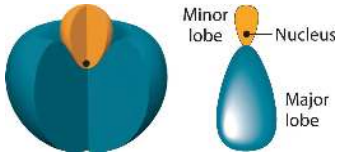


Figure 1.2.3.0: The position of the atomic nucleus with respect to an sp hybrid orbital. The nucleus is actually located slightly inside the minor lobe, not at the node separating the major and minor lobes.

Because the difference A − B can also be written as A + (−B), in Figure **1.2.3.1** 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 11.3.1, 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.

$$sp = \frac{1}{\sqrt{2}}(2s + 2p_z) \tag{1.2.3.1}$$

and

$$sp = \frac{1}{\sqrt{2}}(2s - 2p_z) \tag{1.2.3.2}$$

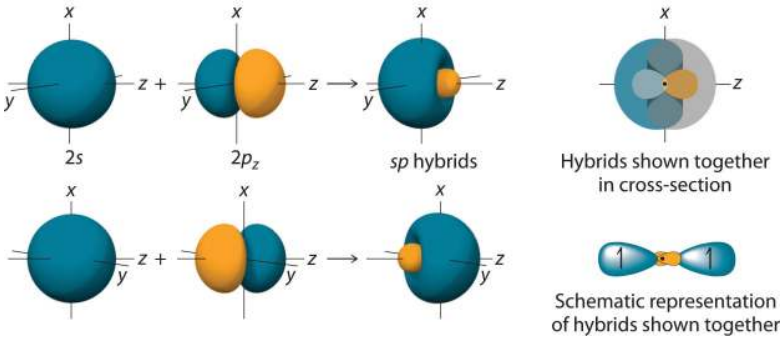


Figure **1.2.3.1**: The Formation of *sp* Hybrid Orbitals. Taking the sum and difference of an *ns* and an *np* atomic orbital where *n* = 2 gives two equivalent *sp* hybrid orbitals oriented at 180° to each other.

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:

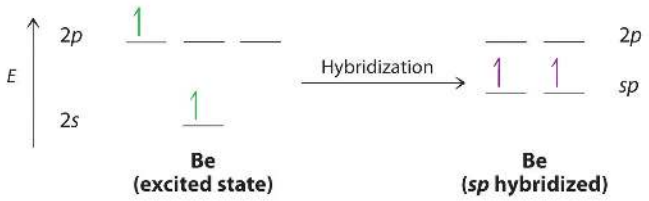


Figure **1.2.3.2**, each *sp* orbital on Be has the correct orientation for the major lobes to overlap with the 1*s* atomic orbital of an H atom. The formation of two energetically equivalent Be–H bonds produces a linear $\boldsymbol{BeH_2}$ molecule. Thus valence bond theory does what neither the Lewis 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.

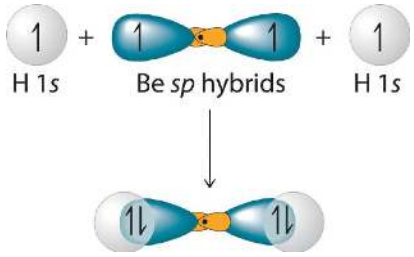


Figure **1.2.3.2**: Explanation of the Bonding in BeH_2 Using *sp* Hybrid Orbitals. Each singly occupied *sp* hybrid orbital on beryllium can form an electron-pair bond with the singly occupied 1*s* orbital of a hydrogen atom. Because the two *sp* hybrid orbitals are oriented at a 180° angle, the BeH_2 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 **1.2.3.3**). 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.

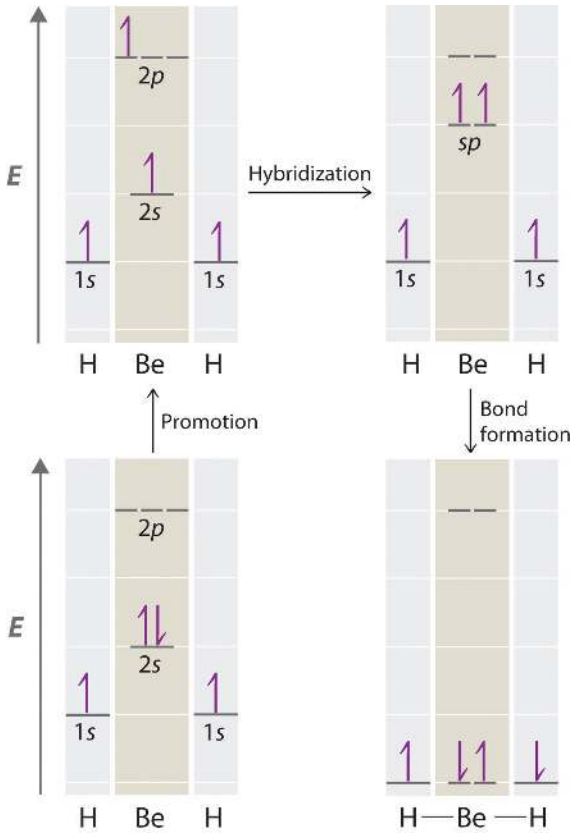


Figure **1.2.3.3**: A Hypothetical Stepwise Process for the Formation of BeH_2 from a Gaseous Be Atom and Two Gaseous H Atoms. The promotion of an electron from the 2*s* orbital of beryllium to one of the 2*p* orbitals is energetically uphill. The overall process of forming a BeH_2 molecule from a Be 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.

The concept of hybridization also explains why boron, with a $2s^22p^1$ valence electron configuration, forms three bonds with fluorine to produce BF_3, as predicted by the Lewis and VSEPR approaches. With only a single unpaired electron in its ground state, boron should form only a single covalent bond. By the promotion of one of its 2*s* electrons to an unoccupied 2*p* orbital, however, followed by the hybridization of the three singly occupied orbitals (the 2*s* and two 2*p* orbitals), boron acquires a set of three equivalent hybrid orbitals with one electron each, as shown here:

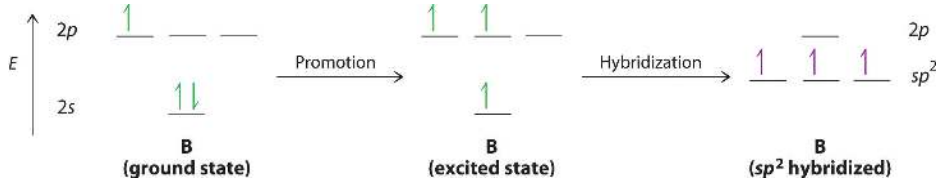


Figure **1.2.3.4**). Because the hybrid atomic orbitals are formed from one *s* and two *p* orbitals, boron is said to be sp^2 *hybridized* (pronounced "s-p-two" or "s-p-squared"). The singly occupied sp^2 hybrid atomic orbitals can overlap with the singly occupied orbitals on each of the three F atoms to form a trigonal planar structure with three energetically equivalent B–F bonds.

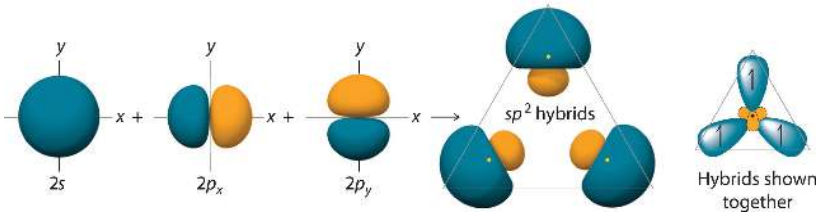
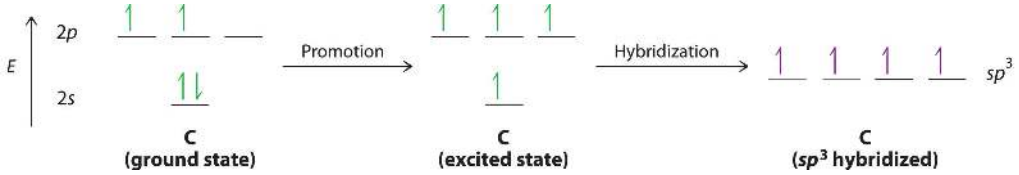


Figure **1.2.3.4**: Formation of sp^2 Hybrid Orbitals. Combining one *ns* and two *np* atomic orbitals gives three equivalent sp^2 hybrid orbitals in a trigonal planar arrangement; that is, oriented at 120° to one another.

Looking at the $2s^22p^2$ valence electron configuration of carbon, we might expect carbon to use its two unpaired 2*p* electrons to form compounds with only two covalent bonds. We know, however, that carbon typically forms compounds with four covalent

bonds. We can explain this apparent discrepancy by the hybridization of the 2*s* orbital and the three 2*p* orbitals on carbon to give a set of four degenerate sp^3 ("s-p-three" or "s-p-cubed") hybrid orbitals, each with a single electron:



The large lobes of the hybridized orbitals are oriented toward the vertices of a tetrahedron, with 109.5° angles between them (Figure **1.2.3.5**). Like all the hybridized orbitals discussed earlier, the sp^3 hybrid atomic orbitals are predicted to be equal in energy.

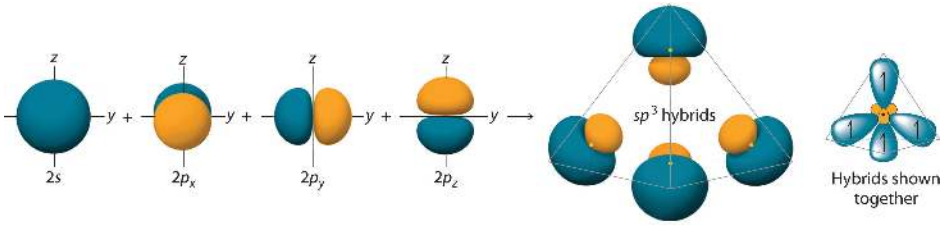
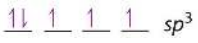


Figure **1.2.3.5**: Formation of sp^3 Hybrid Orbitals. Combining one *ns* and three *np* atomic orbitals results in four sp^3 hybrid orbitals oriented at 109.5° to one another in a tetrahedral arrangement.

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 form in only 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 $2s^22p^3$ 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 CH_4 and NH_3, the hybridized orbitals are *not* entirely equivalent in energy, making this bonding model an active area of research.



Valence Bond Method & sp3 Hybridization: https://youtu.be/2hxKLGWQ5EQ

Example 1.2.3.1

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 VPSER 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 1.2.3.1

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.
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.

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 **1.2.3.6**). 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 **1.2.3.6**). 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.

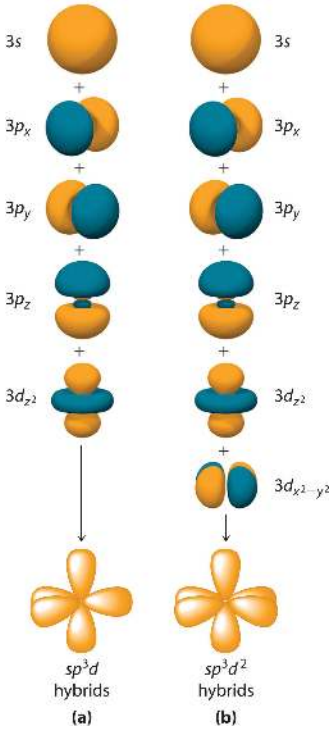


Figure **1.2.3.6**: Hybrid Orbitals Involving *d* Orbitals. The formation of a set of (a) five sp^3d hybrid orbitals and (b) six sp^3d^2 hybrid orbitals from *ns*, *np*, and *nd* atomic orbitals where $n = 4$.

Example 1.2.3.2

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 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 1.2.3.2

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
b. sp^3d with three Br–F bonds and two lone pairs
c. 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 1.2.3.3: 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 1.2.3.3

What is the hybridization of the boron atom in BF_6^{3-}? Is this ion likely to exist?

Answer sp^3d^2 hybridization; no



Expanded Octet Hybridization: https://youtu.be/1WpxXcKl_Io

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*^{3}*d*^{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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1.2.4: Molecular Orbital Theory

Learning Objectives

- To use molecular orbital theory to predict bond order
- To apply Molecular Orbital Theory to the diatomic homonuclear molecule from the elements in the second period.

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.

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.

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 discussed previously, 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*:

$$\begin{aligned} MO(1) &= AO(atom\ A) + AO(atom B) \\ MO(1) &= AO(atom\ A) - AO(atom B) \end{aligned} \tag{1.2.4.1}$$

The molecular orbitals created from Equation 1.2.4.1 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.

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 **1.2.4.1**). In a sigma (σ) orbital, 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.

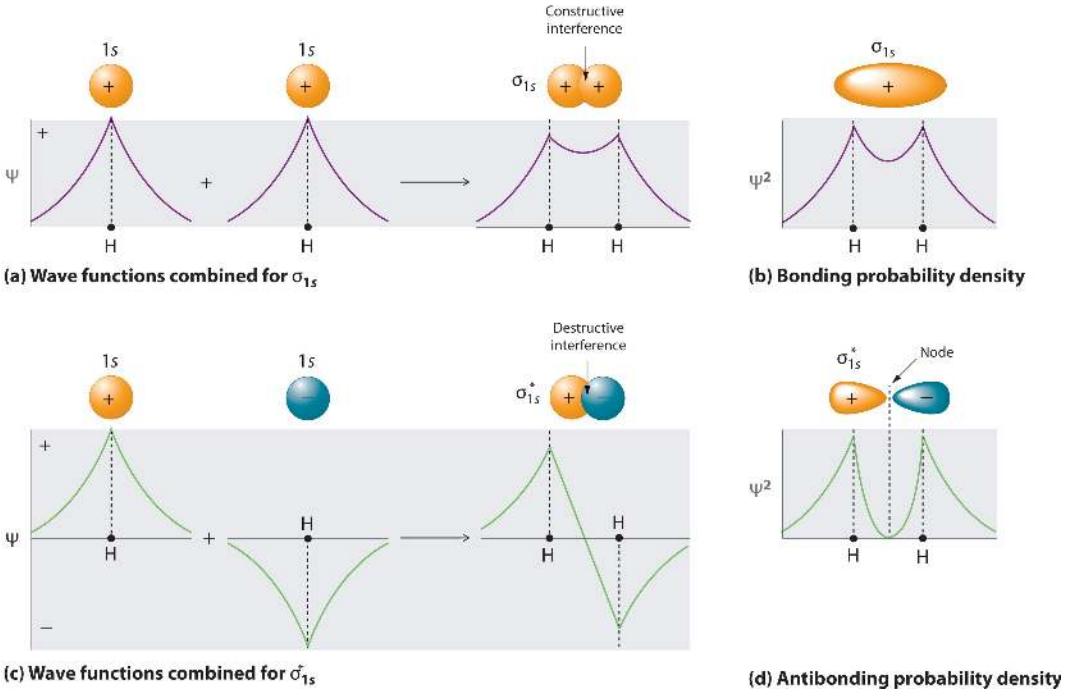


Figure **1.2.4.1**: Molecular Orbitals for the H_2 Molecule**.** (a) This diagram shows the formation of a bonding σ_{1s} molecular orbital for H_2 as the sum of the wave functions (Ψ) of two H 1s atomic orbitals. (b) This plot of the square of the wave function (Ψ^2) for the bonding σ_{1s} molecular 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 1s 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.

$$\sigma_{1s} \approx 1s\,(A) + 1s\,(B) \tag{1.2.4.2}$$

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 **1.2.4.1**). 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:

$$\sigma^*_{1s} \approx 1s\,(A) - 1s\,(B) \tag{1.2.4.3}$$

> *A molecule must have as many molecular orbitals as there are atomic orbitals.*

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.*

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 **1.2.4.2**

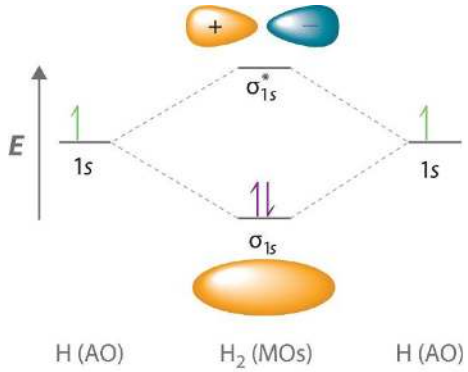


Figure **1.2.4.2**: Molecular Orbital Energy-Level Diagram for H_2. The two available electrons (one from each H atom) in this diagram fill the bonding σ_{1s} molecular orbital. Because the energy of the σ_{1s} molecular orbital is lower than that of the two H 1*s* atomic orbitals, the H_2 molecule is 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 **1.2.4.2**). 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.

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:

$$\textit{bond order} = \frac{\textit{number of bonding electrons} - \textit{number of antibonding electrons}}{2} \tag{1.2.4.4}$$

To calculate the bond order of H_2, we see from Figure **1.2.4.2** 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

$$\frac{2-0}{2} = 1 \tag{1.2.4.5}$$

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 **1.2.4.2** 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.

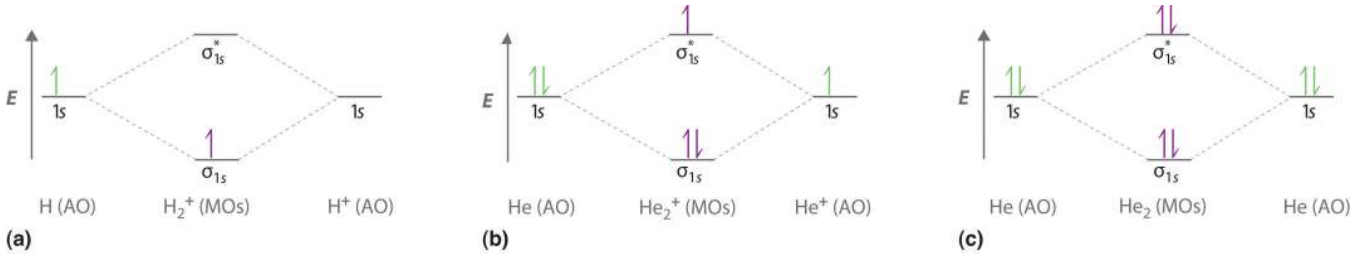


Figure **1.2.4.3**: Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1*s* Atomic Orbitals. (a) The H_2^+ ion, (b) the He_2^+ ion, and (c) the He_2 molecule are shown here.

Part (a) in Figure **1.2.4.3** 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 (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 **1.2.4.1**, these predictions agree with the experimental data.

Part (b) in Figure **1.2.4.3** 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 (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 **1.2.4.1**).

Table **1.2.4.1**: 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. Part (c) in Figure **1.2.4.3** 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 $(\sigma_{1s})^2(\sigma^*_{1s})^1$ electron configuration, with a predicted bond order of $(2 - 2) \div 2 = 0$, 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.

Molecular Orbital Theory: https://youtu.be/XgtOG0ezw78

In contrast to Lewis electron structures and the valence bond approach, molecular orbital theory can accommodate systems with an odd number of electrons.

Example 1.2.4.1

Use a molecular orbital energy-level diagram, such as those in Figure **1.2.4.3**, to predict the bond order in the He_2^{2+} ion. Is this a stable species?

Given: chemical species

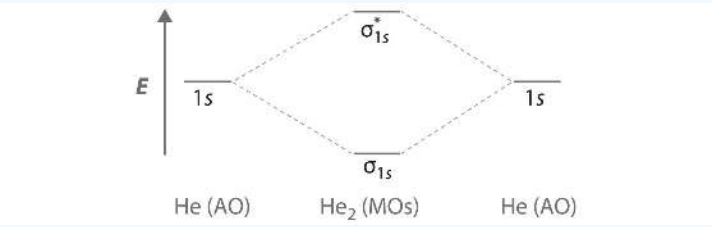
Asked for: molecular orbital energy-level diagram, bond order, and stability

Strategy:

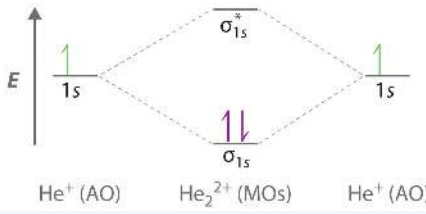
A. Combine the two He valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for the system.
B. Determine the total number of valence electrons in the He_2^{2+} ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.
C. Calculate the bond order and predict whether the species is stable.

Solution:

A Two He 1*s* atomic orbitals combine to give two molecular orbitals: a σ_{1s} bonding orbital at lower energy than the atomic orbitals and a 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:



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 1.2.4.1

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 **1.2.4.4**, 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 **1.2.4.2**. Experimentally, all are found to be stable in the gas phase, and some are even stable in solution.

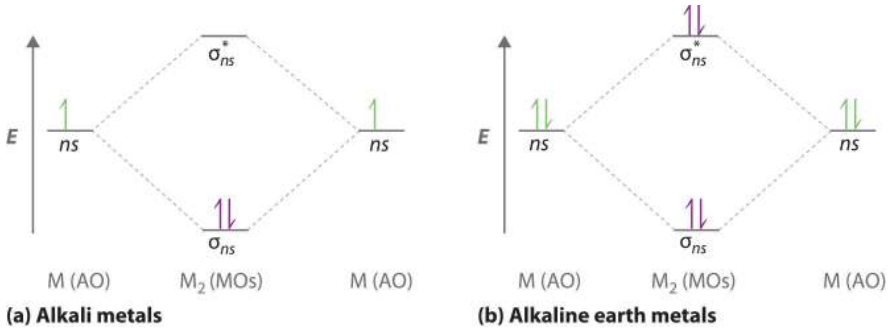


Figure **1.2.4.4**: Molecular Orbital Energy-Level Diagrams for Alkali Metal and Alkaline Earth Metal Diatomic (M_2) Molecules. *(a) For alkali metal diatomic molecules, the two valence electrons are enough to fill the σ_{ns} (bonding) level, giving a bond order of 1. (b) For alkaline earth metal diatomic 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 **1.2.4.3** As shown in part (b) in Figure **1.2.4.4**, 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 1.2.4.2

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

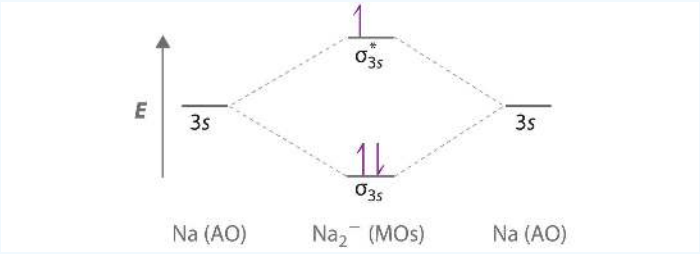
Asked for: molecular orbital energy-level diagram, valence electron configuration, bond order, and stability

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 1.2.4.2

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.

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.

$$\sigma_{np_z} = np_z(A) - np_z(B) \tag{1.2.4.6}$$

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 **1.2.4.5**, 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):

$$\sigma_{np_z} = np_z(A) - np_z(B) \tag{1.2.4.7}$$

The other possible combination of the two np_z orbitals is the mathematical sum:

$$\sigma_{np_z} = np_z(A) + np_z(B) \tag{1.2.4.8}$$

In this combination, shown in part (b) in Figure **1.2.4.5**, 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).

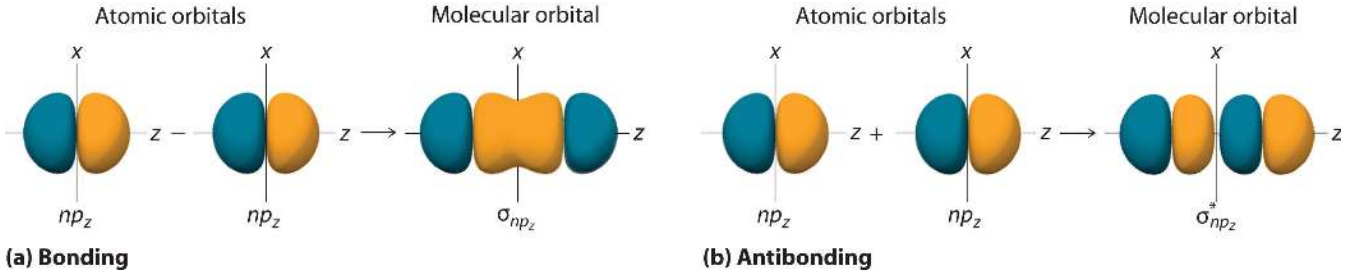


Figure **1.2.4.5**: Formation of Molecular Orbitals from np_z Atomic Orbitals on Adjacent Atoms.(a) By convention, in a linear molecule or ion, the *z*-axis always corresponds to the internuclear axis, with +*z* to the right. As a result, the signs of the lobes of the np_z atomic orbitals on the two 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 **1.2.4.6**, 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..

$$\pi_{np_z} = np_x(A) + np_x(B) \tag{1.2.4.9}$$

$$\pi^*_{np_z} = np_x(A) - np_x(B) \tag{1.2.4.10}$$

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.

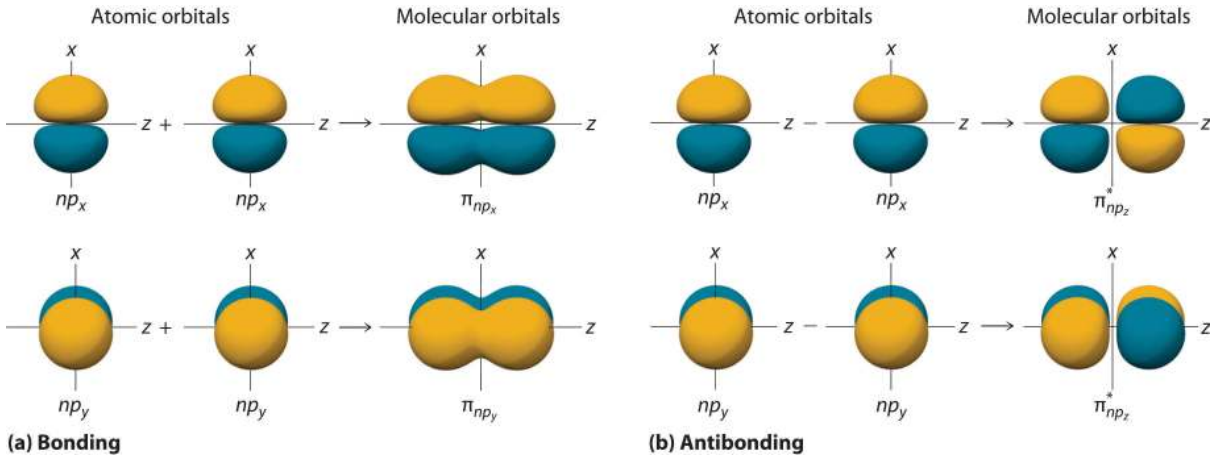


Figure 1.2.4.6: Formation of π Molecular Orbitals from np_x and np_y Atomic Orbitals on Adjacent Atoms.(a) Because the signs of the lobes of both the np_x and the np_y atomic orbitals on adjacent atoms are the same, in both cases the mathematical sum corresponds to a π (bonding) molecular orbital. (b) 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 1.2.4.7 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.

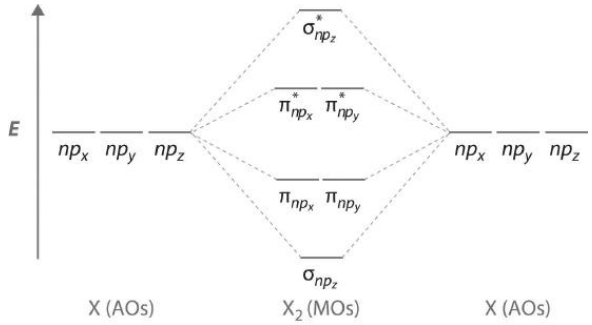


Figure 1.2.4.7: The Relative Energies of the σ and π Molecular Orbitals Derived from np_x, np_y, and np_z Orbitals on Identical Adjacent Atoms. Because the two np_z orbitals point directly at each other, their orbital overlap is greater, so the difference in energy between the σ and σ* molecular orbitals 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 1.2.4.8, 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.

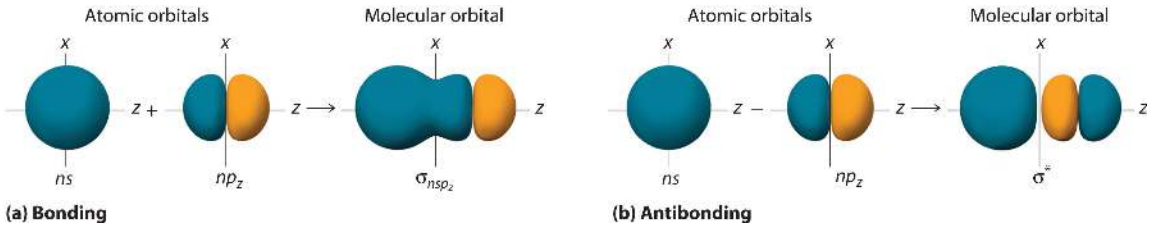


Figure **1.2.4.8**: Formation of Molecular Orbitals from an ns Atomic Orbital on One Atom and an np_z Atomic Orbital on an Adjacent Atom.(a) The mathematical sum results in a σ (bonding) molecular orbital, with increased probability density between the nuclei. (b) The mathematical difference results in a σ* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis.

Second Row Diatomic Molecules

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. When we draw a molecular orbital diagram for a molecule, there are four key points to remember:

1. The number of molecular orbitals produced is the same as the number of atomic orbitals used to create them (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.

> The number of molecular orbitals is **always** equal to the total number of atomic orbitals we started with.

We illustrate how to use these points by constructing a molecular orbital energy-level diagram for F_2. We use the diagram in part (a) in Figure **1.2.4.9**; 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) ÷ 2 = 1. Thus F_2 is predicted to have a stable F–F single bond, in agreement with experimental data.

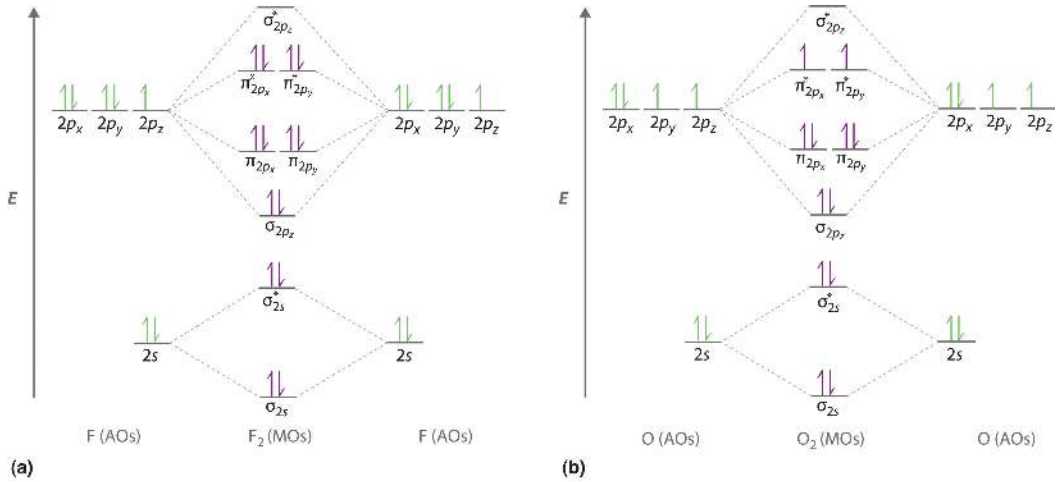


Figure **1.2.4.9**: Molecular Orbital Energy-Level Diagrams for Homonuclear Diatomic Molecules.(a) For F_2, with 14 valence electrons (7 from each F atom), all of the energy levels except the highest, $\sigma^*_{2p_z}$ are filled. This diagram shows 8 electrons in bonding orbitals and 6 in antibonding 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 **1.2.4.9**. 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 **1.2.4.10**, 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 **1.2.4.10**: 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 https://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 $\pi^*_{np_x}$ 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 **1.2.4.11** Experimentally, it is found that the energy gap between the *ns* and *np* atomic orbitals *increases* as the nuclear charge increases (Figure **1.2.4.11**). Thus for example, the σ_{2p_z} molecular orbital is at a lower energy than the $\pi_{2p_{x,y}}$ pair.

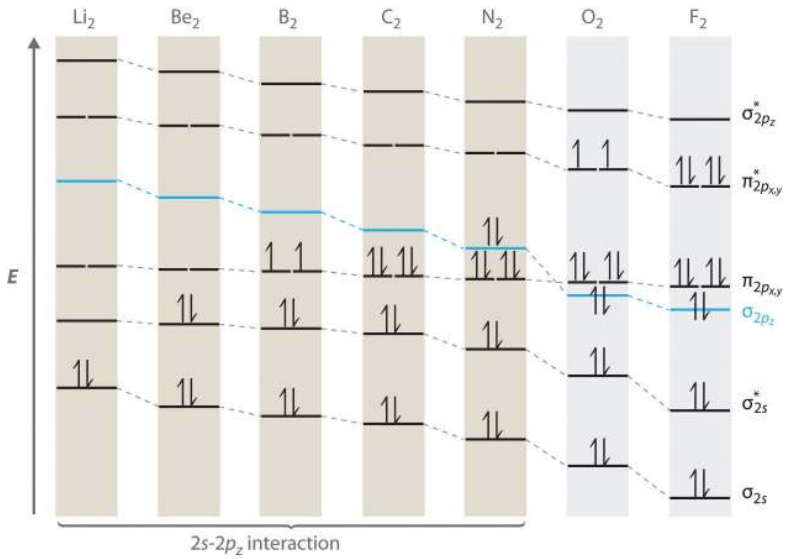


Figure **1.2.4.11**: Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements. Unlike earlier diagrams, only the molecular orbital energy levels for the molecules are shown here. For simplicity, the atomic orbital energy levels for the component *atoms* have been omitted. 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 **1.2.4.3**

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

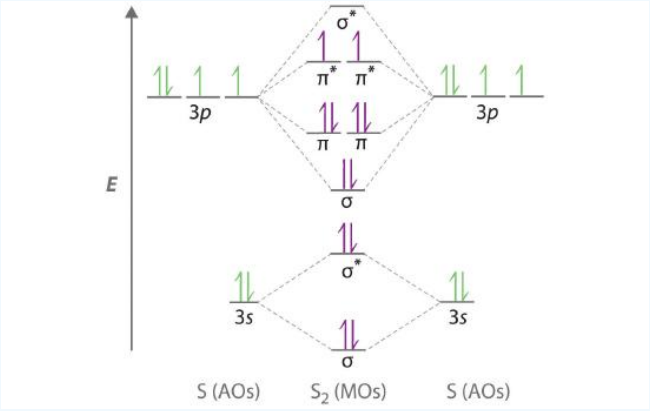
Strategy:

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 **1.2.4.9** and Figure **1.2.4.11**, we need to know how close in energy the 3*s* and 3*p* atomic orbitals are because their energy separation will determine whether the $\pi_{3p_{x,y}}$ or the σ_{3p_z}> molecular orbital is higher in energy. Because the *ns*–*np* energy gap *increases* as the nuclear charge increases (Figure **1.2.4.11**), the σ_{3p_z} molecular orbital will be lower in energy than the $\pi_{3p_{x,y}}$ pair.

B The molecular orbital energy-level diagram is as follows:



Each sulfur atom contributes 6 valence electrons, for a total of 12 valence electrons.

C Ten valence electrons are used to fill the orbitals through π_{3p_x} and π_{3p_y}, leaving 2 electrons to occupy the degenerate $\pi^*_{3p_x}$ 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 $(\sigma_{3s})^2(\sigma^*_{3s})^2(\sigma_{3p_z})^2(\pi_{3p_{x,y}})^4(\pi^*_{3p_{x,y}})^2$ with 2 unpaired electrons. The bond order is (8 − 4) ÷ 2 = 2, so we predict an S=S double bond.

? Exercise 1.2.4.3

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

$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p_z})^2(\pi_{2p_{x,y}})^4(\pi^*_{2p_{x,y}})^4$

bond order of 1;

no unpaired electrons

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 **1.2.4.12**. 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.

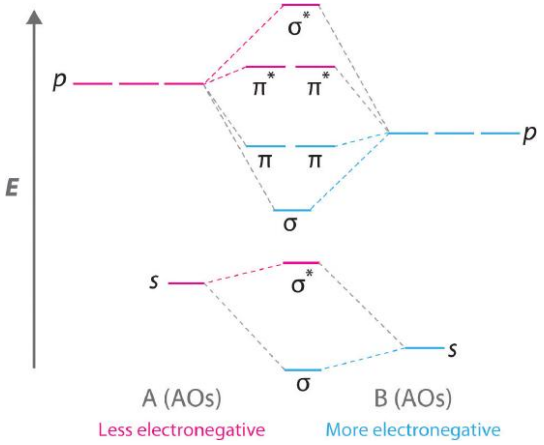


Figure **1.2.4.12**: Molecular Orbital Energy-Level Diagram for a Heteronuclear Diatomic Molecule AB, Where $\chi_B > \chi_A$. The bonding molecular orbitals are closer in energy to the atomic orbitals of the more electronegative B atom. Consequently, the electrons in the bonding orbitals are not shared 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 **1.2.4.13**) shows that the general pattern is similar to that for the O_2 molecule (Figure **1.2.4.11**). 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.

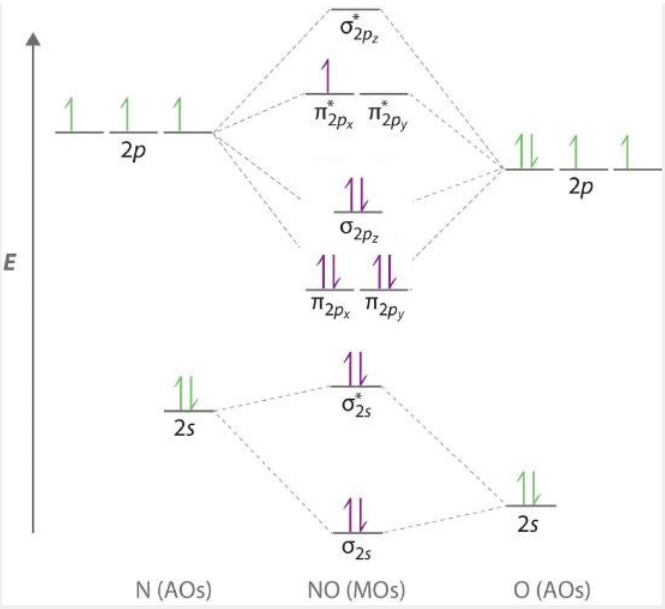


Figure **1.2.4.13**: Molecular Orbital Energy-Level Diagram for **NO**. Because **NO** has 11 valence electrons, it is paramagnetic, with a single electron occupying the $\left(\pi^*_{2p_x}, \pi^*_{2p_y}\right)$ pair of orbitals.

Note that electronic structure studies show the ground state configuration of **NO** to be $(\sigma_{2s})^2 (\sigma^*_{2s})^2 \left(\pi_{2p_{x,y}}\right)^4 (\sigma_{2p_z})^2 \left(\pi_{2p^*_{x,y}}\right)^2$ 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 **1.2.4.11**).

Molecular orbital theory can also tell us something about the *chemistry* of ***NO***. As indicated in the energy-level diagram in Figure **1.2.4.13**, 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.



Molecular Orbital Bonding for Second Row Elements: https://youtu.be/A_5Xa3sK_YE

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 **1.2.4.14** 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 $H^{\delta+}-\!-Cl^{\delta-}$.

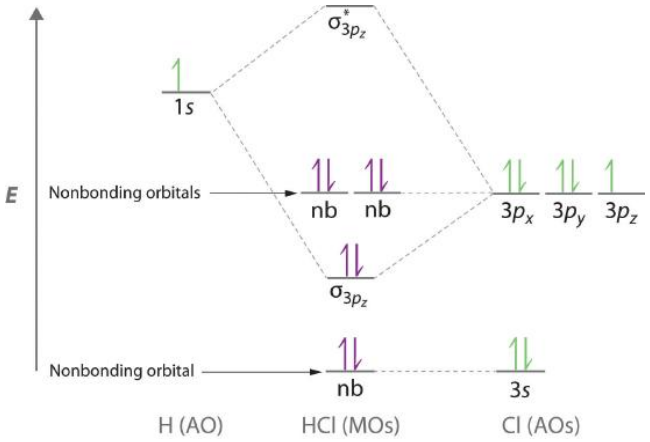


Figure **1.2.4.14**: Molecular Orbital Energy-Level Diagram for HCl. The hydrogen 1*s* atomic orbital interacts most strongly with the 3p_z orbital on chlorine, producing a bonding/antibonding pair of molecular orbitals. The other electrons on Cl are best viewed as nonbonding. As a result, only the bonding σ orbital is occupied by electrons, giving a bond order of 1.

> *Electrons in nonbonding molecular orbitals have **no effect** on bond order.*

Example 1.2.4.4

Use a "skewed" molecular orbital energy-level diagram like the one in Figure **1.2.4.12** 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

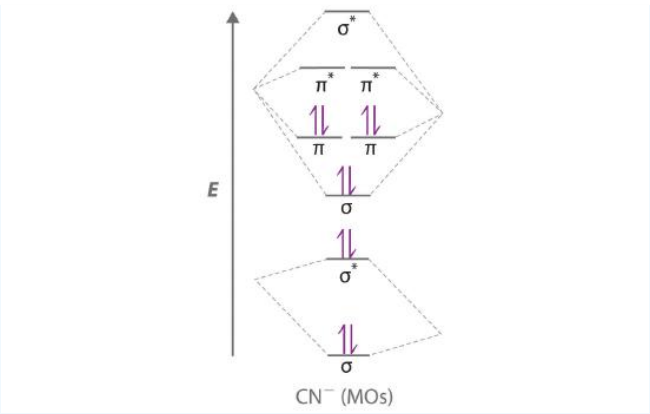
Strategy:

A. Calculate the total number of valence electrons in CN^-. Then place these electrons in a molecular orbital energy-level diagram like Figure **1.2.4.12** 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 **1.2.4.12** 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 $(8 - 2) \div 2 = 3$, indicating that the CN^- ion has a triple bond, analogous to that in N_2.

? Exercise 1.2.4.4

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.

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.

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.

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.

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.

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1.2.5: Multiple Covalent Bonds

Learning Objectives

- To explain resonance structures using molecular orbitals.

So far in our molecular 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.

Non-singular 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. Thus each carbon forms a set of three σ bonds: two C–H (sp^2 + *s*) and one C–C (sp^2 + sp^2) (part (a) in Figure **1.2.5.1**). The sp^2 hybridization can be represented as follows:

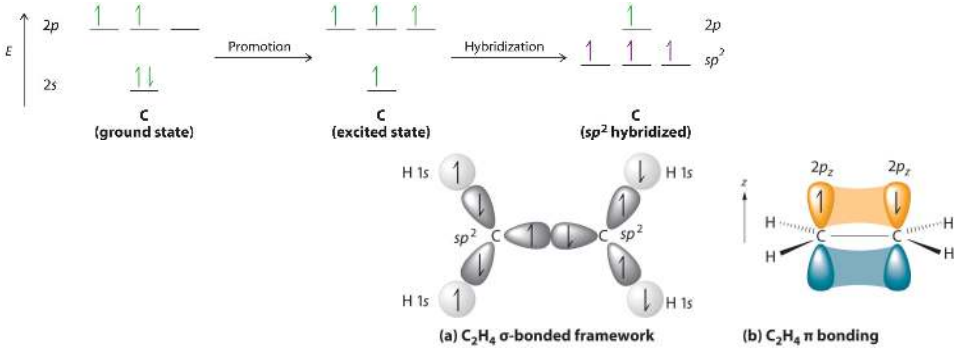


Figure **1.2.5.1**: Bonding in Ethylene. (a) The σ-bonded framework is formed by the overlap of two sets of singly occupied carbon sp^2 hybrid orbitals and four singly occupied hydrogen 1*s* orbitals to form electron-pair bonds. This uses 10 of the 12 valence electrons to form a total of five σ bonds (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.)

After hybridization, each carbon still has one unhybridized $2p_z$ orbital that is perpendicular to the hybridized lobes and contains a single electron (part (b) in Figure **1.2.5.1**). The two singly occupied $2p_z$ orbitals can overlap to form a π bonding orbital and a π^* antibonding orbital, which produces the energy-level diagram shown in Figure **1.2.5.2**. With the formation of a π bonding orbital, electron density increases in the plane between the carbon nuclei. The π^* orbital lies outside the internuclear region and has a nodal plane perpendicular to the internuclear axis. 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.

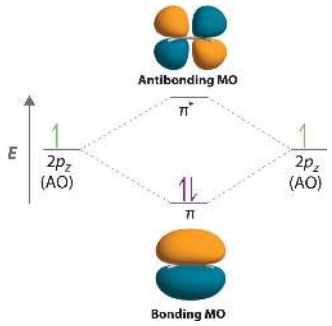


Figure **1.2.5.2**: Molecular Orbital Energy-Level Diagram for π Bonding in Ethylene. As in the diatomic molecules discussed previously, the singly occupied $2p_z$ orbitals in ethylene can overlap to form a bonding/antibonding pair of π molecular orbitals. The two electrons remaining are enough to fill only the bonding π orbital. With one σ bond plus one π bond, the carbon–carbon bond order in ethylene is 2.



sp2 Hybridization: https://youtu.be/EepTvePnfBA

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 **1.2.5.3**).

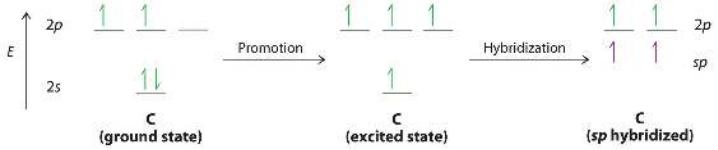


Figure **1.2.5.3**). Because each of the unhybridized 2*p* orbitals has a single electron, four electrons are available for π bonding, which is enough to occupy only the bonding molecular orbitals. Acetylene must therefore have a carbon–carbon triple bond, which consists of a C–C σ bond and two mutually 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.

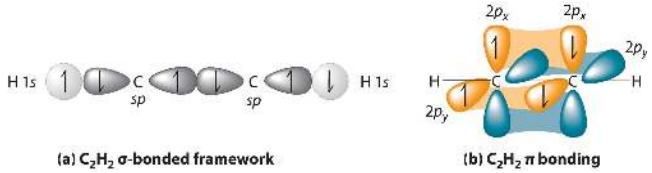


***Figure* 1.2.5.3:** *Bonding in Acetylene (a) In the formation of the σ-bonded framework, two sets of singly occupied carbon sp hybrid orbitals and two singly occupied hydrogen 1s orbitals overlap. (b) In the formation of two carbon–carbon π bonds in acetylene, two singly occupied unhybridized $2p_{x,y}$ orbitals on each carbon atom overlap. With one σ bond plus two π bonds, the carbon–carbon bond order in acetylene is 3.*

Note

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 1.2.5.1

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

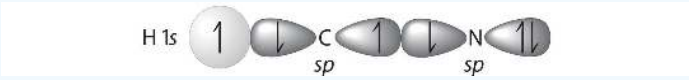
Asked for: bonding description using hybrid atomic orbitals and molecular orbitals

Strategy:

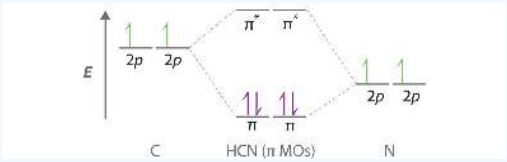
A. From the geometry given, predict the hybridization in HCN. Use the hybrid orbitals to form the σ-bonded framework of the molecule and determine the number of valence electrons that are used for σ bonding.
B. Determine the number of remaining valence electrons. Use any remaining unhybridized *p* orbitals 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

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.



sp Hybridization: https://youtu.be/epQXzG9WDRw

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.

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1.2.6: Exercises

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CHAPTER OVERVIEW

2: Nuclear Chemistry

UC Davis

Chemistry 2C

Unit 1: Electrochemistry ● Unit 2: Coordination Chemistry ● Unit 3: Descriptive Chemistry ● Unit 4: Chemical Kinetics ● Unit 5: Nuclear Chemistry

Agenda ● Textbook ● ADAPT ● Worksheets

Nuclear reactions differ from other chemical processes in one critical way: in a nuclear reaction, the identities of the elements change. In addition, nuclear reactions are often accompanied by the release of enormous amounts of energy, as much as a billion times more than the energy released by chemical reactions. Moreover, the yields and rates of a nuclear reaction are generally unaffected by changes in temperature, pressure, or the presence of a catalyst.

2.1: Components of the Nucleus
2.2: Nuclear Reactions
2.3: Nuclear Radiation
2.4: Rates of Radioactive Decay
2.5: Stability of the Atomic Nucleus
2.6: The Origin of the Elements
2.7: Transmutation of the Elements
2.8: Nuclear Fission
2.9: Nuclear Fusion
2.10: Nuclear Chemistry (Exercises)

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2.1: Components of the Nucleus

24.03: Components of the Nucleus

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2.2: Nuclear Reactions

Learning Objectives

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

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

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

Classes of Radioactive Nuclei

The three general classes of radioactive nuclei are characterized by a different decay process or set of processes:

1. **Neutron-rich nuclei.** The nuclei on the upper left side of the band of stable nuclei have a neutron-to-proton ratio that is too high to give a stable nucleus. These nuclei decay by a process that *converts a neutron to a proton*, thereby *decreasing* the neutron-to-proton ratio.
2. **Neutron-poor nuclei.** Nuclei on the lower right side of the band of stable nuclei have a neutron-to-proton ratio that is too low to give a stable nucleus. These nuclei decay by processes that have the net effect of *converting a proton to a neutron*, thereby *increasing* the neutron-to-proton ratio.
3. **Heavy nuclei.** With very few exceptions, heavy nuclei (those with $A \geq 200$) are intrinsically unstable regardless of the neutron-to-proton ratio, and all nuclei with $Z > 83$ are unstable. This is presumably due to the cumulative effects of electrostatic repulsions between the large number of positively charged protons, which cannot be totally overcome by the strong nuclear force, regardless of the number of neutrons present. Such nuclei tend to decay by emitting an α particle (a helium nucleus, $^{4}_{2}\mathrm{He}$, which decreases the number of protons and neutrons in the original nucleus by 2. Because the neutron-to-proton ratio in an α particle is 1, the net result of alpha emission is an increase in the neutron-to-proton ratio.

> *Nuclear decay reactions always produce daughter nuclei that have a more favorable neutron-to- proton ratio and hence are more stable than the parent nucleus.*

Nuclear Decay Reactions

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

To describe nuclear decay reactions, chemists have extended the $^{A}_{Z}\mathrm{X}$ notation for nuclides to include radioactive emissions. Table **2.2.1** lists the name and symbol for each type of emitted radiation. The most notable addition is the **positron**, a particle that has the same mass as an electron but a positive charge rather than a negative charge.

Table **2.2.1**: Nuclear Decay Emissions and Their Symbols

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

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

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

There are six fundamentally different kinds of nuclear decay reactions, and each releases a different kind of particle or energy. The essential features of each reaction are shown in Figure **2.2.1**. The most common are alpha and beta decay and gamma emission, but the others are essential to an understanding of nuclear decay reactions.

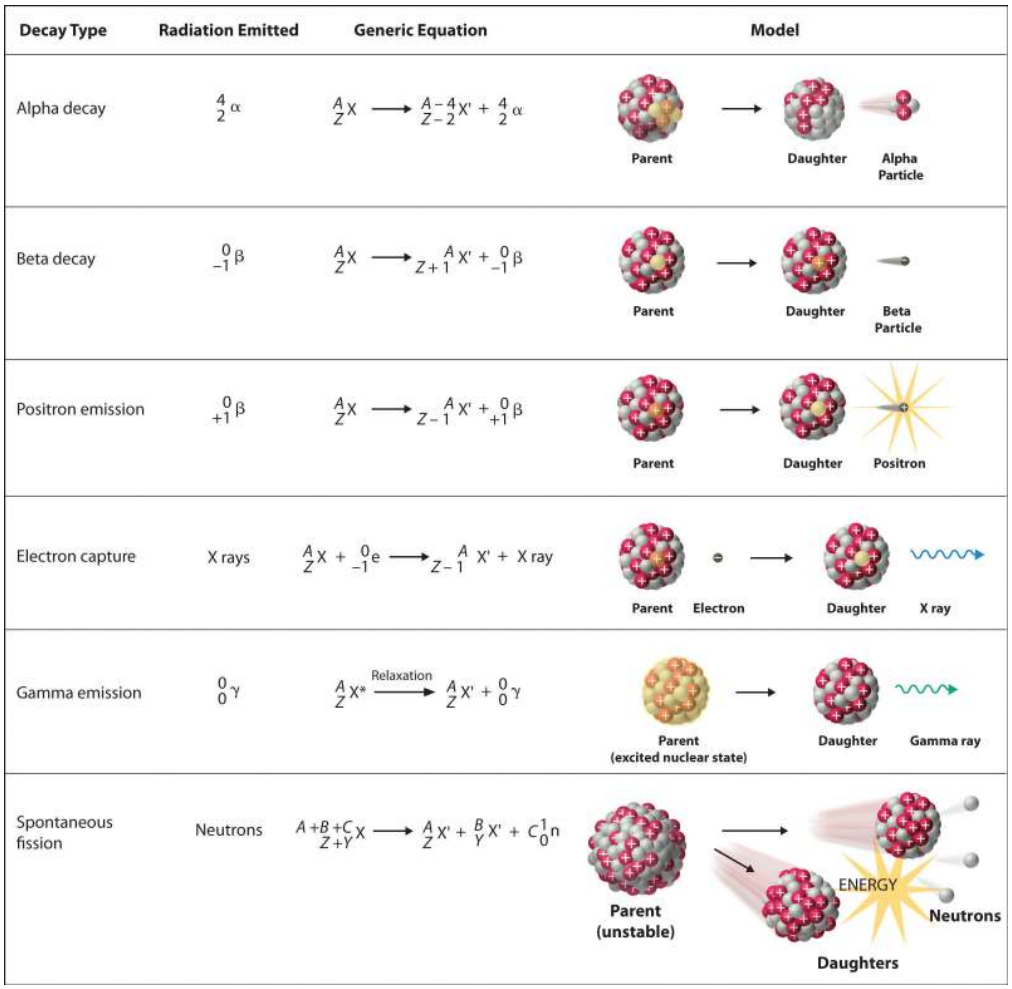


Figure 2.2.1: Common Modes of Nuclear Decay

Alpha Decay

Many nuclei with mass numbers greater than 200 undergo **alpha (α) decay**, which results in the emission of a helium-4 nucleus as an **alpha (α) particle**, $^4_2\alpha$. The general reaction is as follows:

$$\underset{\text{parent}}{^A_Z\text{X}} \rightarrow \underset{\text{daughter}}{^{A-4}_{Z-2}\text{X}'} + \underset{\substack{\text{alpha}\\\text{particle}}}{^4_2\alpha} \tag{2.2.1}$$

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

$$^{226}_{88}\text{Ra} \rightarrow ^{222}_{86}\text{Rn} + ^4_2\alpha \tag{2.2.2}$$

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

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

Beta Decay

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

$$\underset{\substack{\text{unstable}\\\text{neutron in}\\\text{nucleus}}}{{}^{1}_{0}\text{n}} \rightarrow \underset{\substack{\text{proton}\\\text{retained}\\\text{by nucleus}}}{{}^{1}_{1}\text{p}} + \underset{\substack{\text{beta particle}\\\text{emitted by}\\\text{nucleus}}}{{}^{0}_{-1}\beta} \tag{2.2.3}$$

The general reaction for beta decay is therefore

$$\underset{\text{parent}}{{}^{A}_{Z}\text{X}} \rightarrow \underset{\text{daughter}}{{}^{A}_{Z+1}\text{X}'} + \underset{\text{beta particle}}{{}^{0}_{-1}\beta} \tag{2.2.4}$$

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

$${}^{14}_{6}\text{C} \rightarrow {}^{14}_{7}\text{N} + {}^{0}_{-1}\beta \tag{2.2.5}$$

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

Positron Emission

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

$${}^{1}_{1}\text{p}^{+} \rightarrow {}^{1}_{0}\text{n} + {}^{0}_{+1}\beta^{+} \tag{2.2.6}$$

The general reaction for positron emission is therefore

$$\underset{\text{parent}}{{}^{A}_{Z}\text{X}} \rightarrow \underset{\text{daughter}}{{}^{A}_{Z-1}\text{X}'} + \underset{\text{positron}}{{}^{0}_{+1}\beta^{+}} \tag{2.2.7}$$

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

$${}^{11}_{6}\text{C} \rightarrow {}^{11}_{5}\text{B} + {}^{0}_{+1}\beta^{+} \tag{2.2.8}$$

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

Electron Capture

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

$${}^{1}_{1}\text{p} + {}^{0}_{-1}\text{e} \rightarrow {}^{1}_{0}\text{n} \tag{2.2.9}$$

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

$$\underset{\text{parent}}{{}^{A}_{Z}\text{X}} + \underset{\text{electron}}{{}^{0}_{-1}\text{e}} \rightarrow \underset{\text{daughter}}{{}^{A}_{Z-1}\text{X}'} + \text{x-ray} \tag{2.2.10}$$

Electron capture does not change the mass number of the nucleus because both the proton that is lost and the neutron that is formed have a mass number of 1. As with positron emission, however, the atomic number of the daughter nucleus is lower by 1 than that of

the parent. Once again, the neutron-to-proton ratio has increased, moving the nucleus toward the band of stable nuclei. For example, iron-55 decays by electron capture to form manganese-55, which is often written as follows:

$$^{55}_{26}\text{Fe} \xrightarrow{\text{EC}} {}^{55}_{25}\text{Mn} + \text{x-ray} \tag{2.2.11}$$

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

$$^{55}_{26}\text{Fe} + {}^{0}_{-1}\text{e} \rightarrow {}^{55}_{25}\text{Mn} + \text{x-ray} \tag{2.2.12}$$

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

Gamma Emission

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

$$^{238}_{92}\text{U} \rightarrow \underbrace{^{234}_{90}\text{Th}^*}_{\substack{\text{excited}\\ \text{nuclear}\\ \text{state}}} + {}^{4}_{2}\alpha \xrightarrow{\text{relaxation}} {}^{234}_{90}\text{Th} + {}^{0}_{0}\gamma \tag{2.2.13}$$

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

$$^{234}_{88}\text{Th}^* \rightarrow {}^{234}_{88}\text{Th} + {}^{0}_{0}\gamma \tag{2.2.14}$$

or more generally,

$$^{A}_{Z}\text{X}^* \rightarrow {}^{A}_{Z}\text{X} + {}^{0}_{0}\gamma \tag{2.2.15}$$

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

Spontaneous Fission

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

$$^{254}_{98}\text{Cf} \rightarrow {}^{118}_{46}\text{Pd} + {}^{132}_{52}\text{Te} + 4{}^{1}_{0}\text{n} \tag{2.2.16}$$

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

✔ Example 2.2.1

Write a balanced nuclear equation to describe each reaction.

a. the beta decay of $^{35}_{16}\text{S}$
b. the decay of $^{201}_{80}\text{Hg}$ by electron capture

c. the decay of $^{30}_{15}\mathrm{P}$ by positron emission

Given: radioactive nuclide and mode of decay

Asked for: balanced nuclear equation

Strategy:

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

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

Solution

a.

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

$$^{35}_{16}\mathrm{S} \rightarrow {}^{A}_{Z}\mathrm{X} + {}^{0}_{-1}\beta \tag{2.2.17}$$

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

$$^{35}_{16}\mathrm{S} \rightarrow {}^{35}_{17}\mathrm{Cl} + {}^{0}_{-1}\beta \tag{2.2.18}$$

b.

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

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

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

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

c.

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

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

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

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

? Exercise 2.2.1

Write a balanced nuclear equation to describe each reaction.

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

Answer

a. $^{11}_{6}\mathrm{C} \rightarrow {}^{11}_{5}\mathrm{B} + {}^{0}_{+1}\beta$
b. $^{99}_{42}\mathrm{Mo} \rightarrow {}^{99m}_{43}\mathrm{Tc} + {}^{0}_{-1}\beta$
c. $^{185}_{74}\mathrm{W} \rightarrow {}^{181}_{72}\mathrm{Hf} + {}^{4}_{2}\alpha + {}^{0}_{0}\gamma$

Example 2.2.2

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

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

Given: nuclide

Asked for: type of nuclear decay

Strategy:

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

Solution

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

Exercise 2.2.2

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

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

Answer

a. beta decay
b. positron emission or electron capture
c. alpha decay

Radioactive Decay Series

The nuclei of all elements with atomic numbers greater than 83 are unstable. Thus all isotopes of all elements beyond bismuth in the periodic table are radioactive. Because alpha decay decreases *Z* by only 2, and positron emission or electron capture decreases *Z* by only 1, it is impossible for any nuclide with $Z > 85$ to decay to a stable daughter nuclide in a single step, except via nuclear fission. Consequently, radioactive isotopes with $Z > 85$ usually decay to a daughter nucleus that is radiaoctive, which in turn decays to a second radioactive daughter nucleus, and so forth, until a stable nucleus finally results. This series of sequential alpha- and

beta-decay reactions is called a **radioactive decay series**. The most common is the uranium-238 decay series, which produces lead-206 in a series of 14 sequential alpha- and beta-decay reactions (Figure **2.2.2**). Although a radioactive decay series can be written for almost any isotope with $Z > 85$, only two others occur naturally: the decay of uranium-235 to lead-207 (in 11 steps) and thorium-232 to lead-208 (in 10 steps). A fourth series, the decay of neptunium-237 to bismuth-209 in 11 steps, is known to have occurred on the primitive Earth. With a half-life of "only" 2.14 million years, all the neptunium-237 present when Earth was formed decayed long ago, and today all the neptunium on Earth is synthetic.

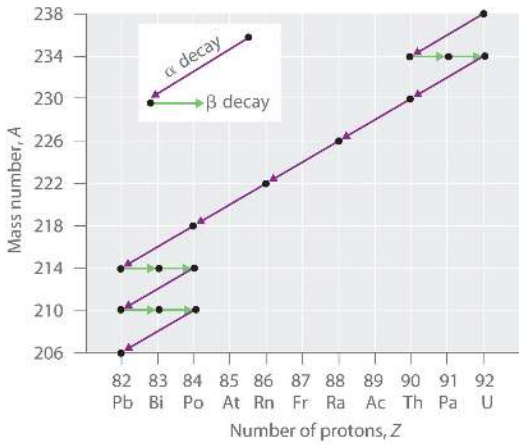


Figure **2.2.1**: A Radioactive Decay Series. Three naturally occurring radioactive decay series are known to occur currently: the uranium-238 decay series, the decay of uranium-235 to lead-207, and the decay of thorium-232 to lead-208.

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

Induced Nuclear Reactions

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

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

$$^{4}_{2}\alpha + {}^{14}_{7}\mathrm{N} \rightarrow {}^{17}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{p} \tag{2.2.19}$$

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

$$^{4}_{2}\alpha + {}^{9}_{4}\mathrm{Be} \rightarrow {}^{12}_{6}\mathrm{C} + {}^{1}_{0}\mathrm{n} \tag{2.2.20}$$

Because α particles and atomic nuclei are both positively charged, electrostatic forces cause them to repel each other. Only α particles with very high kinetic energy can overcome this repulsion and collide with a nucleus (Figure **2.2.3**). Neutrons have no electrical charge, however, so they are not repelled by the nucleus. Hence bombardment with neutrons is a much easier way to prepare new isotopes of the lighter elements. In fact, carbon-14 is formed naturally in the atmosphere by bombarding nitrogen-14 with neutrons generated by cosmic rays:

$$^{1}_{0}\mathrm{n} + {}^{14}_{7}\mathrm{N} \rightarrow {}^{14}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{p} \tag{2.2.21}$$

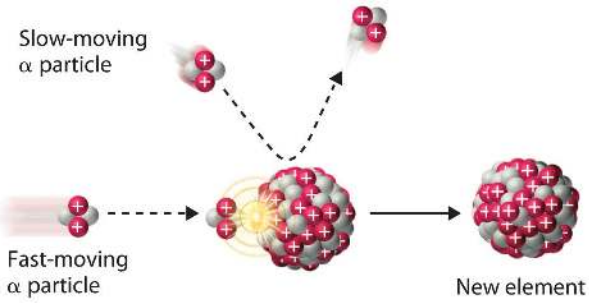


Figure **2.2.3**: A Nuclear Transmutation Reaction. Bombarding a target of one element with high-energy nuclei or subatomic particles can create new elements. Electrostatic repulsions normally prevent a positively charged particle from colliding and reacting with a positively charged nucleus. If the positively charged particle is moving at a very high speed, however, its kinetic energy may be great enough to overcome the electrostatic repulsions, and it may collide with the target nucleus. Such collisions can result in a nuclear transmutation reaction.

Example 2.2.3

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

Given: reactants in a nuclear transmutation reaction

Asked for: product nuclide and balanced nuclear equation

Strategy:

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

B Write the balanced nuclear equation for the reaction.

Solution

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

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

$$^{27}_{13}\mathrm{Al} + {}^{4}_{2}\alpha \rightarrow {}^{30}_{15}\mathrm{P} + {}^{1}_{0}\mathrm{n} \tag{2.2.22}$$

Exercise 2.2.1

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

Answer

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

We noted earlier in this section that very heavy nuclides, corresponding to $Z \geq 104$, tend to decay by spontaneous fission. Nuclides with slightly lower values of Z, such as the isotopes of uranium (Z = 92) and plutonium (Z = 94), do not undergo spontaneous fission at any significant rate. Some isotopes of these elements, however, such as ${}^{235}_{92}\mathrm{U}$ and ${}^{239}_{94}\mathrm{Pu}$ undergo induced nuclear fission when they are bombarded with relatively low-energy neutrons, as shown in the following equation for uranium-235 and in Figure **2.2.3**:

$$ {}^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{236}_{92}\mathrm{U} \rightarrow {}^{141}_{56}\mathrm{Ba} + {}^{92}_{36}\mathrm{Kr} + 3{}^{1}_{0}\mathrm{n} \tag{2.2.23} $$

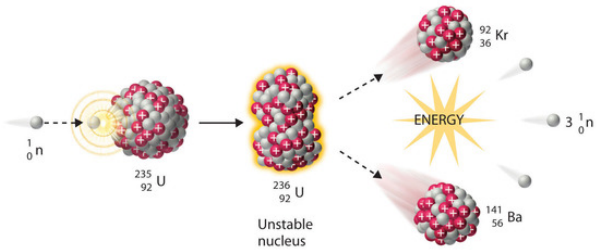


Figure **2.2.4**: Neutron-Induced Nuclear Fission. Collision of a relatively slow-moving neutron with a fissile nucleus can split it into two smaller nuclei with the same or different masses. Neutrons are also released in the process, along with a great deal of energy.

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

During nuclear fission, the nucleus usually divides asymmetrically rather than into two equal parts, as shown in Figure **2.2.4**. Moreover, every fission event of a given nuclide does not give the same products; more than 50 different fission modes have been identified for uranium-235, for example. Consequently, nuclear fission of a fissile nuclide can never be described by a single equation. Instead, as shown in Figure **2.2.5**, a distribution of many pairs of fission products with different yields is obtained, but the mass ratio of each pair of fission products produced by a single fission event is always roughly 3:2.

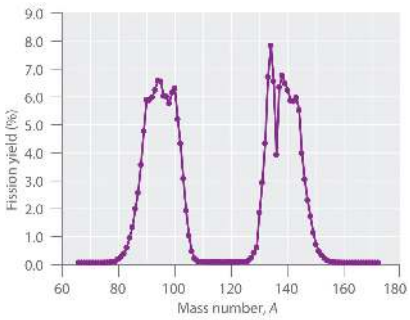


Figure **2.2.5**: Mass Distribution of Nuclear Fission Products of ^{235}U. Nuclear fission usually produces a range of products with different masses and yields, although the mass ratio of each pair of fission products from a fission event is approximately 3:2. As shown in this plot, more than 50 different fission products are known for235U. Data source: T. R. England and B. F. Rider, Los Alamos National Laboratory, LA-UR-94-3106, ENDF-349 (1993).

Synthesis of Transuranium Elements

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

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

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

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

Bombarding the target with more massive nuclei creates elements that have atomic numbers significantly greater than that of the target nucleus (Table **2.2.2**). Such techniques have resulted in the creation of the superheavy elements 114 and 116, both of which lie in or near the “island of stability."

Table **2.2.2**: Some Reactions Used to Synthesize Transuranium Elements

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

A device called a particle accelerator is used to accelerate positively charged particles to the speeds needed to overcome the electrostatic repulsions between them and the target nuclei by using electrical and magnetic fields. Operationally, the simplest particle accelerator is the linear accelerator (Figure **2.2.6**), in which a beam of particles is injected at one end of a long evacuated tube. Rapid alternation of the polarity of the electrodes along the tube causes the particles to be alternately accelerated toward a region of opposite charge and repelled by a region with the same charge, resulting in a tremendous acceleration as the particle travels down the tube. A modern linear accelerator such as the Stanford Linear Accelerator (SLAC) at Stanford University is about 2 miles long.

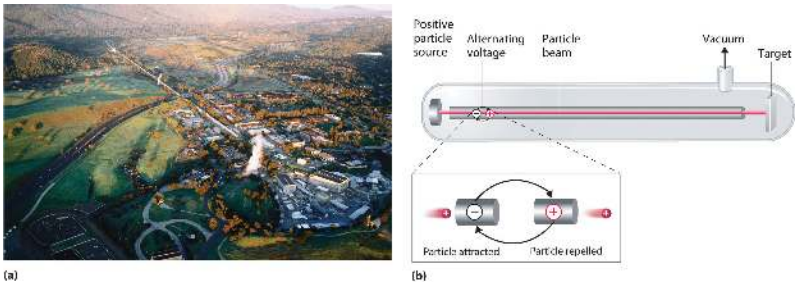


Figure **2.2.6**: A Linear Particle Accelerator. (a) An aerial view of the SLAC, the longest linear particle accelerator in the world; the overall length of the tunnel is 2 miles. (b) Rapidly reversing the polarity of the electrodes in the tube causes the charged particles to be alternately attracted as they enter one section of the tube and repelled as they leave that section. As a result, the particles are continuously accelerated along the length of the tube.

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

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

Summary

In **nuclear decay reactions (or radioactive decay)**, the parent nucleus is converted to a more stable daughter nucleus. Nuclei with too many neutrons decay by converting a neutron to a proton, whereas nuclei with too few neutrons decay by converting a proton to a neutron. Very heavy nuclei (with $A \geq 200$ and $Z > 83$) are unstable and tend to decay by emitting an **α particle**. When an unstable nuclide undergoes radioactive decay, the total number of nucleons is conserved, as is the total positive charge. Six different kinds of nuclear decay reactions are known. *Alpha decay* results in the emission of an α particle, $^{4}_{2}\alpha$, and produces a daughter nucleus with a mass number that is lower by 4 and an atomic number that is lower by 2 than the parent nucleus. **Beta decay** converts a neutron to a proton and emits a high-energy electron, producing a daughter nucleus with the same mass number as

the parent and an atomic number that is higher by 1. **Positron emission** is the opposite of beta decay and converts a proton to a neutron plus a positron. Positron emission does not change the mass number of the nucleus, but the atomic number of the daughter nucleus is lower by 1 than the parent. In **electron capture (EC)**, an electron in an inner shell reacts with a proton to produce a neutron, with emission of an x-ray. The mass number does not change, but the atomic number of the daughter is lower by 1 than the parent. In **gamma emission**, a daughter nucleus in a nuclear excited state undergoes a transition to a lower-energy state by emitting a γ ray. Very heavy nuclei with high neutron-to-proton ratios can undergo **spontaneous fission**, in which the nucleus breaks into two pieces that can have different atomic numbers and atomic masses with the release of neutrons. Many very heavy nuclei decay via a **radioactive decay series**—a succession of some combination of alpha- and beta-decay reactions. In **nuclear transmutation reactions**, a target nucleus is bombarded with energetic subatomic particles to give a product nucleus that is more massive than the original. All **transuranium elements**—elements with $Z > 92$—are artificial and must be prepared by nuclear transmutation reactions. These reactions are carried out in particle accelerators such as linear accelerators, cyclotrons, and synchrotrons.

Key Takeaway

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

Key Equations

alpha decay

Equation 20.1: $^{A}_{Z}\mathrm{X} \rightarrow {}^{A-4}_{Z-2}\mathrm{X}' + {}^{4}_{2}\alpha$

beta decay

Equation 20.4: $^{A}_{Z}\mathrm{X} \rightarrow {}^{A}_{Z+1}\mathrm{X}' + {}^{0}_{-1}\beta$

positron emission

Equation 20.7: $^{A}_{Z}\mathrm{X} \rightarrow {}^{A}_{Z-1}\mathrm{X}' + {}^{0}_{+1}\beta$

electron capture

Equation 20.10: $^{A}_{Z}\mathrm{X} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{A}_{Z-1}\mathrm{X}' + \text{x-ray}$

gamma emission

Equation 20.15: $^{A}_{Z}\mathrm{X}^{*} \rightarrow {}^{A}_{Z}\mathrm{X} + {}^{0}_{0}\gamma$

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2.3: Nuclear Radiation

Learning Objectives

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

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

$$^{A}_{Z}\mathrm{X} \tag{2.3.1}$$

where

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

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

Protons and neutrons, collectively called nucleons, are packed together tightly in a nucleus. With a radius of about 10^{-15} meters, a nucleus is quite small compared to the radius of the entire atom, which is about 10^{-10} meters. Nuclei are extremely dense compared to bulk matter, averaging 1.8×10^{14} grams per cubic centimeter. For example, water has a density of 1 gram per cubic centimeter, and iridium, one of the densest elements known, has a density of 22.6 g/cm^3. If the earth's density were equal to the average nuclear density, the earth's radius would be only about 200 meters (earth's actual radius is approximately 6.4×10^6 meters, 30,000 times larger).

Changes of nuclei that result in changes in their atomic numbers, mass numbers, or energy states are nuclear reactions. To describe a nuclear reaction, we use an equation that identifies the nuclides involved in the reaction, their mass numbers and atomic numbers, and the other particles involved in the reaction.

Nuclear Equations

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

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

If the atomic number and the mass number of all but one of the particles in a nuclear reaction are known, we can identify the particle by balancing the reaction. For instance, we could determine that $^{17}_{8}\mathrm{O}$ is a product of the nuclear reaction of $^{14}_{7}\mathrm{N}$ and $^{4}_{2}\mathrm{He}$ if we knew that a proton, $^{1}_{1}\mathrm{H}$, was one of the two products. Example 2.3.1 shows how we can identify a nuclide by balancing the nuclear reaction.

Example 2.3.1: Balancing Equations for Nuclear Reactions

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

Solution

The nuclear reaction can be written as:

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

where

- **A** is the mass number and
- **Z** is the atomic number of the new nuclide, **X**.

Because the sum of the mass numbers of the reactants must equal the sum of the mass numbers of the products:

$$25 + 4 = A + 1$$

so

$$A = 28$$

Similarly, the charges must balance, so:

$$12 + 2 = Z + 1$$

so

$$Z = 13$$

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

Exercise 2.3.1

The nuclide $^{125}_{53}\mathrm{I}$ combines with an electron and produces a new nucleus and no other massive particles. What is the equation for this reaction?

Answer

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

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

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

Nuclear Decay Reactions

Just as we use the number and type of atoms present to balance a chemical equation, we can use the number and type of nucleons present to write a balanced nuclear equation for a nuclear decay reaction. This procedure also allows us to predict the identity of

either the parent or the daughter nucleus if the identity of only one is known. Regardless of the mode of decay, the total number of nucleons is conserved in all nuclear reactions.

To describe nuclear decay reactions, chemists have extended the ${}^{A}_{Z}\mathrm{X}$ notation for nuclides to include radioactive emissions. Table **2.3.1** lists the name and symbol for each type of emitted radiation. The most notable addition is the **positron**, a particle that has the same mass as an electron but a positive charge rather than a negative charge.

Table **2.3.1**: Nuclear Decay Emissions and Their Symbols

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

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

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

There are six fundamentally different kinds of nuclear decay reactions, and each releases a different kind of particle or energy. The essential features of each reaction are shown in Figure **2.3.1**. The most common are alpha and beta decay and gamma emission, but the others are essential to an understanding of nuclear decay reactions.

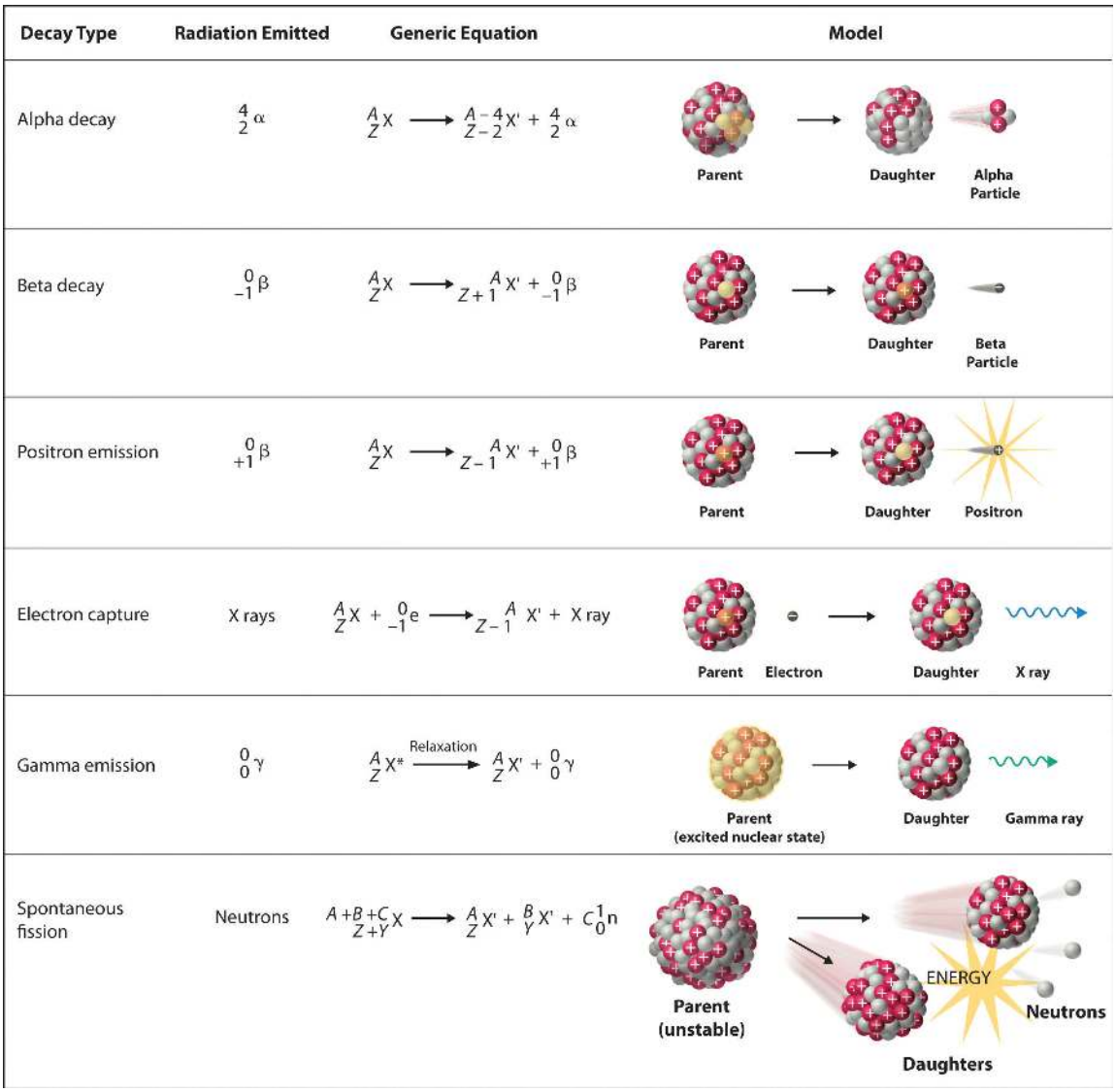


Figure **2.3.1**: Common Modes of Nuclear Decay

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

Alpha α Decay

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

$$\underset{\text{parent}}{{}^{A}_{Z}\mathrm{X}} \rightarrow \underset{\text{daughter}}{{}^{A-4}_{Z-2}\mathrm{X}'} + \underset{\text{alpha particle}}{{}^{4}_{2}\alpha} \tag{2.3.2}$$

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

$${}^{226}_{88}\mathrm{Ra} \rightarrow {}^{222}_{86}\mathrm{Rn} + {}^{4}_{2}\alpha \tag{2.3.3}$$

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

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

Beta β^- Decay

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

$$\underset{\substack{\text{unstable}\\\text{neutron in}\\\text{nucleus}}}{{}^{1}_{0}\text{n}} \rightarrow \underset{\substack{\text{proton}\\\text{retained}\\\text{by nucleus}}}{{}^{1}_{1}\text{p}} + \underset{\substack{\text{beta particle}\\\text{emitted by}\\\text{nucleus}}}{{}^{0}_{-1}\beta} \tag{2.3.4}$$

The general reaction for beta decay is therefore

$$\underset{\text{parent}}{{}^{A}_{Z}\text{X}} \rightarrow \underset{\text{daughter}}{{}^{A}_{Z+1}\text{X}'} + \underset{\text{beta particle}}{{}^{0}_{-1}\beta} \tag{2.3.5}$$

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

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

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

Positron β^+ Emission

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

$${}^{1}_{1}\text{p}^{+} \rightarrow {}^{1}_{0}\text{n} + {}^{0}_{+1}\beta^{+} \tag{2.3.6}$$

The general reaction for positron emission is therefore

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

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

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

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

Electron Capture

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

$${}^{1}_{1}\text{p} + {}^{0}_{-1}\text{e} \rightarrow {}^{1}_{0}\text{n} \tag{2.3.7}$$

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

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

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

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

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

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

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

Gamma γ Emission

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

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

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

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

or more generally,

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

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

Spontaneous Fission

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

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

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

Example 2.3.2

Write a balanced nuclear equation to describe each reaction.

a. the beta decay of $^{35}_{16}\mathrm{S}$
b. the decay of $^{201}_{80}\mathrm{Hg}$ by electron capture
c. the decay of $^{30}_{15}\mathrm{P}$ by positron emission

Given: radioactive nuclide and mode of decay

Asked for: balanced nuclear equation

Strategy:

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

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

Solution

a.

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

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

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

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

b.

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

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

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

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

c.

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

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

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

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

Exercise 2.3.2

Write a balanced nuclear equation to describe each reaction.

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

Answer a

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

Answer d

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

Answer c

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

Example 2.3.3

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

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

Given: nuclide

Asked for: type of nuclear decay

Strategy:

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

Solution

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

Exercise 2.3.3

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

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

Answer a

beta decay

Answer d

positron emission or electron capture

Answer c

alpha decay

Radioactive Decay Series

The nuclei of all elements with atomic numbers greater than 83 are unstable. Thus all isotopes of all elements beyond bismuth in the periodic table are radioactive. Because alpha decay decreases Z by only 2, and positron emission or electron capture decreases Z by only 1, it is impossible for any nuclide with $Z > 85$ to decay to a stable daughter nuclide in a single step, except via nuclear fission. Consequently, radioactive isotopes with $Z > 85$ usually decay to a daughter nucleus that is radiaoctive, which in turn decays to a second radioactive daughter nucleus, and so forth, until a stable nucleus finally results. This series of sequential alpha- and beta-decay reactions is called a **radioactive decay series**. The most common is the uranium-238 decay series, which produces lead-206 in a series of 14 sequential alpha- and beta-decay reactions (Figure **2.3.2**). Although a radioactive decay series can be written for almost any isotope with $Z > 85$, only two others occur naturally: the decay of uranium-235 to lead-207 (in 11 steps) and thorium-232 to lead-208 (in 10 steps). A fourth series, the decay of neptunium-237 to bismuth-209 in 11 steps, is known to have occurred on the primitive Earth. With a half-life of "only" 2.14 million years, all the neptunium-237 present when Earth was formed decayed long ago, and today all the neptunium on Earth is synthetic.

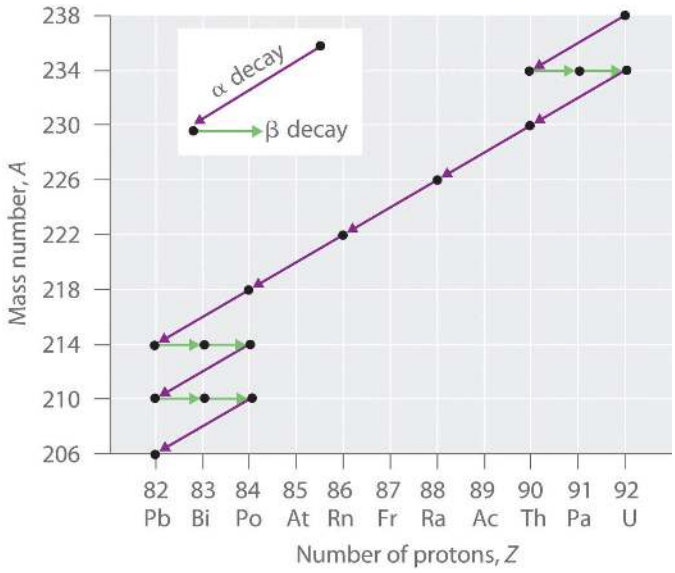


Figure **2.3.2** A Radioactive Decay Series. Three naturally occurring radioactive decay series are known to occur currently: the uranium-238 decay series, the decay of uranium-235 to lead-207, and the decay of thorium-232 to lead-208.

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

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

Induced Nuclear Reactions

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

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

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

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

$$^{4}_{2}\alpha + {}^{9}_{4}\mathrm{Be} \rightarrow {}^{12}_{6}\mathrm{C} + {}^{1}_{0}\mathrm{n} \tag{2.3.8}$$

Because α particles and atomic nuclei are both positively charged, electrostatic forces cause them to repel each other. Only α particles with very high kinetic energy can overcome this repulsion and collide with a nucleus (Figure **2.3.3**). Neutrons have no electrical charge, however, so they are not repelled by the nucleus. Hence bombardment with neutrons is a much easier way to prepare new isotopes of the lighter elements. In fact, carbon-14 is formed naturally in the atmosphere by bombarding nitrogen-14 with neutrons generated by cosmic rays:

$$^{1}_{0}\mathrm{n} + {}^{14}_{7}\mathrm{N} \rightarrow {}^{14}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{p} \tag{2.3.9}$$

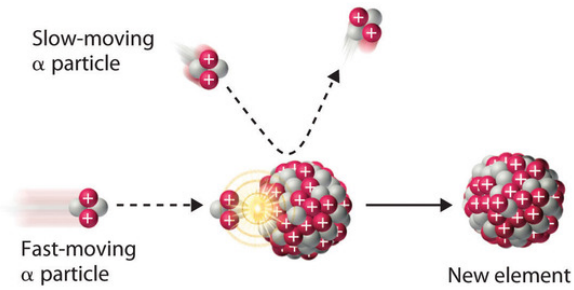


Figure **2.3.3**: A Nuclear Transmutation Reaction. Bombarding a target of one element with high-energy nuclei or subatomic particles can create new elements. Electrostatic repulsions normally prevent a positively charged particle from colliding and reacting with a positively charged nucleus. If the positively charged particle is moving at a very high speed, however, its kinetic energy may be great enough to overcome the electrostatic repulsions, and it may collide with the target nucleus. Such collisions can result in a nuclear transmutation reaction.

✔ Example 2.3.4

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

Given: reactants in a nuclear transmutation reaction

Asked for: product nuclide and balanced nuclear equation

Strategy:

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

B Write the balanced nuclear equation for the reaction.

Solution

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

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

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

? Exercise 2.3.4

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

Answer

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

We noted earlier in this section that very heavy nuclides, corresponding to $Z \geq 104$, tend to decay by spontaneous fission. Nuclides with slightly lower values of Z, such as the isotopes of uranium (Z = 92) and plutonium (Z = 94), do not undergo spontaneous fission at any significant rate. Some isotopes of these elements, however, such as $^{235}_{92}\mathrm{U}$ and $^{239}_{94}\mathrm{Pu}$ undergo induced nuclear fission when they are bombarded with relatively low-energy neutrons, as shown in the following equation for uranium-235 and in Figure **2.3.4**:

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{236}_{92}\mathrm{U} \rightarrow {}^{141}_{56}\mathrm{Ba} + {}^{92}_{36}\mathrm{Kr} + 3{}^{1}_{0}\mathrm{n} \tag{2.3.10}$$

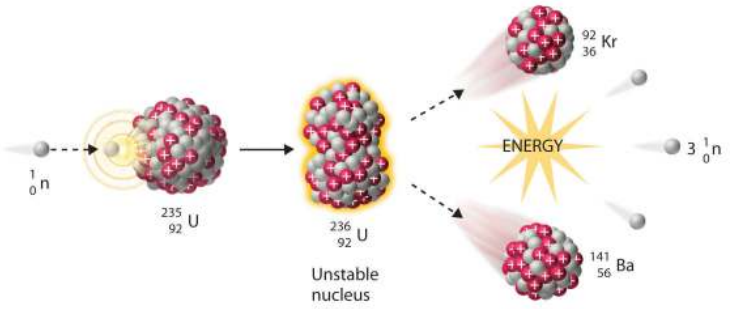


Figure **2.3.4** Neutron-Induced Nuclear Fission. Collision of a relatively slow-moving neutron with a fissile nucleus can split it into two smaller nuclei with the same or different masses. Neutrons are also released in the process, along with a great deal of energy.

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

During nuclear fission, the nucleus usually divides asymmetrically rather than into two equal parts, as shown in Figure **2.3.4**. Moreover, every fission event of a given nuclide does not give the same products; more than 50 different fission modes have been identified for uranium-235, for example. Consequently, nuclear fission of a fissile nuclide can never be described by a single equation. Instead, as shown in Figure **2.3.5**, a distribution of many pairs of fission products with different yields is obtained, but the mass ratio of each pair of fission products produced by a single fission event is always roughly 3:2.

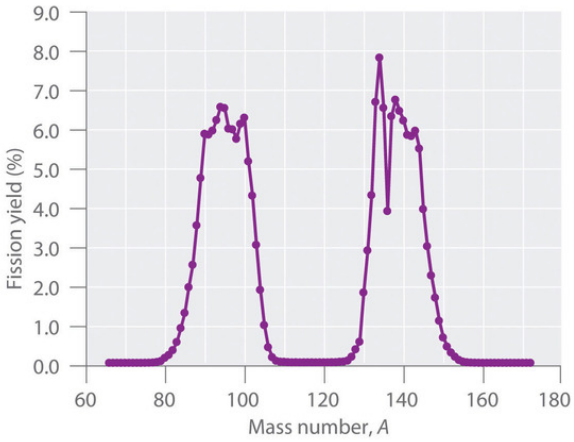


Figure **2.3.5**: Mass Distribution of Nuclear Fission Products of ^{235}U. Nuclear fission usually produces a range of products with different masses and yields, although the mass ratio of each pair of fission products from a fission event is approximately 3:2. As shown in this plot, more than 50 different fission products are known for^{235}U. Data source: T. R. England and B. F. Rider, Los Alamos National Laboratory, LA-UR-94-3106, ENDF-349 (1993).

Synthesis of Transuranium Elements

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

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

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

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

Bombarding the target with more massive nuclei creates elements that have atomic numbers significantly greater than that of the target nucleus (Table **2.3.2**). Such techniques have resulted in the creation of the superheavy elements 114 and 116, both of which lie in or near the “island of stability."

Table **2.3.2**: Some Reactions Used to Synthesize Transuranium Elements

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

A device called a particle accelerator is used to accelerate positively charged particles to the speeds needed to overcome the electrostatic repulsions between them and the target nuclei by using electrical and magnetic fields. Operationally, the simplest particle accelerator is the linear accelerator (Figure **2.3.6**), in which a beam of particles is injected at one end of a long evacuated tube. Rapid alternation of the polarity of the electrodes along the tube causes the particles to be alternately accelerated toward a region of opposite charge and repelled by a region with the same charge, resulting in a tremendous acceleration as the particle travels down the tube. A modern linear accelerator such as the Stanford Linear Accelerator (SLAC) at Stanford University is about 2 miles long.

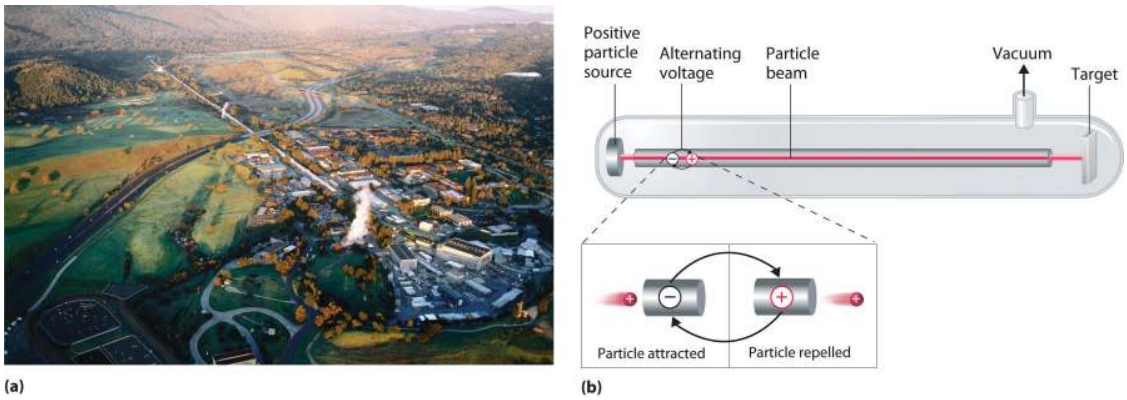


Figure **2.3.6**: A Linear Particle Accelerator. (a) An aerial view of the SLAC, the longest linear particle accelerator in the world; the overall length of the tunnel is 2 miles. (b) Rapidly reversing the polarity of the electrodes in the tube causes the charged particles to be alternately attracted as they enter one section of the tube and repelled as they leave that section. As a result, the particles are continuously accelerated along the length of the tube.

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

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

Summary and Key Takeaway

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

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

Key Equations

alpha decay

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

beta decay

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

positron emission

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

electron capture

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

gamma emission

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

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2.4: Rates of Radioactive Decay

Learning Objectives

- To know how to use half-lives to describe the rates of first-order reactions

The rate of radioactive decay is an intrinsic property of each radioactive isotope that is independent of the chemical and physical form of the radioactive isotope. The rate is also independent of temperature. In this section, we will describe radioactive decay rates and how half-lives can be used to monitor radioactive decay processes.

A Quick Primer from Chemical Kinetics

As discussed previously, the half-life of a first-order reaction is independent of the concentration of the reactants. This becomes evident when we rearrange the integrated rate law for a first-order reaction to produce the following equation:

$$\ln \frac{[\mathrm{A}]_0}{[\mathrm{A}]} = kt \tag{2.4.1}$$

Substituting $[\mathrm{A}]_{0/2}$ for [A] and $t_{1/2}$ for t (to indicate a half-life) into Equation 2.4.1 gives

$$\ln \frac{[\mathrm{A}]_0}{[\mathrm{A}]_0/2} = \ln 2 = kt_{1/2} \tag{2.4.2}$$

Substituting $\ln 2 \approx 0.693$ into the equation results in the expression for the half-life of a first-order reaction:

$$t_{1/2} = \frac{0.693}{k} \tag{2.4.3}$$

Thus, for a first-order reaction, each successive half-life is the same length of time. Since radioactivity follows first order decay kinetics, these equations are also applicable for this type of nuclear reactions.

In any sample of a given radioactive substance, the number of atoms of the radioactive isotope must decrease with time as their nuclei decay to nuclei of a more stable isotope. Using N to represent the number of atoms of the radioactive isotope, we can define the **rate of decay** of the sample, which is also called its **activity** (A) as the decrease in the number of the radioisotope's nuclei per unit time:

$$A = -\frac{\Delta N}{\Delta t} \tag{2.4.4}$$

Activity is usually measured in disintegrations per second (dps) or disintegrations per minute (dpm).

The activity of a sample is directly proportional to the number of atoms of the radioactive isotope in the sample:

$$A = kN \tag{2.4.5}$$

Here, the symbol k is the radioactive decay constant, which has units of inverse time (e.g., s^{-1}, yr^{-1}) and a characteristic value for each radioactive isotope. If we combine Equation 2.4.4 and Equation 2.4.5, we obtain the relationship between the number of decays per unit time and the number of atoms of the isotope in a sample:

$$-\frac{\Delta N}{\Delta t} = kN \tag{2.4.6}$$

Equation 2.4.6 is the same as the equation for the reaction rate of a first-order reaction, except that it uses numbers of atoms instead of concentrations. In fact, radioactive decay is a first-order process and can be described in terms of either the differential rate law (Equation 2.4.6) or the integrated rate law:

$$N = N_0 e^{-kt} \tag{2.4.7}$$

$$\ln \frac{N}{N_0} = -kt \tag{2.4.8}$$

Because radioactive decay is a first-order process, the time required for half of the nuclei in any sample of a radioactive isotope to decay is a constant, called the half-life of the isotope. The half-life tells us how radioactive an isotope is (the number of decays per unit time); thus it is the most commonly cited property of any radioisotope. For a given number of atoms, isotopes with shorter half-lives decay more rapidly, undergoing a greater number of radioactive decays per unit time than do isotopes with longer half-lives. The half-lives of several isotopes are listed in Table **2.4.1**, along with some of their applications.

Table **2.4.1**: Half-Lives and Applications of Some Radioactive Isotopes

Radioactive Isotope	Half-Life	Typical Uses
hydrogen-3 (tritium)	12.32 yr	biochemical tracer
carbon-11	20.33 min	positron emission tomography (biomedical imaging)
carbon-14	5.70×10^3 yr	dating of artifacts
sodium-24	14.951 h	cardiovascular system tracer
phosphorus-32	14.26 days	biochemical tracer
potassium-40	1.248×10^9 yr	dating of rocks
iron-59	44.495 days	red blood cell lifetime tracer
cobalt-60	5.2712 yr	radiation therapy for cancer
technetium-99*m**	6.006 h	biomedical imaging
iodine-131	8.0207 days	thyroid studies tracer
radium-226	1.600×10^3 yr	radiation therapy for cancer
uranium-238	4.468×10^9 yr	dating of rocks and Earth's crust
americium-241	432.2 yr	smoke detectors

*The *m* denotes metastable, where an excited state nucleus decays to the ground state of the same isotope.

Radioisotope Dating Techniques

In our earlier discussion, we used the half-life of a first-order reaction to calculate how long the reaction had been occurring. Because nuclear decay reactions follow first-order kinetics and have a rate constant that is independent of temperature and the chemical or physical environment, we can perform similar calculations using the half-lives of isotopes to estimate the ages of geological and archaeological artifacts. The techniques that have been developed for this application are known as radioisotope dating techniques.

The most common method for measuring the age of ancient objects is carbon-14 dating. The carbon-14 isotope, created continuously in the upper regions of Earth's atmosphere, reacts with atmospheric oxygen or ozone to form $^{14}CO_2$. As a result, the CO_2 that plants use as a carbon source for synthesizing organic compounds always includes a certain proportion of $^{14}CO_2$ molecules as well as nonradioactive $^{12}CO_2$ and $^{13}CO_2$. Any animal that eats a plant ingests a mixture of organic compounds that contains approximately the same proportions of carbon isotopes as those in the atmosphere. When the animal or plant dies, the carbon-14 nuclei in its tissues decay to nitrogen-14 nuclei by a radioactive process known as beta decay, which releases low-energy electrons (β particles) that can be detected and measured:

$$^{14}C \rightarrow {}^{14}N + \beta^- \tag{2.4.9}$$

The half-life for this reaction is 5700 ± 30 yr.

The $^{14}C/^{12}C$ ratio in living organisms is 1.3×10^{-12}, with a decay rate of 15 dpm/g of carbon (Figure **2.4.1**). Comparing the disintegrations per minute per gram of carbon from an archaeological sample with those from a recently living sample enables

scientists to estimate the age of the artifact, illustrated below. Using this method implicitly assumes that the $^{14}CO_2/^{12}CO_2$ ratio in the atmosphere is constant, which is not strictly correct. Other methods, such as tree-ring dating, have been used to calibrate the dates obtained by radiocarbon dating, and all radiocarbon dates reported are now corrected for minor changes in the $^{14}CO_2/^{12}CO_2$ ratio over time.

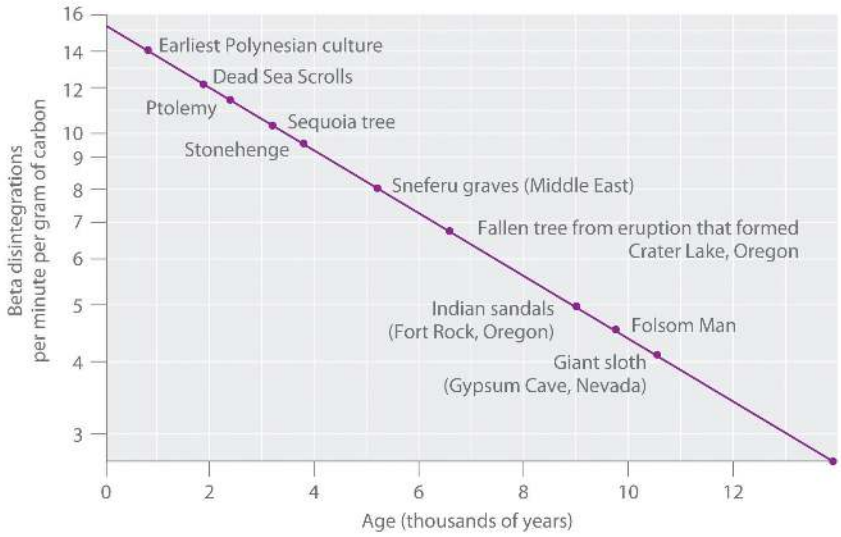


Figure **2.4.1**: Radiocarbon Dating. A plot of the specific activity of ^{14}C versus age for a number of archaeological samples shows an inverse linear relationship between ^{14}C content (a log scale) and age (a linear scale).

Example 2.4.1

In 1990, the remains of an apparently prehistoric man were found in a melting glacier in the Italian Alps. Analysis of the ^{14}C content of samples of wood from his tools gave a decay rate of 8.0 dpm/g carbon. How long ago did the man die?

Given: isotope and final activity

Asked for: elapsed time

Strategy:

A Use Equation 2.4.5 to calculate N_0/N. Then substitute the value for the half-life of ^{14}C into Equation 2.4.3 to find the rate constant for the reaction.

B Using the values obtained for N_0/N and the rate constant, solve Equation 2.4.8 to obtain the elapsed time.

Solution

We know the initial activity from the isotope's identity (15 dpm/g), the final activity (8.0 dpm/g), and the half-life, so we can use the integrated rate law for a first-order nuclear reaction (Equation 2.4.8) to calculate the elapsed time (the amount of time elapsed since the wood for the tools was cut and began to decay).

$$\ln \frac{N}{N_0} = -kt$$

$$\frac{\ln(N/N_0)}{k} = t$$

A From Equation 2.4.5, we know that $A = kN$. We can therefore use the initial and final activities (A_0 = 15 dpm and A = 8.0 dpm) to calculate N_0/N:

$$dfracA_0A = \frac{kN_0}{kN} = \frac{N_0}{N} = \frac{15}{8.0}$$

Now we need only calculate the rate constant for the reaction from its half-life (5730 yr) using Equation 2.4.3:

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

This equation can be rearranged as follows:

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730\ \text{yr}} = 1.22 \times 10^{-4}\ \text{yr}^{-1}$$

B Substituting into the equation for *t*,

$$t = \frac{\ln(N_0/N)}{k} = \frac{\ln(15/8.0)}{1.22 \times 10^{-4}\ \text{yr}^{-1}} = 5.2 \times 10^{3}\ \text{yr}$$

From our calculations, the man died 5200 yr ago.

Exercise 2.4.1

It is believed that humans first arrived in the Western Hemisphere during the last Ice Age, presumably by traveling over an exposed land bridge between Siberia and Alaska. Archaeologists have estimated that this occurred about 11,000 yr ago, but some argue that recent discoveries in several sites in North and South America suggest a much earlier arrival. Analysis of a sample of charcoal from a fire in one such site gave a ^{14}C decay rate of 0.4 dpm/g of carbon. What is the approximate age of the sample?

Answer

30,000 yr

Summary

- The half-life of a first-order reaction is independent of the concentration of the reactants.
- The half-lives of radioactive isotopes can be used to date objects.

The half-life of a reaction is the time required for the reactant concentration to decrease to one-half its initial value. The half-life of a first-order reaction is a constant that is related to the rate constant for the reaction: $t_{1/2} = 0.693/k$. Radioactive decay reactions are first-order reactions. The rate of decay, or activity, of a sample of a radioactive substance is the decrease in the number of radioactive nuclei per unit time.

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2.5: Stability of the Atomic Nucleus

Learning Objectives

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

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

Mass–Energy Balance

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

$$E = mc^2 \tag{2.5.1}$$

where c is the speed of light (2.998×10^8 m/s), and E and m are expressed in units of joules and kilograms, respectively. Albert Einstein first derived this relationship in 1905 as part of his special theory of relativity: the mass of a particle is directly proportional to its energy. Thus according to Equation 20.27, every mass has an associated energy, and similarly, any reaction that involves a change in energy must be accompanied by a change in mass. This implies that all exothermic reactions should be accompanied by a decrease in mass, and all endothermic reactions should be accompanied by an increase in mass. Given the law of conservation of mass, how can this be true? The solution to this apparent contradiction is that chemical reactions are indeed accompanied by changes in mass, but these changes are simply too small to be detected. As you may recall, all particles exhibit wavelike behavior, but the wavelength is inversely proportional to the mass of the particle (actually, to its momentum, the product of its mass and velocity). Consequently, wavelike behavior is detectable only for particles with very small masses, such as electrons. For example, the chemical equation for the combustion of graphite to produce carbon dioxide is as follows:

$$\mathrm{C(graphite)} + \frac{1}{2}\mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)} \quad \Delta H^\circ = -393.5\ \mathrm{kJ/mol} \tag{2.5.2}$$

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

$$\Delta E = (\Delta m)c^2 \tag{2.5.3}$$

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

$$\Delta m = \frac{\Delta E}{c^2} \tag{2.5.4}$$

Because 1 J = 1 $(\mathrm{kg \cdot m^2})/\mathrm{s^2}$, the change in mass is as follows:

$$\Delta m = \frac{-393.5\ \mathrm{kJ/mol}}{(2.998 \times 10^8\ \mathrm{m/s})^2} = \frac{-3.935 \times 10^5 (\mathrm{kg \cdot m^2})/(\mathrm{s^2 \cdot mol})}{(2.998 \times 10^8\ \mathrm{m/s})^2} = -4.38 \times 10^{-12}\ \mathrm{kg/mol} \tag{2.5.5}$$

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

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

$$^{14}\mathrm{C} \rightarrow {}^{14}\mathrm{N} + {}^{0}_{-1}\beta \tag{2.5.6}$$

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

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

$$\Delta m = \text{mass}_{\text{products}} - \text{mass}_{\text{reactants}} \tag{2.5.7}$$
$$= 14.003074 \text{ amu} - 14.003242 \text{ amu} = -0.000168 \text{ amu} \tag{2.5.8}$$

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

$$\Delta E = (\Delta m)c^2 = (-1.68 \times 10^{-7} \text{ kg})(2.998 \times 10^8 \text{ m/s})^2 \tag{2.5.9}$$
$$= -1.51 \times 10^{10} (\text{kg} \cdot \text{m}^2)/\text{s}^2 = -1.51 \times 10^{10} \text{ J} = -1.51 \times 10^7 \text{ kJ} \tag{2.5.10}$$

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

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

$$(-1.68 \times 10^{-4} \text{ amu}) \left(\frac{931 \text{ MeV}}{\text{amu}} \right) = -0.156 \text{ MeV} = -156 \text{ keV} \tag{2.5.11}$$

Example 2.5.1

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

Given: nuclear decay reaction

Asked for: changes in mass and energy

Strategy:

A Use the mass values in Table 20.1 to calculate the change in mass for the decay reaction in atomic mass units.

B Use Equation 20.30 to calculate the change in energy in joules per mole.

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

Solution

A Using particle and isotope masses from Table 20.1, we can calculate the change in mass as follows:

$$\Delta m = \text{mass}_{\text{products}} - \text{mass}_{\text{reactants}} = (\text{mass } ^{234}\text{Th} + \text{mass } ^4_2\text{He}) - \text{mass } ^{238}\text{U} \tag{2.5.12}$$
$$= (234.043601 \text{ amu} + 4.002603 \text{ amu}) - 238.050788 \text{ amu} = -0.004584 \text{ amu} \tag{2.5.13}$$

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

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

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

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

? Exercise 2.5.1

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

Answer

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

Nuclear Binding Energies

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

$$m_{^2\mathrm{H}} = m_{\text{neutron}} + m_{\text{proton}} + m_{\text{electron}} \tag{2.5.14}$$

$$= 1.008665 \text{ amu} + 1.007276 \text{ amu} + 0.000549 \text{ amu} = 2.016490 \text{ amu} \tag{2.5.15}$$

The difference between the sum of the masses of the components and the measured atomic mass is called the **mass defect** of the nucleus. Just as a molecule is more stable than its isolated atoms, a nucleus is more stable (lower in energy) than its isolated components. Consequently, when isolated nucleons assemble into a stable nucleus, energy is released. According to Equation 2.5.4, this release of energy must be accompanied by a decrease in the mass of the nucleus.

The amount of energy released when a nucleus forms from its component nucleons is the **nuclear binding energy** (Figure 21.2.1). In the case of deuterium, the mass defect is 0.002388 amu, which corresponds to a nuclear binding energy of 2.22 MeV for the deuterium nucleus. Because the magnitude of the mass defect is proportional to the nuclear binding energy, both values indicate the stability of the nucleus.

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

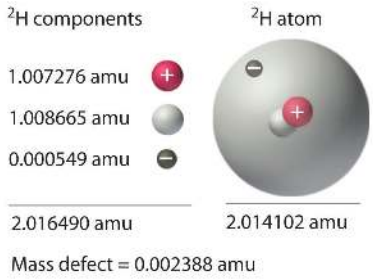


Figure 2.5.1: Nuclear Binding Energy in Deuterium. *The mass of a ^{2}H atom is less than the sum of the masses of a proton, a neutron, and an electron by 0.002388 amu; the difference in mass corresponds to the nuclear binding energy. The larger the value of the mass defect, the greater the nuclear binding energy and the more stable the nucleus.*

Not all nuclei are equally stable. Chemists describe the relative stability of different nuclei by comparing the binding energy per nucleon, which is obtained by dividing the nuclear binding energy by the mass number (A) of the nucleus. As shown in Figure 2.5.2, the binding energy per nucleon increases rapidly with increasing atomic number until about Z = 26, where it levels off to about 8–9 MeV per nucleon and then decreases slowly. The initial increase in binding energy is not a smooth curve but exhibits sharp peaks corresponding to the light nuclei that have equal numbers of protons and neutrons (e.g., ^{4}He, ^{12}C, and ^{16}O). As mentioned earlier, these are particularly stable combinations.

Because the maximum binding energy per nucleon is reached at ^{56}Fe, all other nuclei are thermodynamically unstable with regard to the formation of ^{56}Fe. Consequently, heavier nuclei (toward the right in 2.5.2) should spontaneously undergo reactions such as alpha decay, which result in a decrease in atomic number. Conversely, lighter elements (on the left in Figure 2.5.2) should spontaneously undergo reactions that result in an increase in atomic number. This is indeed the observed pattern.

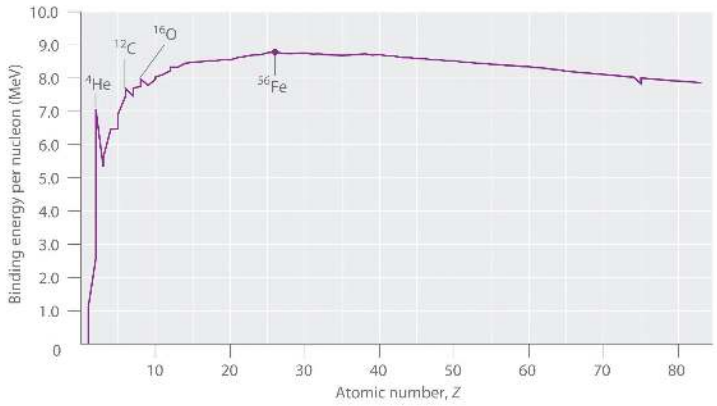


Figure **2.5.3**: The Curve of Nuclear Binding Energy. This plot of the average binding energy per nucleon as a function of atomic number shows that the binding energy per nucleon increases with increasing atomic number until about Z = 26, levels off, and then decreases. The sharp peaks correspond to light nuclei that have equal numbers of protons and neutrons.

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

Example 2.5.2

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

Given: nuclide and mass

Asked for: nuclear binding energy and binding energy per nucleon

Strategy:

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

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

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

Solution

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

$$\text{calculated mass} = 26(\text{mass } {}^{1}_{1}\text{H}) + 30(\text{mass } {}^{1}_{0}\text{n}) \tag{2.5.16}$$

$$= 26(1.007825)\text{amu} + 30(1.008665)\text{amu} = 56.463400 \text{ amu} \tag{2.5.17}$$

$$\text{experimental mass} = 55.934938 \tag{2.5.18}$$

B We subtract to find the mass defect:

$$\text{mass defect} = \text{calculated mass} - \text{experimental mass} \tag{2.5.19}$$

$$= 56.463400 \text{ amu} - 55.934938 \text{ amu} = 0.528462 \text{ amu} \tag{2.5.20}$$

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

Exercise 2.5.2

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

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

Nuclear Fission and Fusion

N**uclear fission** is the splitting of a heavy nucleus into two lighter ones. Fission was discovered in 1938 by the German scientists Otto Hahn, Lise Meitner, and Fritz Strassmann, who bombarded a sample of uranium with neutrons in an attempt to produce new elements with Z > 92. They observed that lighter elements such as barium (Z = 56) were formed during the reaction, and they realized that such products had to originate from the neutron-induced fission of uranium-235:

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{141}_{56}\mathrm{Ba} + {}^{92}_{36}\mathrm{Kr} + 3{}^{1}_{0}\mathrm{n} \tag{2.5.21}$$

This hypothesis was confirmed by detecting the krypton-92 fission product. The nucleus usually divides asymmetrically rather than into two equal parts, and the fission of a given nuclide does not give the same products every time.

In a typical nuclear fission reaction, more than one neutron is released by each dividing nucleus. When these neutrons collide with and induce fission in other neighboring nuclei, a self-sustaining series of nuclear fission reactions known as a **nuclear chain reaction** can result (Figure **2.5.3**). For example, the fission of ^{235}U releases two to three neutrons per fission event. If absorbed by other ^{235}U nuclei, those neutrons induce additional fission events, and the rate of the fission reaction increases geometrically. Each series of events is called a generation. Experimentally, it is found that some minimum mass of a fissile isotope is required to sustain a nuclear chain reaction; if the mass is too low, too many neutrons are able to escape without being captured and inducing a fission reaction. The minimum mass capable of supporting sustained fission is called the **critical mass**. This amount depends on the purity of the material and the shape of the mass, which corresponds to the amount of surface area available from which neutrons can escape, and on the identity of the isotope. If the mass of the fissile isotope is greater than the critical mass, then under the right conditions, the resulting supercritical mass can release energy explosively. The enormous energy released from nuclear chain reactions is responsible for the massive destruction caused by the detonation of nuclear weapons such as fission bombs, but it also forms the basis of the nuclear power industry.

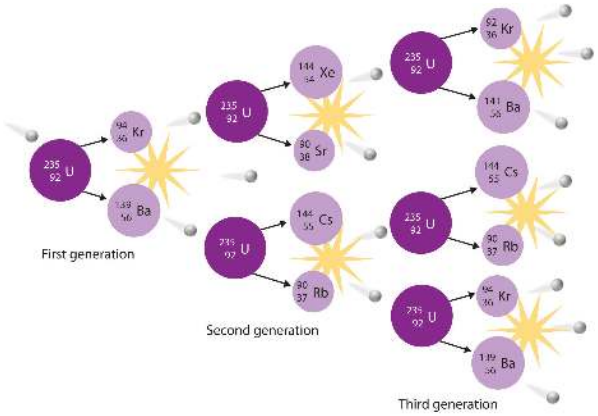


Figure **2.5.3**: A Nuclear Chain Reaction. The process is initiated by the collision of a single neutron with a ^{235}U nucleus, which undergoes fission, as shown in Figure 20.6. Because each neutron released can cause the fission of another ^{235}U nucleus, the rate of a fission reaction accelerates geometrically. Each series of events is a generation.

Nuclear fusion, in which two light nuclei combine to produce a heavier, more stable nucleus, is the opposite of nuclear fission. As in the nuclear transmutation reactions discussed in Section 20.2, the positive charge on both nuclei results in a large electrostatic energy barrier to fusion. This barrier can be overcome if one or both particles have sufficient kinetic energy to overcome the electrostatic repulsions, allowing the two nuclei to approach close enough for a fusion reaction to occur. The principle is similar to adding heat to increase the rate of a chemical reaction. As shown in the plot of nuclear binding energy per nucleon versus atomic number in Figure 21.2.3, fusion reactions are most exothermic for the lightest element. For example, in a typical fusion reaction, two deuterium atoms combine to produce helium-3, a process known as deuterium–deuterium fusion (D–D fusion):

$$2{}^{2}_{1}\mathrm{H} \rightarrow {}^{3}_{2}\mathrm{He} + {}^{1}_{0}\mathrm{n} \tag{2.5.22}$$

In another reaction, a deuterium atom and a tritium atom fuse to produce helium-4 (Figure **2.5.4**), a process known as deuterium–tritium fusion (D–T fusion):

$${}^{2}_{1}\mathrm{H} + {}^{3}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{1}_{0}\mathrm{n} \tag{2.5.23}$$

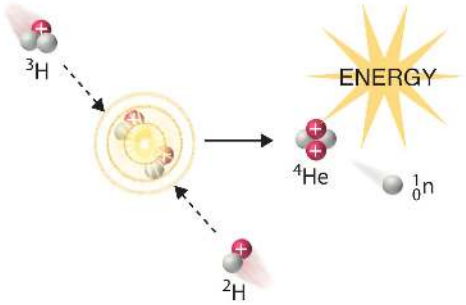


Figure 2.5.4: Nuclear Fusion. In a nuclear fusion reaction, lighter nuclei combine to produce a heavier nucleus. As shown, fusion of ^{3}H and ^{2}H to give ^{4}He and a neutron releases an enormous amount of energy. In principle, nuclear fusion can produce much more energy than fission, but very high kinetic energy is required to overcome electrostatic repulsions between the positively charged nuclei and initiate the fusion reaction.

Initiating these reactions, however, requires a temperature comparable to that in the interior of the sun (approximately 1.5×10^7 K). Currently, the only method available on Earth to achieve such a temperature is the detonation of a fission bomb. For example, the so-called hydrogen bomb (or H bomb) is actually a deuterium–tritium bomb (a D–T bomb), which uses a nuclear fission reaction to create the very high temperatures needed to initiate fusion of solid lithium deuteride (^{6}LiD), which releases neutrons that then react with ^{6}Li, producing tritium. The deuterium-tritium reaction releases energy explosively. Example 9 and its corresponding exercise demonstrate the enormous amounts of energy produced by nuclear fission and fusion reactions. In fact, fusion reactions are the power sources for all stars, including our sun.

Example 2.5.3

Calculate the amount of energy (in electronvolts per atom and kilojoules per mole) released when the neutron-induced fission of ^{235}U produces ^{144}Cs, ^{90}Rb, and two neutrons:

$$^{235}_{92}\text{U} + {}^{1}_{0}\text{n} \rightarrow {}^{144}_{55}\text{Cs} + {}^{90}_{37}\text{Rb} + 2{}^{1}_{0}\text{n}$$

Given: balanced nuclear reaction

Asked for: energy released in electronvolts per atom and kilojoules per mole

Strategy:

A Following the method used in Example 2.5.1, calculate the change in mass that accompanies the reaction. Convert this value to the change in energy in electronvolts per atom.

B Calculate the change in mass per mole of ^{235}U. Then use Equation 2.5.3 to calculate the change in energy in kilojoules per mole.

Solution

A The change in mass that accompanies the reaction is as follows:

$$\Delta m = \text{mass}_{\text{products}} - \text{mass}_{\text{reactants}} = \text{mass}({}^{144}_{55}\text{Cs} + {}^{90}_{37}\text{Rb} + {}^{1}_{0}\text{n}) - \text{mass } {}^{235}_{92}\text{U} \quad (2.5.24)$$

$$= (143.932077 \text{ amu} + 89.914802 \text{ amu} + 1.008665 \text{ amu}) - 235.043930 \text{ amu} \quad (2.5.25)$$

$$= -0.188386 \text{ amu} \quad (2.5.26)$$

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

$$\Delta E = (-0.188386 \text{ amu})(931 \text{ MeV/amu}) = -175 \text{ MeV}$$

B The change in mass per mole of $^{235}_{92}$U is −0.188386 g = -1.88386×10^{-4} kg, so the change in energy in kilojoules per mole is as follows:

$$\Delta E = (\Delta m)c^2 = (-1.88386 \times 10^{-4} \text{ kg})(2.998 \times 10^8 \text{ m/s})^2 \quad (2.5.27)$$

$$= -1.693 \times 10^{13} \text{ J/mol} = -1.693 \times 10^{10} \text{ kJ/mol} \quad (2.5.28)$$

? Exercise 2.5.3

Calculate the amount of energy (in electronvolts per atom and kilojoules per mole) released when deuterium and tritium fuse to give helium-4 and a neutron:

$$^{2}_{1}\mathrm{H} + {}^{3}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{1}_{0}\mathrm{n}$$

Answer

$\Delta E = -17.6$ MeV/atom $= -1.697 \times 10^{9}$ kJ/mol

Summary

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

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2.6: The Origin of the Elements

Learning Objectives

- To understand how nuclear transmutation reactions lead to the formation of the elements in stars and how they can be used to synthesize transuranium elements.

The relative abundances of the elements in the known universe vary by more than 12 orders of magnitude. For the most part, these differences in abundance cannot be explained by differences in nuclear stability. Although the ^{56}Fe nucleus is the most stable nucleus known, the most abundant element in the known universe is not iron, but hydrogen (^{1}H), which accounts for about 90% of all atoms. In fact, ^{1}H is the raw material from which all other elements are formed. In this section, we explain why ^{1}H and ^{2}He together account for at least 99% of all the atoms in the known universe. We also describe the nuclear reactions that take place in stars, which transform one nucleus into another and create all the naturally occurring elements.

Relative Abundances of the Elements on Earth and in the Known Universe

The relative abundances of the elements in the known universe and on Earth relative to silicon are shown in Figure **2.6.1**. The data are estimates based on the characteristic emission spectra of the elements in stars, the absorption spectra of matter in clouds of interstellar dust, and the approximate composition of Earth as measured by geologists. The data in Figure **2.6.1** illustrate two important points. First, except for hydrogen, the most abundant elements have even atomic numbers. Not only is this consistent with the known trends in nuclear stability, but it also suggests that heavier elements are formed by combining helium nuclei (Z = 2). Second, the relative abundances of the elements in the known universe and on Earth are often very different, as indicated by the data in Table **2.6.1** for some common elements.

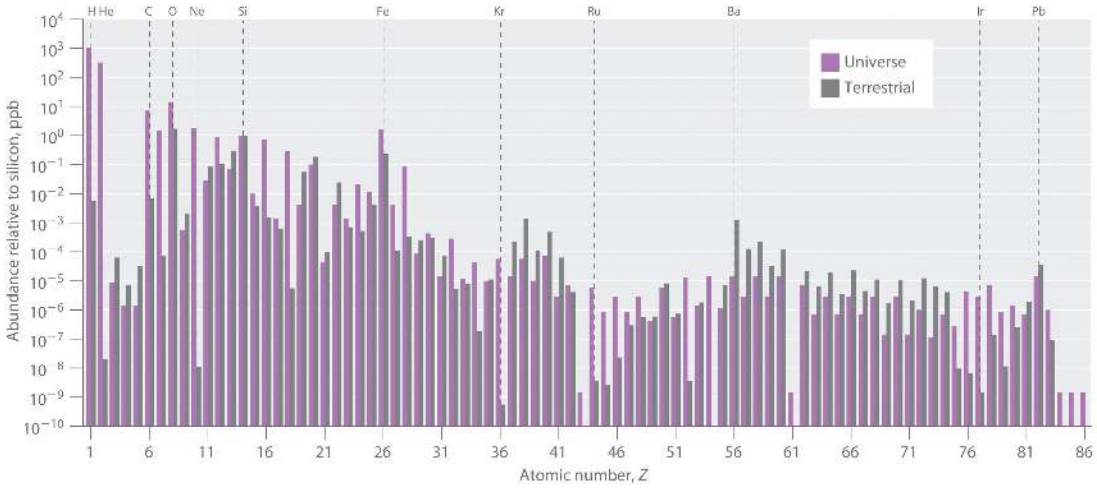


Figure **2.6.1**: The Relative Abundances of the Elements in the Universe and on Earth. In this logarithmic plot, the relative abundances of the elements relative to that of silicon (arbitrarily set equal to 1) in the universe (green bars) and on Earth (purple bars) are shown as a function of atomic number. Elements with even atomic numbers are generally more abundant in the universe than elements with odd atomic numbers. Also, the relative abundances of many elements in the universe are very different from their relative abundances on Earth. (CC BY-NC-SA 3.0; anonymous)

Bar graph of abundance realtive to silicon in pbb against atomic number. The purple bars are universe elements while the gray bars are terrestrial elements.

Some of these differences are easily explained. For example, nonmetals such as H, He, C, N, O, Ne, and Kr are much less abundant relative to silicon on Earth than they are in the rest of the universe. These elements are either noble gases (He, Ne, and Kr) or elements that form volatile hydrides, such as NH_3, CH_4, and H_2O. Because Earth's gravity is not strong enough to hold such light substances in the atmosphere, these elements have been slowly diffusing into outer space ever since our planet was formed. Argon is an exception; it is relatively abundant on Earth compared with the other noble gases because it is continuously produced in rocks by the radioactive decay of isotopes such as ^{40}K. In contrast, many metals, such as Al, Na, Fe, Ca, Mg, K, and Ti, are relatively abundant on Earth because they form nonvolatile compounds, such as oxides, that cannot escape into space. Other metals, however,

are much less abundant on Earth than in the universe; some examples are Ru and Ir. This section explains some of the reasons for the great differences in abundances of the metallic elements.

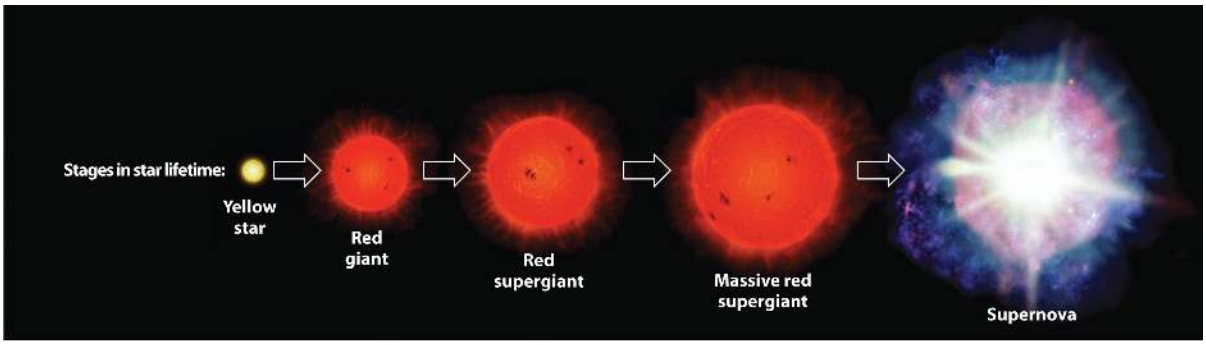
Table **2.6.1**: Relative Abundances of Elements on Earth and in the Known Universe

Terrestrial/Universal Element	Abundance Ratio
H	0.0020
He	2.4×10^{-8}
C	0.36
N	0.02
O	46
Ne	1.9×10^{-6}
Na	1200
Mg	48
Al	1600
Si	390
S	0.84
K	5000
Ca	710
Ti	2200
Fe	57

All the elements originally present on Earth (and on other planets) were synthesized from hydrogen and helium nuclei in the interiors of stars that have long since exploded and disappeared. Six of the most abundant elements in the universe (C, O, Ne, Mg, Si, and Fe) have nuclei that are integral multiples of the helium-4 nucleus, which suggests that helium-4 is the primary building block for heavier nuclei.

Synthesis of the Elements in Stars

Elements are synthesized in discrete stages during the lifetime of a star, and some steps occur only in the most massive stars known (Figure **2.6.2**). Initially, all stars are formed by the aggregation of interstellar “dust,” which is mostly hydrogen. As the cloud of dust slowly contracts due to gravitational attraction, its density eventually reaches about 100 g/cm^3, and the temperature increases to about 1.5×10^7 K, forming a dense plasma of ionized hydrogen nuclei. At this point, self-sustaining nuclear reactions begin, and the star “ignites,” creating a yellow star like our sun.



Core Temperature:	1.5×10^7 K	2×10^8 K	7×10^8 K	3×10^9 K	1×10^{11} K
Primary Nuclear Reaction:	^{1}H fusion	^{4}He fusion	$^4He + ^{12}C$ $^{12}C + ^{12}C$ $^{12}C + ^{16}O$	Proton–neutron exchange reactions	Multiple neutron captures
Elements Formed:	He	C, O, Ne, Mg	Na, Si, S, Ar, Ca	Fe, Ni	Elements with $Z \geq 28$

Figure **2.6.2**: Nuclear Reactions during the Life Cycle of a Massive Star. At each stage in the lifetime of a star, a different fuel is used for nuclear fusion, resulting in the formation of different elements. Fusion of hydrogen to give helium is the primary fusion reaction in young stars. As the star ages, helium accumulates and begins to "burn," undergoing fusion to form heavier elements such as carbon and oxygen. As the adolescent star matures, significant amounts of iron and nickel are formed by fusion of the heavier elements formed previously. The heaviest elements are formed only during the final death throes of the star—the formation of a nova or supernova.

The stages in a stare lifetime are yellow star, red giant, red supergiant, massive red supergiant and finally supernova.

In the first stage of its life, the star is powered by a series of nuclear fusion reactions that convert hydrogen to helium:

$$\begin{aligned} {}^1_1\mathrm{H} + {}^1_1\mathrm{H} &\rightarrow {}^2_1\mathrm{H} + {}^0_{+1}\beta \\ {}^2_1\mathrm{H} + {}^1_1\mathrm{H} &\rightarrow {}^3_2\mathrm{He} + {}^0_0\gamma \\ {}^3_2\mathrm{He} + {}^3_2\mathrm{He} &\rightarrow {}^4_2\mathrm{He} + 2{}^1_1\mathrm{H} \end{aligned} \tag{2.6.1}$$

The overall reaction is the conversion of four hydrogen nuclei to a helium-4 nucleus, which is accompanied by the release of two positrons, two γ rays, and a great deal of energy:

$$4{}^1_1\mathrm{H} \rightarrow {}^4_2\mathrm{He} + 2{}^0_{+1}\beta + 2{}^0_0\gamma \tag{2.6.2}$$

These reactions are responsible for most of the enormous amount of energy that is released as sunlight and solar heat. It takes several billion years, depending on the size of the star, to convert about 10% of the hydrogen to helium.

Once large amounts of helium-4 have been formed, they become concentrated in the core of the star, which slowly becomes denser and hotter. At a temperature of about 2×10^8 K, the helium-4 nuclei begin to fuse, producing beryllium-8:

$$2{}^4_2\mathrm{He} \rightarrow {}^8_4\mathrm{Be} \tag{2.6.3}$$

Although beryllium-8 has both an even mass number and an even atomic number, its also has a low neutron-to-proton ratio (and other factors beyond the scope of this text) that makes it unstable; it decomposes in only about 10^{-16} s. Nonetheless, this is long enough for it to react with a third helium-4 nucleus to form carbon-12, which is very stable. Sequential reactions of carbon-12 with helium-4 produce the elements with even numbers of protons and neutrons up to magnesium-24:

$${}^8_4\mathrm{Be} \xrightarrow{{}^4_2\mathrm{He}} {}^{12}_6\mathrm{C} \xrightarrow{{}^4_2\mathrm{He}} {}^{16}_8\mathrm{O} \xrightarrow{{}^4_2\mathrm{He}} {}^{20}_{10}\mathrm{Ne} \xrightarrow{{}^4_2\mathrm{He}} {}^{24}_{12}\mathrm{Mg} \tag{2.6.4}$$

So much energy is released by these reactions that it causes the surrounding mass of hydrogen to expand, producing a red giant that is about 100 times larger than the original yellow star.

As the star expands, heavier nuclei accumulate in its core, which contracts further to a density of about 50,000 g/cm3, so the core becomes even hotter. At a temperature of about 7×10^8 K, carbon and oxygen nuclei undergo nuclear fusion reactions to produce sodium and silicon nuclei:

$${}^{12}_6\mathrm{C} + {}^{12}_6\mathrm{C} \rightarrow {}^{23}_{11}\mathrm{Na} + {}^1_1\mathrm{H} \tag{2.6.5}$$

$${}^{12}_6\mathrm{C} + {}^{16}_8\mathrm{O} \rightarrow {}^{28}_{14}\mathrm{Si} + {}^0_0\gamma \tag{2.6.6}$$

At these temperatures, carbon-12 reacts with helium-4 to initiate a series of reactions that produce more oxygen-16, neon-20, magnesium-24, and silicon-28, as well as heavier nuclides such as sulfur-32, argon-36, and calcium-40:

$$^{12}_{6}\text{C} \xrightarrow{^{4}_{2}\text{He}} {}^{16}_{8}\text{O} \xrightarrow{^{4}_{2}\text{He}} {}^{20}_{10}\text{Ne} \xrightarrow{^{4}_{2}\text{He}} {}^{24}_{12}\text{Mg} \xrightarrow{^{4}_{2}\text{He}} {}^{28}_{14}\text{Si} \xrightarrow{^{4}_{2}\text{He}} {}^{32}_{16}\text{S} \xrightarrow{^{4}_{2}\text{He}} {}^{36}_{18}\text{Ar} \xrightarrow{^{4}_{2}\text{He}} {}^{40}_{20}\text{Ca} \tag{2.6.7}$$

The energy released by these reactions causes a further expansion of the star to form a red supergiant, and the core temperature increases steadily. At a temperature of about 3×10^9 K, the nuclei that have been formed exchange protons and neutrons freely. This equilibration process forms heavier elements up to iron-56 and nickel-58, which have the most stable nuclei known.

The Formation of Heavier Elements in Supernovas

None of the processes described so far produces nuclei with Z > 28. All naturally occurring elements heavier than nickel are formed in the rare but spectacular cataclysmic explosions called supernovas (Figure **2.6.2**). When the fuel in the core of a very massive star has been consumed, its gravity causes it to collapse in about 1 s. As the core is compressed, the iron and nickel nuclei within it disintegrate to protons and neutrons, and many of the protons capture electrons to form neutrons. The resulting neutron star is a dark object that is so dense that atoms no longer exist. Simultaneously, the energy released by the collapse of the core causes the supernova to explode in what is arguably the single most violent event in the universe. The force of the explosion blows most of the star's matter into space, creating a gigantic and rapidly expanding dust cloud, or nebula (Figure **2.6.3**). During the extraordinarily short duration of this event, the concentration of neutrons is so great that multiple neutron-capture events occur, leading to the production of the heaviest elements and many of the less stable nuclides. Under these conditions, for example, an iron-56 nucleus can absorb as many as 64 neutrons, briefly forming an extraordinarily unstable iron isotope that can then undergo multiple rapid β-decay processes to produce tin-120:

$$^{56}_{26}\text{Fe} + 64\,^{1}_{0}\text{n} \rightarrow {}^{120}_{26}\text{Fe} \rightarrow {}^{120}_{50}\text{Sn} + 24\,^{0}_{-1}\beta \tag{2.6.8}$$

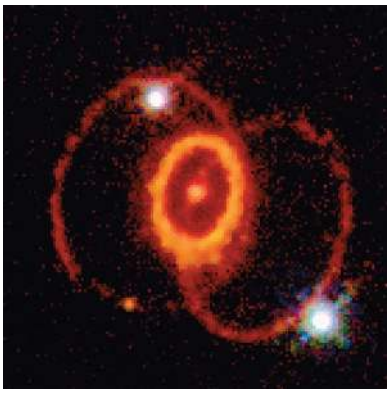


Figure **2.6.3**: A Supernova. A view of the remains of Supernova 1987A, located in the Large Magellanic Cloud, showing the circular halo of expanding debris produced by the explosion. Multiple neutron-capture events occur during a supernova explosion, forming both the heaviest elements and many of the less stable nuclides.

Although a supernova occurs only every few hundred years in a galaxy such as the Milky Way, these rare explosions provide the only conditions under which elements heavier than nickel can be formed. The force of the explosions distributes these elements throughout the galaxy surrounding the supernova, and eventually they are captured in the dust that condenses to form new stars. Based on its elemental composition, our sun is thought to be a second- or third-generation star. It contains a considerable amount of cosmic debris from the explosion of supernovas in the remote past.

✔ Example 2.6.1: Carbon Burning Stars

The reaction of two carbon-12 nuclei in a carbon-burning star can produce elements other than sodium. Write a balanced nuclear equation for the formation of

a. magnesium-24.
b. neon-20 from two carbon-12 nuclei.

Given: reactant and product nuclides

Asked for: balanced nuclear equation

Strategy:

Use conservation of mass and charge to determine the type of nuclear reaction that will convert the reactant to the indicated product. Write the balanced nuclear equation for the reaction.

Solution

a. A magnesium-24 nucleus (Z = 12, A = 24) has the same nucleons as two carbon-12 nuclei (Z = 6, A = 12). The reaction is therefore a fusion of two carbon-12 nuclei, and no other particles are produced: $^{12}_{6}\mathrm{C} + {}^{12}_{6}\mathrm{C} \rightarrow {}^{24}_{12}\mathrm{Mg}$.

b. The neon-20 product has Z = 10 and A = 20. The conservation of mass requires that the other product have A = (2 × 12) − 20 = 4; because of conservation of charge, it must have Z = (2 × 6) − 10 = 2. These are the characteristics of an α particle. The reaction is therefore $^{12}_{6}\mathrm{C} + {}^{12}_{6}\mathrm{C} \rightarrow {}^{20}_{10}\mathrm{Ne} + {}^{4}_{2}\alpha$.

? Exercise 2.6.1

How many neutrons must an iron-56 nucleus absorb during a supernova explosion to produce an arsenic-75 nucleus? Write a balanced nuclear equation for the reaction.

Answer

19 neutrons; $^{56}_{26}\mathrm{Fe} + 19\,^{1}_{0}\mathrm{n} \rightarrow {}^{75}_{26}\mathrm{Fe} \rightarrow {}^{75}_{33}\mathrm{As} + 7\,^{0}_{-1}\beta$

Summary

Hydrogen and helium are the most abundant elements in the universe. Heavier elements are formed in the interior of stars via multiple neutron-capture events. By far the most abundant element in the universe is hydrogen. The fusion of hydrogen nuclei to form helium nuclei is the major process that fuels young stars such as the sun. Elements heavier than helium are formed from hydrogen and helium in the interiors of stars. Successive fusion reactions of helium nuclei at higher temperatures create elements with even numbers of protons and neutrons up to magnesium and then up to calcium. Eventually, the elements up to iron-56 and nickel-58 are formed by exchange processes at even higher temperatures. Heavier elements can only be made by a process that involves multiple neutron-capture events, which can occur only during the explosion of a supernova.

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2.7: Transmutation of the Elements

Although the conversion of one element to another is the basis of natural radioactive decay, it is also possible to convert one element to another experimentally. The conversion of one element to another is the process of transmutation. In 1919 Rutherford converted a stable isotope to an unstable one. By bombarding $^{14}\mathrm{N}$ with α particles he created $^{17}\mathrm{O}$, which is an unstable isotope of oxygen. Transmutation may also be accomplished by bombardment with neutrons.

$$^{14}_{7}\mathrm{N} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{17}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{H} \tag{2.7.1}$$

Historically, part of Alchemy was the study of methods of creating gold from base metals, such lead. Where the Alchemists failed in this quest, we can now succeed. Thus, bombardment of platinum-198 with a neutron creates an unstable isotope of platinum that undergoes beta decay to gold-199. Unfortunately, while we may succeed in making gold, the platinum we make it from is actually worth more than the gold making this particular transmutation economically non-viable!

$$^{198}_{78}\mathrm{Pt} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{199}_{78}\mathrm{Pt} \rightarrow {}^{199}_{79}\mathrm{Au} + {}^{0}_{-1}\beta \tag{2.7.2}$$

Transuranium Elements

Uranium (Z = 92) is the heaviest naturally occurring element. Consequently, all the elements with Z > 92, the **transuranium elements**, are artificial and have been prepared by bombarding suitable target nuclei with smaller particles. The first of the transuranium elements to be prepared was neptunium (Z = 93), which was synthesized in 1940 by bombarding a ^{238}U target with neutrons. As shown in Equation \(\ref{20.41}\) this reaction occurs in two steps. Initially, a neutron combines with a ^{238}U nucleus to form ^{239}U, which is unstable and undergoes beta decay to produce ^{239}Np:

$$^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{239}_{92}\mathrm{U} \rightarrow {}^{239}_{93}\mathrm{Np} + {}^{0}_{-1}\beta \tag{2.7.3}$$

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

$$^{239}_{93}\mathrm{Np} \rightarrow {}^{239}_{94}\mathrm{Pu} + {}^{0}_{-1}\beta \tag{2.7.4}$$

Bombarding the target with more massive nuclei creates elements that have atomic numbers significantly greater than that of the target nucleus (Table **2.7.1**). Such techniques have resulted in the creation of the superheavy elements 114 and 116, both of which lie in or near the “island of stability." As of this writing, 22 transuranium elements have been produced and officially recognized by IUPAC; several other elements have formation claims that are waiting for approval.

Table 2.7.1: Preparation of Some of the Transuranium Elements

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

Particle Accelerators

A device called a particle accelerator is used to accelerate positively charged particles to the speeds needed to overcome the electrostatic repulsions between them and the target nuclei by using electrical and magnetic fields. Operationally, the simplest particle accelerator is the linear accelerator (Figure **2.7.2**), in which a beam of particles is injected at one end of a long evacuated tube. Rapid alternation of the polarity of the electrodes along the tube causes the particles to be alternately accelerated toward a region of opposite charge and repelled by a region with the same charge, resulting in a tremendous acceleration as the particle travels down the tube. A modern linear accelerator such as the Stanford Linear Accelerator (SLAC) at Stanford University is about 2 miles long.

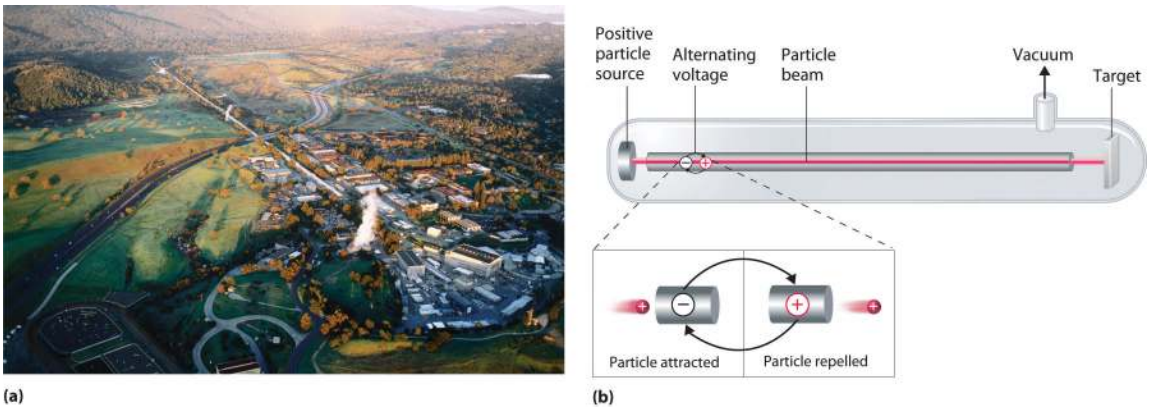


Figure **2.7.2**: A Linear Particle Accelerator. (a) An aerial view of the SLAC, the longest linear particle accelerator in the world; the overall length of the tunnel is 2 miles. (b) Rapidly reversing the polarity of the electrodes in the tube causes the charged particles to be alternately attracted as they enter one section of the tube and repelled as they leave that section. As a result, the particles are continuously accelerated along the length of the tube.

To achieve the same outcome in less space, a particle accelerator called a cyclotron forces the charged particles to travel in a circular path rather than a linear one. The particles are injected into the center of a ring and accelerated by rapidly alternating the

polarity of two large D-shaped electrodes above and below the ring, which accelerates the particles outward along a spiral path toward the target.

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

Contributors and Attributions

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2.8: Nuclear Fission

Skills to Develop

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

Many heavier elements with smaller binding energies per nucleon can decompose into more stable elements that have intermediate mass numbers and larger binding energies per nucleon—that is, mass numbers and binding energies per nucleon that are closer to the "peak" of the binding energy graph near 56. Sometimes neutrons are also produced. This decomposition is called fission, the breaking of a large nucleus into smaller pieces. The breaking is rather random with the formation of a large number of different products. Fission usually does not occur naturally, but is induced by bombardment with neutrons. The first reported nuclear fission occurred in 1939 when three German scientists, Lise Meitner, Otto Hahn, and Fritz Strassman, bombarded uranium-235 atoms with slow-moving neutrons that split the U-238 nuclei into smaller fragments that consisted of several neutrons and elements near the middle of the periodic table. Since then, fission has been observed in many other isotopes, including most actinide isotopes that have an odd number of neutrons. A typical nuclear fission reaction is shown in Figure **2.8.1**.

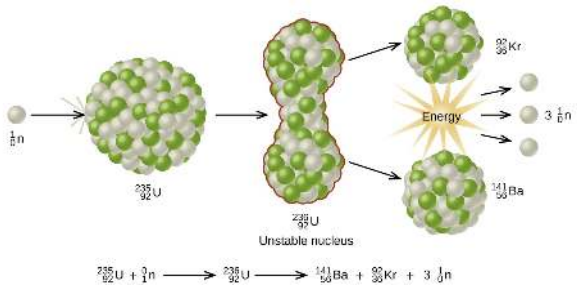


Figure **2.8.1**: When a slow neutron hits a fissionable U-235 nucleus, it is absorbed and forms an unstable U-236 nucleus. The U-236 nucleus then rapidly breaks apart into two smaller nuclei (in this case, Ba-141 and Kr-92) along with several neutrons (usually two or three), and releases a very large amount of energy.

Among the products of Meitner, Hahn, and Strassman's fission reaction were barium, krypton, lanthanum, and cerium, all of which have nuclei that are more stable than uranium-235. Since then, hundreds of different isotopes have been observed among the products of fissionable substances. A few of the many reactions that occur for U-235, and a graph showing the distribution of its fission products and their yields, are shown in Figure **2.8.2**.. Similar fission reactions have been observed with other uranium isotopes, as well as with a variety of other isotopes such as those of plutonium.

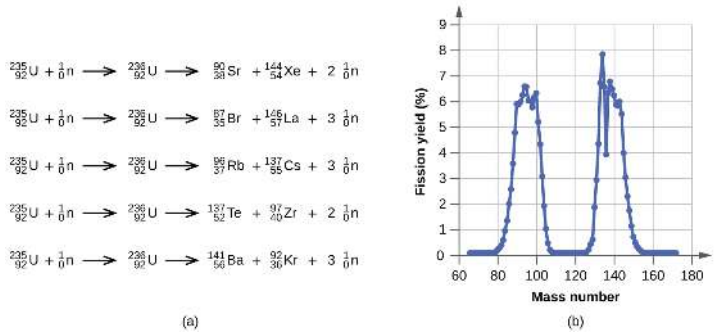


Figure **2.8.2**: (a) Nuclear fission of U-235 produces a range of fission products. (b) The larger fission products of U-235 are typically one isotope with a mass number around 85–105, and another isotope with a mass number that is about 50% larger, that is, about 130–150.

A tremendous amount of energy is produced by the fission of heavy elements. For instance, when one mole of U-235 undergoes fission, the products weigh about 0.2 grams less than the reactants; this "lost" mass is converted into a very large amount of energy, about 1.8×10^{10} kJ per mole of U-235. Nuclear fission reactions produce incredibly large amounts of energy compared to chemical reactions. The fission of 1 kilogram of uranium-235, for example, produces about 2.5 million times as much energy as is produced by burning 1 kilogram of coal.

As described earlier, when undergoing fission U-235 produces two "medium-sized" nuclei, and two or three neutrons. These neutrons may then cause the fission of other uranium-235 atoms, which in turn provide more neutrons that can cause fission of even more nuclei, and so on. If this occurs, we have a nuclear chain reaction (Figure **2.8.3**). On the other hand, if too many neutrons escape the bulk material without interacting with a nucleus, then no chain reaction will occur.

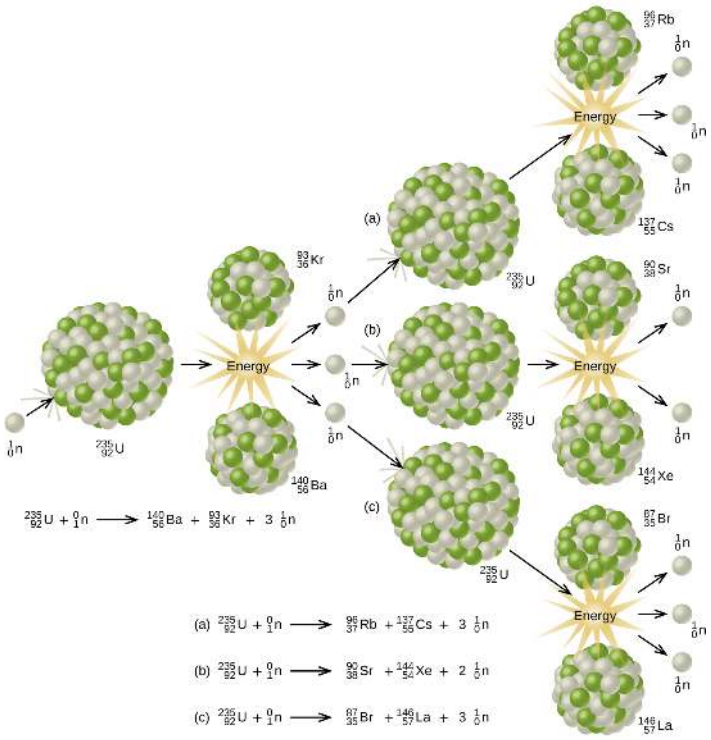


Figure **2.8.3**: The fission of a large nucleus, such as U-235, produces two or three neutrons, each of which is capable of causing fission of another nucleus by the reactions shown. If this process continues, a nuclear chain reaction occurs.

Material that can sustain a nuclear fission chain reaction is said to be fissile or fissionable. (Technically, fissile material can undergo fission with neutrons of any energy, whereas fissionable material requires high-energy neutrons.) Nuclear fission becomes self-sustaining when the number of neutrons produced by fission equals or exceeds the number of neutrons absorbed by splitting nuclei plus the number that escape into the surroundings. The amount of a fissionable material that will support a self-sustaining chain reaction is a critical mass. An amount of fissionable material that cannot sustain a chain reaction is a subcritical mass. An amount of material in which there is an increasing rate of fission is known as a supercritical mass. The critical mass depends on the type of material: its purity, the temperature, the shape of the sample, and how the neutron reactions are controlled (Figure **2.8.4**).

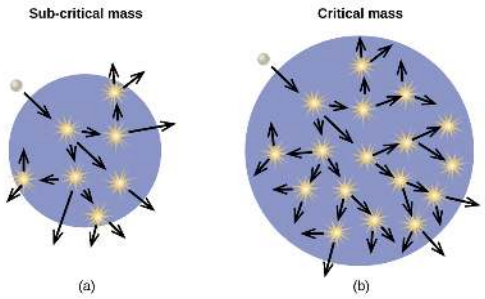


Figure **2.8.4**: (a) In a subcritical mass, the fissile material is too small and allows too many neutrons to escape the material, so a chain reaction does not occur. (b) In a critical mass, a large enough number of neutrons in the fissile material induce fission to create a chain reaction.

An atomic bomb (Figure **2.8.5**) contains several pounds of fissionable material, $^{235}_{92}\mathbf{U}$ or $^{239}_{94}\mathbf{Pu}$, a source of neutrons, and an explosive device for compressing it quickly into a small volume. When fissionable material is in small pieces, the proportion of neutrons that escape through the relatively large surface area is great, and a chain reaction does not take place. When the small pieces of fissionable material are brought together quickly to form a body with a mass larger than the critical mass, the relative number of escaping neutrons decreases, and a chain reaction and explosion result.

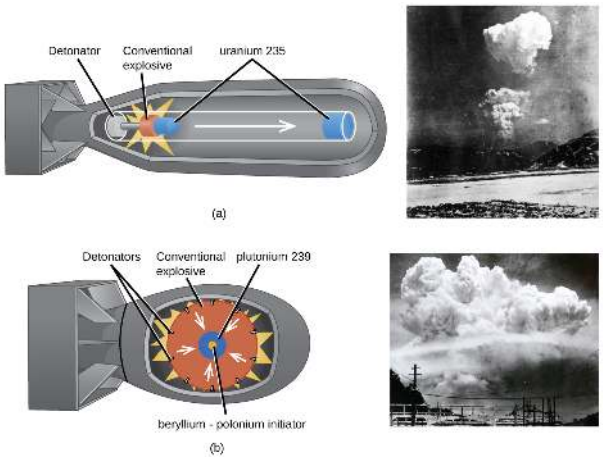


Figure **2.8.5**: (a) The nuclear fission bomb that destroyed Hiroshima on August 6, 1945, consisted of two subcritical masses of U-235, where conventional explosives were used to fire one of the subcritical masses into the other, creating the critical mass for the nuclear explosion. (b) The plutonium bomb that destroyed Nagasaki on August 12, 1945, consisted of a hollow sphere of plutonium that was rapidly compressed by conventional explosives. This led to a concentration of plutonium in the center that was greater than the critical mass necessary for the nuclear explosion.

Fission Reactors

Chain reactions of fissionable materials can be controlled and sustained without an explosion in a nuclear reactor (Figure **2.8.6**). Any nuclear reactor that produces power via the fission of uranium or plutonium by bombardment with neutrons must have at least five components: nuclear fuel consisting of fissionable material, a nuclear moderator, reactor coolant, control rods, and a shield and containment system. We will discuss these components in greater detail later in the section. The reactor works by separating the fissionable nuclear material such that a critical mass cannot be formed, controlling both the flux and absorption of neutrons to allow shutting down the fission reactions. In a nuclear reactor used for the production of electricity, the energy released by fission reactions is trapped as thermal energy and used to boil water and produce steam. The steam is used to turn a turbine, which powers a generator for the production of electricity.

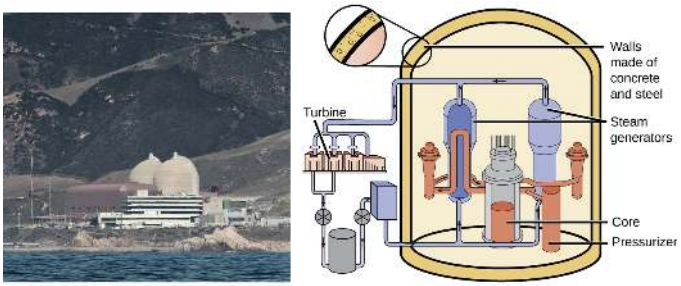


Figure **2.8.6**: (a) The Diablo Canyon Nuclear Power Plant near San Luis Obispo is the only nuclear power plant currently in operation in California. The domes are the containment structures for the nuclear reactors, and the brown building houses the turbine where electricity is generated. Ocean water is used for cooling. (b) The Diablo Canyon uses a pressurized water reactor, one of a few different fission reactor designs in use around the world, to produce electricity. Energy from the nuclear fission reactions in the core heats water in a closed, pressurized system. Heat from this system produces steam that drives a turbine, which in turn produces electricity. (credit a: modification of work by “Mike” Michael L. Baird; credit b: modification of work by the Nuclear Regulatory Commission)

Nuclear Fuels

Nuclear fuel consists of a fissionable isotope, such as uranium-235, which must be present in sufficient quantity to provide a self-sustaining chain reaction. In the United States, uranium ores contain from 0.05–0.3% of the uranium oxide U_3O_8; the uranium in the ore is about 99.3% nonfissionable U-238 with only 0.7% fissionable U-235. Nuclear reactors require a fuel with a higher concentration of U-235 than is found in nature; it is normally enriched to have about 5% of uranium mass as U-235. At this concentration, it is not possible to achieve the supercritical mass necessary for a nuclear explosion. Uranium can be enriched by gaseous diffusion (the only method currently used in the US), using a gas centrifuge, or by laser separation.

In the gaseous diffusion enrichment plant where U-235 fuel is prepared, UF_6 (uranium hexafluoride) gas at low pressure moves through barriers that have holes just barely large enough for UF_6 to pass through. The slightly lighter $^{235}UF_6$ molecules diffuse through the barrier slightly faster than the heavier $^{238}UF_6$ molecules. This process is repeated through hundreds of barriers, gradually increasing the concentration of $^{235}UF_6$ to the level needed by the nuclear reactor. The basis for this process, Graham’s law, is described in the chapter on gases. The enriched UF_6 gas is collected, cooled until it solidifies, and then taken to a fabrication facility where it is made into fuel assemblies. Each fuel assembly consists of fuel rods that contain many

thimble-sized, ceramic-encased, enriched uranium (usually UO_2) fuel pellets. Modern nuclear reactors may contain as many as 10 million fuel pellets. The amount of energy in each of these pellets is equal to that in almost a ton of coal or 150 gallons of oil.

Nuclear Moderators

Neutrons produced by nuclear reactions move too fast to cause fission (Figure **2.8.4**). They must first be slowed to be absorbed by the fuel and produce additional nuclear reactions. A nuclear moderator is a substance that slows the neutrons to a speed that is low enough to cause fission. Early reactors used high-purity graphite as a moderator. Modern reactors in the US exclusively use heavy water ($\mathbf{^2_1H_2O}$) or light water (ordinary H_2O), whereas some reactors in other countries use other materials, such as carbon dioxide, beryllium, or graphite.

Reactor Coolants

A nuclear reactor coolant is used to carry the heat produced by the fission reaction to an external boiler and turbine, where it is transformed into electricity. Two overlapping coolant loops are often used; this counteracts the transfer of radioactivity from the reactor to the primary coolant loop. All nuclear power plants in the US use water as a coolant. Other coolants include molten sodium, lead, a lead-bismuth mixture, or molten salts.

Control Rods

Nuclear reactors use control rods (Figure **2.8.8**) to control the fission rate of the nuclear fuel by adjusting the number of slow neutrons present to keep the rate of the chain reaction at a safe level. Control rods are made of boron, cadmium, hafnium, or other elements that are able to absorb neutrons. Boron-10, for example, absorbs neutrons by a reaction that produces lithium-7 and alpha particles:

$$\mathbf{^{10}_5B + ^1_0n \longrightarrow ^7_3Li + ^4_2He} \tag{2.8.1}$$

When control rod assemblies are inserted into the fuel element in the reactor core, they absorb a larger fraction of the slow neutrons, thereby slowing the rate of the fission reaction and decreasing the power produced. Conversely, if the control rods are removed, fewer neutrons are absorbed, and the fission rate and energy production increase. In an emergency, the chain reaction can be shut down by fully inserting all of the control rods into the nuclear core between the fuel rods.

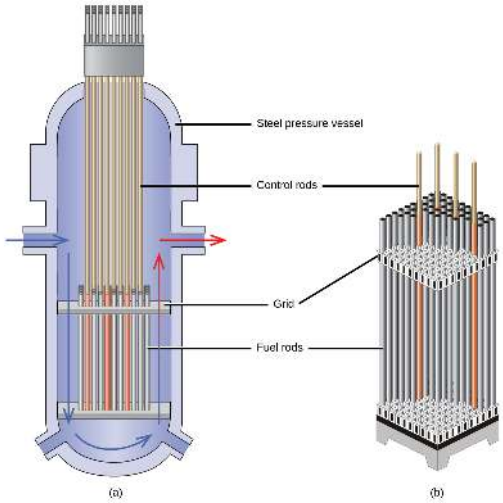


Figure **2.8.7**: The nuclear reactor core shown in (a) contains the fuel and control rod assembly shown in (b). (credit: modification of work by E. Generalic)

Shield and Containment System

During its operation, a nuclear reactor produces neutrons and other radiation. Even when shut down, the decay products are radioactive. In addition, an operating reactor is thermally very hot, and high pressures result from the circulation of water or another coolant through it. Thus, a reactor must withstand high temperatures and pressures, and must protect operating personnel from the radiation. Reactors are equipped with a containment system (or shield) that consists of three parts:

1. The reactor vessel, a steel shell that is 3–20-centimeters thick and, with the moderator, absorbs much of the radiation produced by the reactor
2. A main shield of 1–3 meters of high-density concrete
3. A personnel shield of lighter materials that protects operators from γ rays and X-rays

In addition, reactors are often covered with a steel or concrete dome that is designed to contain any radioactive materials might be released by a reactor accident.



Video* 2.8.1*: *Click here to watch a 3-minute video from the Nuclear Energy Institute on how nuclear reactors work.*

Nuclear power plants are designed in such a way that they cannot form a supercritical mass of fissionable material and therefore cannot create a nuclear explosion. But as history has shown, failures of systems and safeguards can cause catastrophic accidents, including chemical explosions and nuclear meltdowns (damage to the reactor core from overheating). The following Chemistry in Everyday Life feature explores three infamous meltdown incidents.

Nuclear Accidents

The importance of cooling and containment are amply illustrated by three major accidents that occurred with the nuclear reactors at nuclear power generating stations in the United States (Three Mile Island), the former Soviet Union (Chernobyl), and Japan (Fukushima).

In March 1979, the cooling system of the Unit 2 reactor at Three Mile Island Nuclear Generating Station in Pennsylvania failed, and the cooling water spilled from the reactor onto the floor of the containment building. After the pumps stopped, the reactors overheated due to the high radioactive decay heat produced in the first few days after the nuclear reactor shut down. The temperature of the core climbed to at least 2200 °C, and the upper portion of the core began to melt. In addition, the zirconium alloy cladding of the fuel rods began to react with steam and produced hydrogen:

$$\mathrm{Zr}(s) + 2\,\mathrm{H_2O}(g) \longrightarrow \mathrm{ZrO_2}(s) + 2\,\mathrm{H_2}(g) \tag{2.8.2}$$

The hydrogen accumulated in the confinement building, and it was feared that there was danger of an explosion of the mixture of hydrogen and air in the building. Consequently, hydrogen gas and radioactive gases (primarily krypton and xenon) were vented from the building. Within a week, cooling water circulation was restored and the core began to cool. The plant was closed for nearly 10 years during the cleanup process.

Although zero discharge of radioactive material is desirable, the discharge of radioactive krypton and xenon, such as occurred at the Three Mile Island plant, is among the most tolerable. These gases readily disperse in the atmosphere and thus do not produce highly radioactive areas. Moreover, they are noble gases and are not incorporated into plant and animal matter in the food chain. Effectively none of the heavy elements of the core of the reactor were released into the environment, and no cleanup of the area outside of the containment building was necessary (Figure 2.8.8).

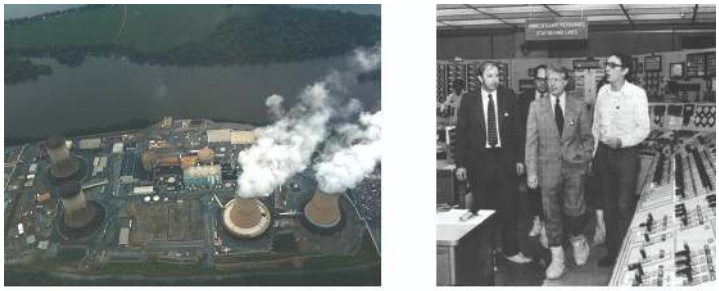


Figure 2.8.8: (a) In this 2010 photo of Three Mile Island, the remaining structures from the damaged Unit 2 reactor are seen on the left, whereas the separate Unit 1 reactor, unaffected by the accident, continues generating power to this day (right). (b) President Jimmy Carter visited the Unit 2 control room a few days after the accident in 1979.

Another major nuclear accident involving a reactor occurred in April 1986, at the Chernobyl Nuclear Power Plant in Ukraine, which was still a part of the former Soviet Union. While operating at low power during an unauthorized experiment with some of its safety devices shut off, one of the reactors at the plant became unstable. Its chain reaction became uncontrollable and increased to a level far beyond what the reactor was designed for. The steam pressure in the reactor rose to between 100 and 500 times the full power pressure and ruptured the reactor. Because the reactor was not enclosed in a containment building, a large amount of radioactive material spewed out, and additional fission products were released, as the graphite (carbon) moderator of the core ignited and burned. The fire was controlled, but over 200 plant workers and firefighters developed acute radiation sickness and at least 32 soon died from the effects of the radiation. It is predicted that about 4000 more deaths will occur among emergency workers and former Chernobyl residents from radiation-induced cancer and leukemia. The reactor has since been encapsulated in steel and concrete, a now-decaying structure known as the sarcophagus. Almost 30 years later, significant radiation problems still persist in the area, and Chernobyl largely remains a wasteland.

In 2011, the Fukushima Daiichi Nuclear Power Plant in Japan was badly damaged by a 9.0-magnitude earthquake and resulting tsunami. Three reactors up and running at the time were shut down automatically, and emergency generators came online to power electronics and coolant systems. However, the tsunami quickly flooded the emergency generators and cut power to the pumps that circulated coolant water through the reactors. High-temperature steam in the reactors reacted with zirconium alloy to produce hydrogen gas. The gas escaped into the containment building, and the mixture of hydrogen and air exploded. Radioactive material was released from the containment vessels as the result of deliberate venting to reduce the hydrogen pressure, deliberate discharge of coolant water into the sea, and accidental or uncontrolled events.

An evacuation zone around the damaged plant extended over 12.4 miles away, and an estimated 200,000 people were evacuated from the area. All 48 of Japan's nuclear power plants were subsequently shut down, remaining shuttered as of December 2014. Since the disaster, public opinion has shifted from largely favoring to largely opposing increasing the use of nuclear power plants, and a restart of Japan's atomic energy program is still stalled (Figure 2.8.10).



Figure 2.8.9: (a) After the accident, contaminated waste had to be removed, and (b) an evacuation zone was set up around the plant in areas that received heavy doses of radioactive fallout. (credit a: modification of work by "Live Action Hero"/Flickr)

The energy produced by a reactor fueled with enriched uranium results from the fission of uranium as well as from the fission of plutonium produced as the reactor operates. As discussed previously, the plutonium forms from the combination of neutrons and the uranium in the fuel. In any nuclear reactor, only about 0.1% of the mass of the fuel is converted into energy. The other 99.9% remains in the fuel rods as fission products and unused fuel. All of the fission products absorb neutrons, and after a period of several months to a few years, depending on the reactor, the fission products must be removed by changing the fuel rods. Otherwise, the concentration of these fission products would increase and absorb more neutrons until the reactor could no longer operate.

Spent fuel rods contain a variety of products, consisting of unstable nuclei ranging in atomic number from 25 to 60, some transuranium elements, including plutonium and americium, and unreacted uranium isotopes. The unstable nuclei and the transuranium isotopes give the spent fuel a dangerously high level of radioactivity. The long-lived isotopes require thousands of years to decay to a safe level. The ultimate fate of the nuclear reactor as a significant source of energy in the United States probably rests on whether or not a politically and scientifically satisfactory technique for processing and storing the components of spent fuel rods can be developed.

Contributors and Attributions

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2.9: Nuclear Fusion

Skills to Develop

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

The process of converting very light nuclei into heavier nuclei is also accompanied by the conversion of mass into large amounts of energy, a process called fusion. The principal source of energy in the sun is a net fusion reaction in which four hydrogen nuclei fuse and produce one helium nucleus and two positrons. This is a net reaction of a more complicated series of events:

$$\underbrace{4{}_1^1\mathrm{H}}_{4\times 1.00794\ u} \longrightarrow \underbrace{{}_2^4\mathrm{He}}_{4.0012\ u} + \underbrace{2{}_1^0\beta^+}_{2\times 0.0005487\ u} \tag{2.9.1}$$

A helium nucleus has a mass that is 0.7% less than that of four hydrogen nuclei; this lost mass is converted into thermal energy during the fusion via Einstein's $E = mc^2$ equation. This reaction produces about 3.6×10^{11} kJ of energy per mole of ${}_2^4\mathrm{He}$ produced. This is somewhat larger than the energy produced by the nuclear fission of one mole of ${}^{235}\mathrm{U}$ (1.8×10^{10} kJ), and over **3 million times larger** than the energy produced by the (chemical) combustion of one mole of octane ($\Delta H = -5471\ kJ$):

$$2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O \tag{2.9.2}$$

It has been determined that the nuclei of the heavy isotopes of hydrogen, a deuteron, ${}_1^2\mathrm{H}$ and a triton, ${}_1^3\mathrm{H}$, undergo fusion at extremely high temperatures (thermonuclear fusion). They form a helium nucleus and a neutron:

$${}_1^2\mathrm{H} + {}_1^3\mathrm{H} \longrightarrow {}_2^4\mathrm{He} + 2{}_0^1\mathrm{n} \tag{2.9.3}$$

This change proceeds with a mass loss of 0.0188 amu, corresponding to the release of 1.69×10^9 kilojoules per mole of ${}_2^4\mathrm{He}$ formed. The very high temperature is necessary to give the nuclei enough kinetic energy to overcome the very strong repulsive forces resulting from the positive charges on their nuclei so they can collide.

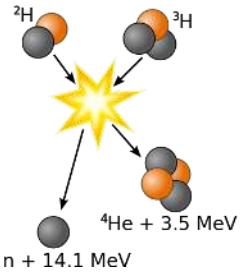


Figure **2.9.1**: Fusion of deuterium with tritium creating helium-4, freeing a neutron, and releasing 17.59 MeV of energy, as an appropriate amount of mass changing forms to appear as the kinetic energy of the products, in agreement with kinetic $E = \Delta mc^2$, where Δm is the change in rest mass of particles.[Image use with permission via Wikipedia (Wykis)

The most important fusion process in nature is the one that powers stars. In the 20th century, it was realized that the energy released from nuclear fusion reactions accounted for the longevity of the Sun and other stars as a source of heat and light. The fusion of nuclei in a star, starting from its initial hydrogen and helium abundance, provides that energy and synthesizes new nuclei as a byproduct of that fusion process. The prime energy producer in the Sun is the fusion of hydrogen to form helium, which occurs at a solar-core temperature of 14 million kelvin. The net result is the fusion of four protons into one alpha particle, with the release of two positrons, two neutrinos (which changes two of the protons into neutrons), and energy (Figure **2.9.2**).

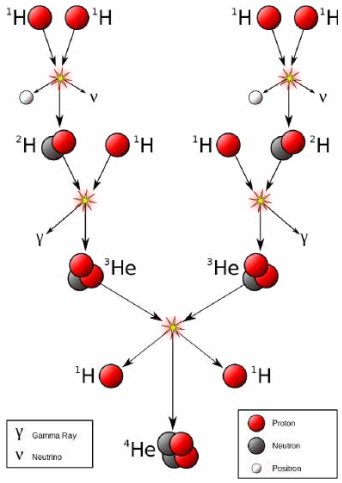


Figure **2.9.2**: (left) The Sun is a main-sequence star, and thus generates its energy by nuclear fusion of hydrogen nuclei into helium. In its core, the Sun fuses 620 million metric tons of hydrogen each second. (right) The proton-proton chain dominates in stars the size of the Sun or smaller.

Example 2.9.1

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

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

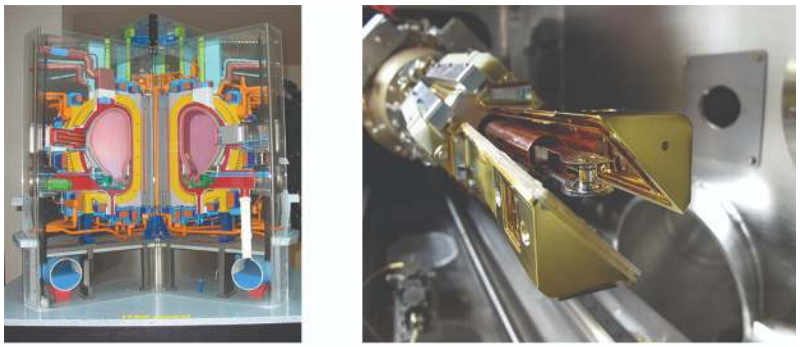
Discuss your results.

a. *Q*a = 3 * 4.0026 - 12.000) amu * (1.4924E-10 J/amu)
= 1.17E-12 J
b. *Q*b = (6*(1.007825 + 1.008665) - 12.00000) amu * (1.4924E-10 J/amu)
= 1.476E-11 J
c. *Q*c = 6*2.014102 - 12.00000 amu * (1.4924E-10 J/amu)
= 1.263E-11 J

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

Nuclear Reactors

Useful fusion reactions require very high temperatures for their initiation—about 15,000,000 K or more. At these temperatures, all molecules dissociate into atoms, and the atoms ionize, forming plasma. These conditions occur in an extremely large number of locations throughout the universe—stars are powered by fusion. Humans have already figured out how to create temperatures high enough to achieve fusion on a large scale in thermonuclear weapons. A thermonuclear weapon such as a hydrogen bomb contains a nuclear fission bomb that, when exploded, gives off enough energy to produce the extremely high temperatures necessary for fusion to occur.



(a) (b)

Figure **2.9.3**: (a) This model is of the International Thermonuclear Experimental Reactor (ITER) reactor. Currently under construction in the south of France with an expected completion date of 2027, the ITER will be the world's largest experimental Tokamak nuclear fusion reactor with a goal of achieving large-scale sustained energy production. (b) In 2012, the National Ignition Facility at Lawrence Livermore National Laboratory briefly produced over 500,000,000,000 watts (500 terawatts, or 500 TW) of peak power and delivered 1,850,000 joules (1.85 MJ) of energy, the largest laser energy ever produced and 1000 times the power usage of the entire United States in any given moment. Although lasting only a few billionths of a second, the 192 lasers attained the conditions needed for nuclear fusion ignition. This image shows the target prior to the laser shot. (credit a: modification of work by Stephan Mosel)

Another much more beneficial way to create fusion reactions is in a fusion reactor, a nuclear reactor in which fusion reactions of light nuclei are controlled. Because no solid materials are stable at such high temperatures, mechanical devices cannot contain the plasma in which fusion reactions occur. Two techniques to contain plasma at the density and temperature necessary for a fusion reaction are currently the focus of intensive research efforts: containment by a magnetic field and by the use of focused laser beams (Figure **2.9.3**). A number of large projects are working to attain one of the biggest goals in science: getting hydrogen fuel to ignite and produce more energy than the amount supplied to achieve the extremely high temperatures and pressures that are required for fusion. At the time of this writing, there are no self-sustaining fusion reactors operating in the world, although small-scale controlled fusion reactions have been run for very brief periods.

Contributors

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2.10: Nuclear Chemistry (Exercises)

21.1: Radioactivity

Q21.1.1

Why are many radioactive substances warm to the touch? Why do many radioactive substances glow?

Q21.1.2

Describe the differences between nonionizing and ionizing radiation in terms of the intensity of energy emitted and the effect each has on an atom or molecule after collision. Which nuclear decay reactions are more likely to produce ionizing radiation? nonionizing radiation?

Q21.1.3

Would you expect nonionizing or ionizing radiation to be more effective at treating cancer? Why?

S21.1.3

Ionizing radiation is higher in energy and causes greater tissue damage, so it is more likely to destroy cancerous cells.

Q21.1.4

Historically, concrete shelters have been used to protect people from nuclear blasts. Comment on the effectiveness of such shelters.

Q21.1.5

Gamma rays are a very high-energy radiation, yet α particles inflict more damage on biological tissue. Why?

Q21.1.6

List the three primary sources of naturally occurring radiation. Explain the factors that influence the dose that one receives throughout the year. Which is the largest contributor to overall exposure? Which is the most hazardous?

S21.1.6

Three primary naturally occurring radiations are radium, uranium and thorium, each all having long half lives. Inhalation of air, ingestion of food and water,terrestrial radation from the ground and cosmic radiation from space are all factors tat influence the does that a person receives throughout the year. Inhalation of the air is the largest contributor to exposure. Radiation can damage DNA or kill cells. When radiation is exposed to your body, it will collide with atoms and this will change and damage your DNA.

Q21.1.7

Because radon is a noble gas, it is inert and generally unreactive. Despite this, exposure to even low concentrations of radon in air is quite dangerous. Describe the physical consequences of exposure to radon gas. Why are people who smoke more susceptible to these effects?

Q21.1.8

Most medical imaging uses isotopes that have extremely short half-lives. These isotopes usually undergo only one kind of nuclear decay reaction. Which kind of decay reaction is usually used? Why? Why would a short half-life be preferred in these cases?

Beta decay. Alfa decay can be easily stopped by paper, which means it can not be used to see inside people's body. Also, Gamma rays are really dangerous for human, that even a short period of time exploding to it will have negative effect on human body. Thus, Beta decay is the perfect choice. It can be used to see through human's body and stopped by aluminum or some other metals.

Since all these radioactive decays are harmful for human body, if the half time of these reactions are short, the time exploding to these reactions will be short too.

Q21.1.9

Which would you prefer: one exposure of 100 rem, or 10 exposures of 10 rem each? Explain your rationale.

S21.1.9

Ten exposures of 10 rem are less likely to cause major damage.

Q21.1.10

A 2.14 kg sample of rock contains 0.0985 g of uranium. How much energy is emitted over 25 yr if 99.27% of the uranium is ^{238}U, which has a half-life of 4.46×10^9 yr, if each decay event is accompanied by the release of 4.039 MeV? If a 180 lb individual absorbs all of the emitted radiation, how much radiation has been absorbed in rads?

Q21.1.11

There is a story about a “radioactive boy scout” who attempted to convert thorium-232, which he isolated from about 1000 gas lantern mantles, to uranium-233 by bombarding the thorium with neutrons. The neutrons were generated via bombarding an aluminum target with α particles from the decay of americium-241, which was isolated from 100 smoke detectors. Write balanced nuclear reactions for these processes. The “radioactive boy scout” spent approximately 2 h/day with his experiment for 2 yr. Assuming that the alpha emission of americium has an energy of 5.24 MeV/particle and that the americium-241 was undergoing 3.5×10^6 decays/s, what was the exposure of the 60.0 kg scout in rads? The intrepid scientist apparently showed no ill effects from this exposure. Why?

241/95 Am---> 4/2 He + 237/93Np---> 4/2He + 233/91Pa----> 1/0n+ 232/91Th---> 1/1 H + 233/92 U

By adding alpha particles to the products side of the reaction, he was able to reduce the mass number by 4 and the atomic number by 2 to get the products he wanted. Bombardment with neutrons and 1 H was required to lower to the mass number to get Th and then raise both the mass number and the atomic number to yield Uranium.

2 hours*365*2= 1460 hours of exposure.*60min/1hr*60s/1min= 5.26*10^6s of exposure

1MeV= (1.6022*10^-13 Joules) * (5.24 MeV/particle)*2 particles= 1.679*10^-12 Joules.

(1.679*10^-12 Joules) * (1 amu/ 1.4924*10^-10 Joules)= 2.51*10^-13 amu

E=mc^2

E=(2.51*10^-13 amu)(1.66*10^-22kg/amu)(2.9998*10^8m/s)^2= (3.75*10^-18 kgm^2/s)*(3.5*10^6 decays/s)= 1.31*10^-11 joules of exposure per second.

The scientist showed no ill effects from this exposure because if we multiple the energy in joules of exposure per second, 1.31*10^-11, by the total amount of seconds of exposure, 5.26*10^6s, we find that he was only exposed to 6.9*10^-5 joules of radiation throughout the span of two years. This is a very small amount of radiation for such a long span of time.

In order to plug in the values for this equation, we must convert the given MeV to Joules with the known conversion rate. Similarly, we must convert Joules to amu with another known conversion rate. Then we can plug in the values and multiply by c^2 but we must not forget to multiple the amu by the conversion rate to kg in order to yield Joules. After all of this is done, we multiple the amount of Joules of exposure per second by the total amount of exposure in seconds in order to find out the total amount of exposure over the two year span.

21.2: Patterns of Nuclear Stability

Q21.2.1

How do chemical reactions compare with nuclear reactions with respect to mass changes? Does either type of reaction violate the law of conservation of mass? Explain your answers.

Q21.2.2

Why is the amount of energy released by a nuclear reaction so much greater than the amount of energy released by a chemical reaction?

Q21.2.3

Explain why the mass of an atom is less than the sum of the masses of its component particles.

Q21.2.4

The stability of a nucleus can be described using two values. What are they, and how do they differ from each other?

Q21.2.5

In the days before true chemistry, ancient scholars (alchemists) attempted to find the philosopher's stone, a material that would enable them to turn lead into gold. Is the conversion of Pb → Au energetically favorable? Explain why or why not.

Q21.2.6

Describe the energy barrier to nuclear fusion reactions and explain how it can be overcome.

Q21.2.7

Imagine that the universe is dying, the stars have burned out, and all the elements have undergone fusion or radioactive decay. What would be the most abundant element in this future universe? Why?

Q21.2.8

Numerous elements can undergo fission, but only a few can be used as fuels in a reactor. What aspect of nuclear fission allows a nuclear chain reaction to occur?

Q21.2.9

How are transmutation reactions and fusion reactions related? Describe the main impediment to fusion reactions and suggest one or two ways to surmount this difficulty.

Q21.2.10

Using the information provided in Chapter 33, complete each reaction and calculate the amount of energy released from each in kilojoules.

a. $^{238}\text{Pa} \rightarrow ? + \beta^-$
b. $^{216}\text{Fr} \rightarrow ? + \alpha$
c. $^{199}\text{Bi} \rightarrow ? + \beta^+$

Q21.2.22

Using the information provided in Chapter 33, complete each reaction and calculate the amount of energy released from each in kilojoules.

a. $^{194}\text{Tl} \rightarrow ? + \beta^+$
b. $^{171}\text{Pt} \rightarrow ? + \alpha$
c. $^{214}\text{Pb} \rightarrow ? + \beta^-$

Q21.2.23

Using the information provided in Chapter 33, complete each reaction and calculate the amount of energy released from each in kilojoules per mole.

a. $^{234}_{91}\mathrm{Pa} \rightarrow ? + {}^{0}_{-1}\beta$
b. $^{226}_{88}\mathrm{Ra} \rightarrow ? + {}^{4}_{2}\alpha$

Q21.2.24

Using the information provided in Chapter 33, complete each reaction and then calculate the amount of energy released from each in kilojoules per mole.

a. $^{60}_{27}\mathrm{Co} \rightarrow ? + {}^{0}_{-1}\beta$ (The mass of cobalt-60 is 59.933817 amu.)
b. technicium-94 (mass = 93.909657 amu) undergoing fission to produce chromium-52 and potassium-40

Q21.2.25

Using the information provided in Chapter 33, predict whether each reaction is favorable and the amount of energy released or required in megaelectronvolts and kilojoules per mole.

a. the beta decay of bismuth-208 (mass = 207.979742 amu)
b. the formation of lead-206 by alpha decay

Q21.2.26

Using the information provided, predict whether each reaction is favorable and the amount of energy released or required in megaelectronvolts and kilojoules per mole.

a. alpha decay of oxygen-16
b. alpha decay to produce chromium-52

Q21.2.27

Calculate the total nuclear binding energy (in megaelectronvolts) and the binding energy per nucleon for ^{87}Sr if the measured mass of ^{87}Sr is 86.908877 amu.

a. the calculated mass
b. the mass defect
c. the nuclear binding energy
d. the nuclear binding energy per nucleon

Q21.2.30

The experimentally determined mass of ^{29}S is 28.996610 amu. Find each of the following.

a. the calculated mass
b. the mass defect
c. the nuclear binding energy
d. the nuclear binding energy per nucleon

Q21.2.31

Calculate the amount of energy that is released by the neutron-induced fission of ^{235}U to give ^{141}Ba, ^{92}Kr (mass = 91.926156 amu), and three neutrons. Report your answer in electronvolts per atom and kilojoules per mole.

Q21.2.31

Calculate the amount of energy that is released by the neutron-induced fission of ^{235}U to give ^{90}Sr, ^{143}Xe, and three neutrons. Report your answer in electronvolts per atom and kilojoules per mole.

Q21.2.33

Calculate the amount of energy released or required by the fusion of helium-4 to produce the unstable beryllium-8 (mass = 8.00530510 amu). Report your answer in kilojoules per mole. Do you expect this to be a spontaneous reaction?

Q21.2.34

Calculate the amount of energy released by the fusion of ^{6}Li and deuterium to give two helium-4 nuclei. Express your answer in electronvolts per atom and kilojoules per mole.

Q21.2.35

How much energy is released by the fusion of two deuterium nuclei to give one tritium nucleus and one proton? How does this amount compare with the energy released by the fusion of a deuterium nucleus and a tritium nucleus, which is accompanied by ejection of a neutron? Express your answer in megaelectronvolts and kilojoules per mole. Pound for pound, which is a better choice for a fusion reactor fuel mixture?

Numerical Answers

1

a. $^{238}_{91}\mathrm{Pa} \rightarrow {}^{238}_{92}\mathrm{U} + {}^{0}_{-1}\beta$; -5.540×10^{-16} kJ
b. $^{216}_{87}\mathrm{Fr} \rightarrow {}^{212}_{85}\mathrm{At} + {}^{4}_{2}\alpha$; -1.470×10^{-15} kJ
c. $^{199}_{83}\mathrm{Bi} \rightarrow {}^{199}_{82}\mathrm{Pb} + {}^{0}_{+1}\beta$; -5.458×10^{-16} kJ

3.

a. $^{234}_{91}\mathrm{Pa} \rightarrow {}^{234}_{92}\mathrm{U} + {}^{0}_{-1}\beta$; 2.118×10^{8} kJ/mol
b. $^{226}_{88}\mathrm{Ra} \rightarrow {}^{222}_{86}\mathrm{Rn} + {}^{4}_{2}\alpha$; 4.700×10^{8} kJ/mol

5.

a. The beta decay of bismuth-208 to polonium is endothermic (ΔE = 1.400 MeV/atom, 1.352×10^{8} kJ/mol).
b. The formation of lead-206 by alpha decay of polonium-210 is exothermic (ΔE = −5.405 MeV/atom, -5.218×10^{8} kJ/mol).

7. 757 MeV/atom, 8.70 MeV/nucleon

9.

a. 53.438245 amu
b. 0.496955 amu
c. 463 MeV/atom
d. 8.74 MeV/nucleon

11. −173 MeV/atom; 1.67×10^{10} kJ/mol

13. $\Delta E = +9.0 \times 10^{6}$ kJ/mol beryllium-8; no

15. D–D fusion: ΔE = −4.03 MeV/tritium nucleus formed = -3.89×10^{8} kJ/mol tritium; D–T fusion: ΔE = −17.6 MeV/tritium nucleus = -1.70×10^{9} kJ/mol; D–T fusion

21.3: Nuclear Transmutations

Q21.3.1

Why do scientists believe that hydrogen is the building block of all other elements? Why do scientists believe that helium-4 is the building block of the heavier elements?

Q21.3.2

How does a star produce such enormous amounts of heat and light? How are elements heavier than Ni formed?

Q21.3.3

Propose an explanation for the observation that elements with even atomic numbers are more abundant than elements with odd atomic numbers.

S21.3.3

The raw material for all elements with Z > 2 is helium (Z = 2), and fusion of helium nuclei will always produce nuclei with an even number of protons.

Q21.3.4

During the lifetime of a star, different reactions that form different elements are used to power the fusion furnace that keeps a star "lit." Explain the different reactions that dominate in the different stages of a star's life cycle and their effect on the temperature of the star.

Q21.3.5

A line in a popular song from the 1960s by Joni Mitchell stated, "We are stardust…." Does this statement have any merit or is it just poetic? Justify your answer.

Q21.3.6

If the laws of physics were different and the primary element in the universe were boron-11 (Z = 5), what would be the next four most abundant elements? Propose nuclear reactions for their formation.

Q21.3.7

Write a balanced nuclear reaction for the formation of each isotope.

a. ^{27}Al from two ^{12}C nuclei
b. ^{9}Be from two ^{4}He nuclei

Q21.3.8

At the end of a star's life cycle, it can collapse, resulting in a supernova explosion that leads to the formation of heavy elements by multiple neutron-capture events. Write a balanced nuclear reaction for the formation of each isotope during such an explosion.

a. ^{106}Pd from nickel-58
b. selenium-79 from iron-56

Q21.3.9

When a star reaches middle age, helium-4 is converted to short-lived beryllium-8 (mass = 8.00530510 amu), which reacts with another helium-4 to produce carbon-12. How much energy is released in each reaction (in megaelectronvolts)? How many atoms of helium must be "burned" in this process to produce the same amount of energy obtained from the fusion of 1 mol of hydrogen atoms to give deuterium?

21.4: Rates of Radioactive Decay

Q21.4.1

What do chemists mean by the half-life of a reaction?

Q21.4.2

If a sample of one isotope undergoes more disintegrations per second than the same number of atoms of another isotope, how do their half-lives compare?

Q21.4.3

Half-lives for the reaction A + B → C were calculated at three values of $[A]_0$, and [B] was the same in all cases. The data are listed in the following table:

$[A]_0$ (M)	$t_{½}$ (s)
0.50	420
0.75	280
1.0	210

Does this reaction follow first-order kinetics? On what do you base your answer?

S21.4.3

1. No; the reaction is second order in A because the half-life decreases with increasing reactant concentration according to $t_{1/2} = 1/k[A_0]$.

Q21.4.4

Ethyl-2-nitrobenzoate ($NO_2C_6H_4CO_2C_2H_5$) hydrolyzes under basic conditions. A plot of $[NO_2C_6H_4CO_2C_2H_5]$ versus t was used to calculate $t½$, with the following results:

$[NO_2C_6H_4CO_2C_2H_5]$ (M/cm^3)	$t_{½}$ (s)
0.050	240
0.040	300
0.030	400

Is this a first-order reaction? Explain your reasoning.

Q21.4.5

Azomethane ($CH_3N_2CH_3$) decomposes at 600 K to C_2H_6 and N_2. The decomposition is first order in azomethane. Calculate $t½$ from the data in the following table:

Time (s)	$P_{CH_3N_2CH_3}$ (atm)
0	8.2×10^{-2}
2000	3.99×10^{-2}
4000	1.94×10^{-2}

How long will it take for the decomposition to be 99.9% complete?

S21.4.5

$t_{1/2} = 1.92 \times 10^3$ s or 1920 s; 19100 s or 5.32 hrs.

Q21.4.6

The first-order decomposition of hydrogen peroxide has a half-life of 10.7 h at 20°C. What is the rate constant (expressed in s^{-1}) for this reaction? If you started with a solution that was 7.5×10^{-3} M H_2O_2, what would be the initial rate of decomposition (M/s)? What would be the concentration of H_2O_2 after 3.3 h?

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CHAPTER OVERVIEW

3: Physical Properties of Gases

Here, 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.

3.1: Properties of Gases
3.2: Gas Pressure
3.3: Relationships among Pressure, Temperature, Volume, and Amount
3.4: 6.4 The Ideal Gas Law
3.5: 6.5 Mixtures of Gases
3.6: Gas Volumes and Stoichiometry
3.7: Kinetic Molecular Theory of Gases
3.8: Connecting Gas Properties to Kinetic Molecular Theory
3.9: Chapter Problems

Thumbnail: Motion of gas molecules. The randomized thermal vibrations of fundamental particles such as atoms and molecules—gives a substance its "kinetic temperature." Here, the size of helium atoms relative to their spacing is shown to scale under 1950 atmospheres of pressure. (CC BY-SA 3.0; Greg L).

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3.1: Properties 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 **3.1.1** compares the three states of matter and illustrates the differences at the molecular level.

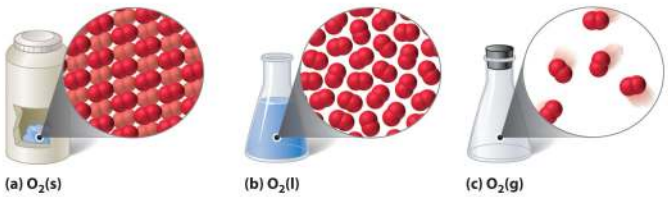


Figure **3.1.1**: A Diatomic Substance (O_2) in the Solid, Liquid, and Gaseous States: (a) Solid O_2 has a fixed volume and shape, and the molecules are packed tightly together. (b) Liquid O_2 conforms to the shape of its container but has a fixed volume; it contains relatively densely packed molecules. (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 **3.1.1**.

Table **3.1.1**: Properties of Water at 1.0 atm

Temperature	State	Density (g/cm^3)
≤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 **3.1.2** 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.

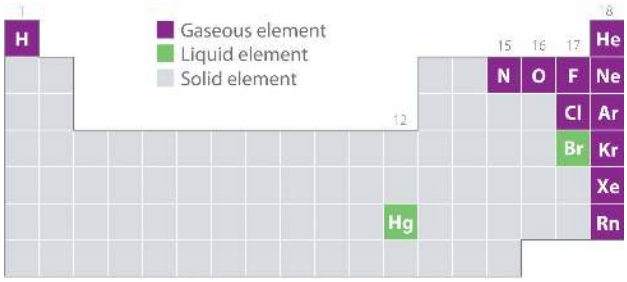


Figure **3.1.2**: Elements That Occur Naturally as Gases, Liquids, and Solids at 25°C and 1 atm. The noble gases and mercury occur as monatomic species, whereas all other gases and bromine are diatomic molecules.

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.



Defining Gas Pressure: https://youtu.be/_CRn3cFs2CI

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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3.2: Gas Pressure

Learning Objectives

- to describe and measure the pressure of a gas.

At the macroscopic level, a complete physical description of a sample of a gas requires four quantities:

- ***temperature*** (expressed in kelvins),
- ***volume*** (expressed in liters),
- ***amount*** (expressed in moles), and
- ***pressure*** (in atmospheres).

As we demonstrated below, these variables are *not* independent (i.e., they cannot be arbitrarily be varied). If we know the values of any *three* of these quantities, we can calculate the fourth and thereby obtain a full physical description of the gas. Temperature, volume, and amount have been discussed in previous chapters. We now discuss pressure and its units of measurement.

Units of Pressure

Any object, whether it is your computer, a person, or a sample of gas, exerts a force on any surface with which it comes in contact. The air in a balloon, for example, exerts a force against the interior surface of the balloon, and a liquid injected into a mold exerts a force against the interior surface of the mold, just as a chair exerts a force against the floor because of its mass and the effects of gravity. If the air in a balloon is heated, the increased kinetic energy of the gas eventually causes the balloon to burst because of the increased pressure (P) of the gas, the force (F) per unit area (A) of surface:

$$P = \frac{\text{Force}}{\text{Area}} = \frac{F}{A} \tag{3.2.1}$$

Pressure is dependent on *both* the force exerted *and* the size of the area to which the force is applied. We know from Equation 3.2.1 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):

$$1\ \text{Pa} = 1\ \text{N/m}^2 \tag{3.2.2}$$

Example 3.2.1

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 3.2.1 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 3.2.1

What pressure does a 60.0 kg student exert on the floor

a. when standing flat-footed in the laboratory in a pair of tennis shoes (the surface area of the soles is approximately 180 cm^2)?
b. as she steps heel-first onto a dance floor wearing high-heeled shoes (the area of the heel = 1.0 cm^2)?

Answer a

3.27×10^4 Pa

Answer b

5.9×10^6 Pa

Barometric Pressure

Just as we exert pressure on a surface because of gravity, so does our atmosphere. We live at the bottom of an ocean of gases that becomes progressively less dense with increasing altitude. Approximately 99% of the mass of the atmosphere lies within 30 km of Earth's surface (Figure **3.2.1**). 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:

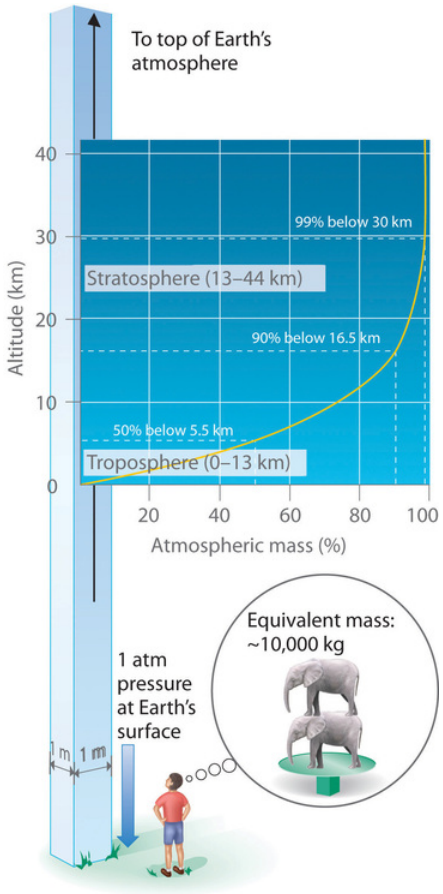


Figure **3.2.1**: Barometric Pressure. Each square meter of Earth's surface supports a column of air that is more than 200 km high and weighs about 10,000 kg at Earth's surface.

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 **3.2.2**). 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:

$$P = \frac{F}{A} \tag{3.2.3}$$

$$= \frac{mg}{A} \tag{3.2.4}$$

$$= \frac{\rho V \cdot g}{A} \tag{3.2.5}$$

$$= \frac{\rho \cdot Ah \cdot g}{A} \tag{3.2.6}$$

$$= \rho gh \tag{3.2.7}$$

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 **3.2.2**. 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.

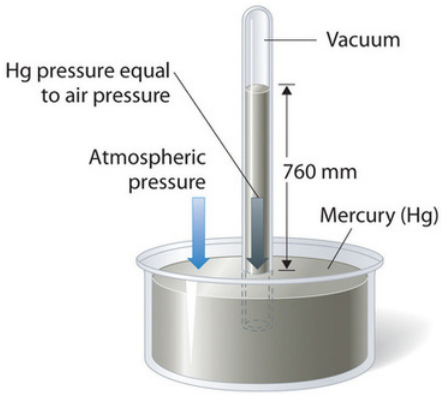


Figure **3.2.2**: A Mercury Barometer. The pressure exerted by the atmosphere on the surface of the pool of mercury supports a column of mercury in the tube that is about 760 mm tall. Because the boiling point of mercury is quite high (356.73°C), there is very little mercury vapor in the space above 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:

$$1\ \text{atm} = 760\ mmHg \tag{3.2.8}$$
$$= 760\ torr \tag{3.2.9}$$
$$= 1.01325 \times 10^5\ Pa \tag{3.2.10}$$
$$= 101.325\ kPa \tag{3.2.11}$$

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 3.2.2: 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 3.2.11 to convert from millimeters of mercury to atmospheres and kilopascals.

Solution:

From Equation 3.2.11, we have 1 atm = 760 mmHg = 101.325 kPa. The pressure at 14,000 ft in atm is thus

$$P = 454 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} \tag{3.2.12}$$
$$= 0.597 \text{ atm}$$

The pressure in bar is given by

$$P = 0.597 \text{ atm} \times \frac{1.01325 \text{ bar}}{1 \text{ atm}} \tag{3.2.13}$$
$$= 0.605 \text{ bar}$$

? Exercise 3.2.2: Barometric Pressure

Mt. Everest, at 29,028 ft above sea level, is the world's tallest mountain. The normal barometric pressure at this altitude is about 0.308 atm. Convert this pressure to

a. millimeters of mercury.
b. bar.

Answer a

234 mmHg;

Answer b

0.312 bar

Manometers

Barometers measure barometric pressure, but manometers measure the pressures of samples of gases contained in an apparatus. The key feature of a manometer is a U-shaped tube containing mercury (or occasionally another nonvolatile liquid). A closed-end manometer is shown schematically in part (a) in Figure **3.2.3**. 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.

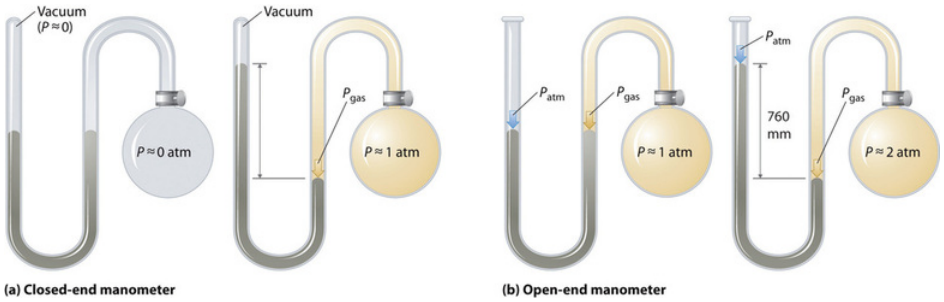


Figure **3.2.3**: The Two Types of Manometer. (a) In a closed-end manometer, the space above the mercury column on the left (the reference arm) is essentially a vacuum ($P \approx 0$), and the difference in the heights of the two columns gives the pressure of the gas contained in the bulb directly. (b) 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 **3.2.3**, 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 3.2.3

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 3.2.3

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 **3.2.3** also tells us the maximum depth of a farmer's well if a simple suction pump will be used to get the water out. The 1.00 atm corresponds to a column height of

$$\begin{aligned} h_{\text{wat}} &= h_{\text{Hg}} \times \frac{d_{\text{Hg}}}{g_{\text{wat}}} \\ &= 760\ \text{mm} \times \frac{13.53\ \text{g/cm}^3}{1.00\ \text{g/cm}^3} \\ &= 1.03 \times 10^4\ mm \\ &= 10.3\ m \end{aligned}$$

A suction pump is just a more sophisticated version of a straw: it creates a vacuum above a liquid and relies on barometric pressure to force the liquid up a tube. If 1 atm pressure corresponds to a 10.3 m (33.8 ft) column of water, then it is physically impossible for barometric pressure to raise the water in a well higher than this. Until electric pumps were invented to push water mechanically from greater depths, this factor greatly limited where people could live because obtaining water from wells deeper than about 33 ft was difficult.

Summary

Pressure is defined as the force exerted per unit area; it can be measured using a barometer or manometer. Four quantities must be known for a complete physical description of a sample of a gas: *temperature*, *volume*, *amount*, and *pressure*. **Pressure** is force per unit area of surface; the SI unit for pressure is the **pascal (Pa)**, defined as 1 newton per square meter (N/m^2). The pressure exerted by an object is proportional to the force it exerts and inversely proportional to the area on which the force is exerted. The pressure exerted by Earth's atmosphere, called *barometric pressure*, is about 101 kPa or 14.7 $lb/in.^2$ at sea level. barometric pressure can be measured with a **barometer**, a closed, inverted tube filled with mercury. The height of the mercury column is proportional to barometric pressure, which is often reported in units of **millimeters of mercury (mmHg)**, also called **torr**. **Standard barometric pressure**, the pressure required to support a column of mercury 760 mm tall, is yet another unit of pressure: 1 **atmosphere (atm)**. A **manometer** is an apparatus used to measure the pressure of a sample of a gas.



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3.3: Relationships among Pressure, Temperature, Volume, and Amount

Learning Objectives

- To understand the relationships among pressure, temperature, volume, and the amount of a gas.

Early scientists explored the relationships among the pressure of a gas (*P*) and its temperature (*T*), volume (*V*), and amount (*n*) by holding two of the four variables constant (amount and temperature, for example), varying a third (such as pressure), and measuring the effect of the change on the fourth (in this case, volume). The history of their discoveries provides several excellent examples of the scientific method.

The Relationship between Pressure and Volume: Boyle's Law

As the pressure on a gas increases, the volume of the gas decreases because the gas particles are forced closer together. Conversely, as the pressure on a gas decreases, the gas volume increases because the gas particles can now move farther apart. Weather balloons get larger as they rise through the atmosphere to regions of lower pressure because the volume of the gas has increased; that is, the atmospheric gas exerts less pressure on the surface of the balloon, so the interior gas expands until the internal and external pressures are equal.

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 **3.3.1**. 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 **3.3.2**). A simple plot of V versus P gives a curve called a hyperbola and reveals an inverse relationship between pressure and volume: as the pressure is doubled, the volume decreases by a factor of two. This relationship between the two quantities is described as follows:

$$PV = \text{constant} \tag{3.3.1}$$

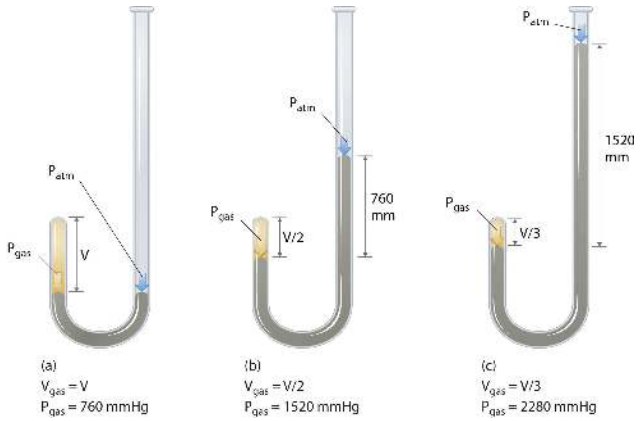


Figure **3.3.1**: Boyle's Experiment Using a J-Shaped Tube to Determine the Relationship between Gas Pressure and Volume. (a) Initially the gas is at a pressure of 1 atm = 760 mmHg (the mercury is at the same height in both the arm containing the sample and the arm open to the atmosphere); its volume 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.

Dividing both sides by P gives an equation illustrating the inverse relationship between P and V:

$$V = \frac{\text{const.}}{P} = \text{const.}\left(\frac{1}{P}\right) \tag{3.3.2}$$

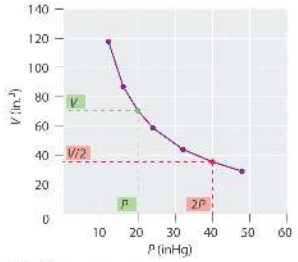
or

$$V \propto \frac{1}{P} \tag{3.3.3}$$

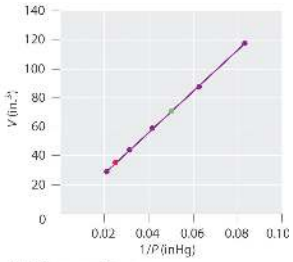
where the ∝ symbol is read “is proportional to.” A plot of V versus $1/P$ is thus a straight line whose slope is equal to the constant in Equation 6.2.1 and Equation 6.2.3. Dividing both sides of Equation 6.2.1 by V instead of P gives a similar relationship between P and $1/V$. The numerical value of 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.*

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 **3.3.2**: 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.



Boyle’s Law: https://youtu.be/lu86VSupPO4

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 **3.3.3**).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 **3.3.3** 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 **3.3.3**, 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.

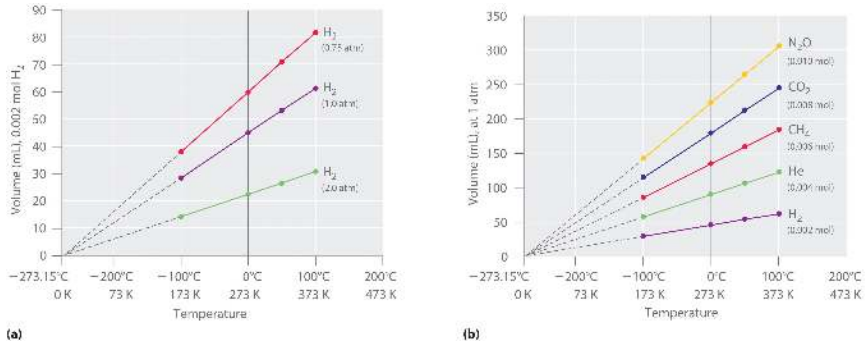


Figure **3.3.3**: The Relationship between Volume and Temperature. (a) In these plots of volume versus temperature for equal-sized samples of H_2 at three different pressures, the solid lines show the experimentally measured data down to −100°C, and the broken lines show the extrapolation of the data 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.

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 **3.3.3** is often referred to as Charles's law and is stated mathematically as

$$V = \text{const.}\, T \tag{3.3.4}$$

or

$$V \propto T \tag{3.3.5}$$

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.



Charles's Law: https://youtu.be/NBf510ZnlR0

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 **3.3.4**). This is the historic "Avogadro's hypothesis."

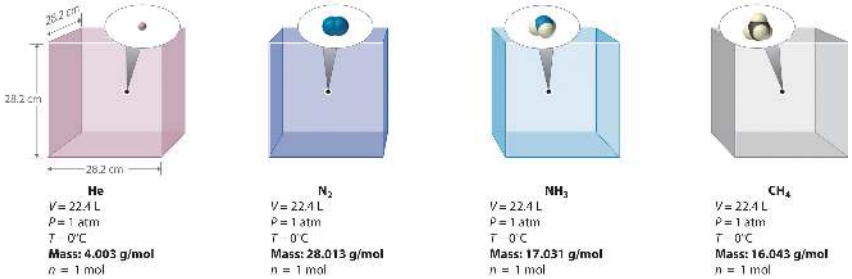


Figure **3.3.4**: Avogadro's Hypothesis. Equal volumes of four different gases at the same temperature and pressure contain the same number of gaseous particles. Because the molar mass of each gas is different, the *mass* of each gas sample is different even though all contain 1 mol of gas.

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,

$$V = \text{const.}\ (n) \tag{3.3.6}$$

or

$$V \propto .n@\ \text{constant T and P} \tag{3.3.7}$$

This relationship is valid for most gases at relatively low pressures, but deviations from strict linearity are observed at elevated pressures.

Note

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 **3.3.5**. Volume *increases* with increasing temperature or amount but *decreases* with increasing pressure.

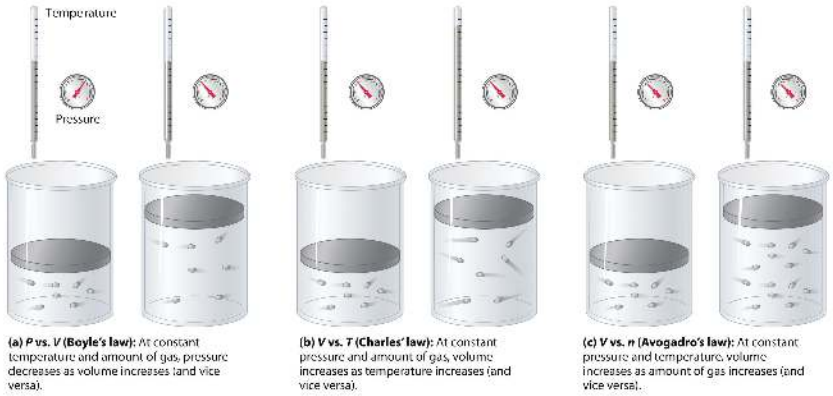


Figure **3.3.5**: The Empirically Determined Relationships among Pressure, Volume, Temperature, and Amount of a Gas. The thermometer and pressure gauge indicate the temperature and the pressure qualitatively, the level in the flask indicates the volume, and the number of particles in each flask indicates relative amounts.



Avogadro's Law: https://youtu.be/dRY3Trl4T24

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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3.4: 6.4 The Ideal Gas Law

Learning Objectives

- To use the ideal gas law to describe the behavior of a gas.

In this module, the relationship between Pressure, Temperature, Volume, and Amount of a gas are described and how these relationships can be combined to give a general expression that describes the behavior of a gas.

Deriving the Ideal Gas Law

Any set of relationships between a single quantity (such as V) and several other variables (P, T, and n) can be combined into a single expression that describes all the relationships simultaneously. The three individual expressions are as follows:

- **Boyle's law**

$$V \propto \frac{1}{P} \text{ @ constant n and T} \tag{3.4.1}$$

- **Charles's law**

$$V \propto T \text{ @ constant n and P} \tag{3.4.2}$$

- **Avogadro's law**

$$V \propto n \text{ @ constant T and P} \tag{3.4.3}$$

Combining these three expressions gives

$$V \propto \frac{nT}{P} \tag{6.3.1}$$

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

$$V = \text{Cons.}\left(\frac{nT}{P}\right) \tag{6.3.2}$$

By convention, the proportionality constant in Equation 6.3.1 is called the gas constant, which is represented by the letter R. Inserting R into Equation 6.3.2 gives

$$V = \frac{Rnt}{P} = \frac{nRT}{P} \tag{6.3.3}$$

Clearing the fractions by multiplying both sides of Equation 6.3.4 by P gives

$$PV = nRT \tag{6.3.4}$$

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.

Note

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

$$R = 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \tag{6.3.5}$$

Because the product PV has the units of energy, R can also have units of J/(K•mol):

$$R = 8.3145 \frac{\text{J}}{\text{K} \cdot \text{mol}} \tag{6.3.6}$$

Standard Conditions of Temperature and Pressure

Scientists have chosen a particular set of conditions to use as a reference: 0°C (273.15 K) and $1 \text{ bar} = 100 \text{ kPa} = 10^5 \text{ Pa}$ pressure, referred to as standard temperature and pressure (**STP**).

$$\text{STP:} \qquad T = 273.15 \text{ K and } P = 1 \text{ bar} = 10^5 \text{ Pa} \tag{3.4.4}$$

Please note that STP was defined differently in the part. The old definition was based on a standard pressure of 1 atm.

We can calculate the volume of 1.000 mol of an ideal gas under standard conditions using the variant of the ideal gas law given in Equation 6.3.4:

$$V = \frac{nRT}{P} \tag{6.3.7}$$

Thus the volume of 1 mol of an ideal gas is **22.71 L at STP** and **22.41 L at 0°C and 1 atm**, approximately equivalent to the volume of three basketballs. The molar volumes of several real gases at 0°C and 1 atm are given in Table 10.3, which shows that the deviations from ideal gas behavior are quite small. Thus the ideal gas law does a good job of approximating the behavior of real gases at 0°C and 1 atm. The relationships described in Section 10.3 as Boyle's, Charles's, and Avogadro's laws are simply special cases of the ideal gas law in which two of the four parameters (P, V, T, and n) are held fixed.

Table **3.4.1**: 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

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 3.4.1

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 6.3.4) for *n*, we obtain

$$745\ \text{mmHg} \times \frac{1\ \text{atm}}{760\ \text{mmHg}} = 0.980\ \text{atm} \tag{3.4.5}$$

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:

$$T = 273 + 30 = 303\text{K} \tag{3.4.6}$$

Substituting these values into the expression we derived for *n*, we obtain

$$n = \frac{PV}{RT} = \frac{0.980\ \text{atm} \times 31150\ \text{L}}{0.08206 \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 303\ \text{K}} = 1.23 \times 10^3\ \text{mol} \tag{3.4.7}$$

Exercise 3.4.1

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 **3.4.1**, 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 **3.4.5**.



The Ideal Gas Law: https://youtu.be/rHGs23368mE

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:

$$\underset{P_iV_i = n_iRT_i}{\text{Initial condition } (i)} \quad \underset{P_fV_f = n_fRT_f}{\text{Final condition}(f)} \tag{3.4.8}$$

Both equations can be rearranged to give:

$$R = \frac{P_iV_i}{n_iT_i} \qquad R = \frac{P_fV_f}{n_fT_f} \tag{3.4.9}$$

The two equations are equal to each other since each is equal to the same constant R. Therefore, we have:

$$\frac{P_iV_i}{n_iT_i} = \frac{P_fV_f}{n_fT_f} \tag{6.3.8}$$

The equation is called the **general gas equation**. The equation is particularly useful when one or two of the gas properties are held constant between the two conditions. In such cases, the equation can be simplified by eliminating these constant gas properties.

Example 3.4.2

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 **3.4.1**?

Given: temperature, pressure, amount, and volume in August; temperature in January

Asked for: volume in January

Strategy:

A. Use the results from Example **3.4.1** 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:

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 × 103 mol	$n_f =$1.23 × 103 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 can be simplified to:

$$\frac{V_i}{T_i} = \frac{V_f}{T_f} \tag{3.4.10}$$

This is the relationship first noted by Charles.

C Solving the equation for V_f, we get:

$$V_f = V_i \times \frac{T_f}{T_i} = 31150\ \text{L} \times \frac{263\ \text{K}}{303\ \text{K}} = 2.70 \times 10^4\ \text{L} \tag{3.4.11}$$

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 3.4.2

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 **3.4.1** 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 **3.4.1** can be applied in *any* such case, as we demonstrate in Example **3.4.2** (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 3.4.3

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 5 (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 **3.4.5**.

Solution:

Prepare a table to determine which parameters change and which are held constant:

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:

$$P_i T_i = P_f T_f \tag{3.4.12}$$

By solving the equation for P_f, we get:

$$P_f = P_i \times \frac{T_i}{T_f} = 1.5\ \text{atm} \times \frac{1023\ \text{K}}{298\ \text{K}} = 5.1\ \text{atm} \tag{3.4.13}$$

This pressure is more than enough to rupture a thin sheet metal container and cause an explosion!

? Exercise 3.4.3

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 Example **3.4.1** and Example **3.4.2**, 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 3.4.4

We saw in Example **3.4.1** 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 **3.4.5**.

Solution:

Begin by setting up a table of the two sets of conditions:

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 6.3.8 is simplified to:

$$\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f} \tag{3.4.14}$$

By solving the equation for V_f, we get:

$$V_f = V_i \times \frac{P_i}{P_f}\frac{T_f}{T_i} = 3.115 \times 10^4\ \text{L} \times \frac{0.980\ \text{atm}}{0.411\ \text{atm}}\frac{243\ \text{K}}{303\ \text{K}} = 5.96 \times 10^4\ \text{L} \tag{3.4.15}$$

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 3.4.4

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



Second Type of Ideal Gas Law Problems: https://youtu.be/WQDJOqddPI0

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

$$\frac{n}{V} = \frac{P}{RT} \tag{6.3.9}$$

The left side has the units of moles per unit volume (mol/L). The number of moles of a substance equals its mass (m, in grams) divided by its molar mass (M, in grams per mole):

$$n = \frac{m}{M} \tag{6.3.10}$$

Substituting this expression for n into Equation 6.3.9 gives

$$\frac{m}{MV} = \frac{P}{RT} \tag{6.3.11}$$

Because m/V is the density d of a substance, we can replace m/V by d and rearrange to give

$$\rho = \frac{m}{V} = \frac{MP}{RT} \tag{6.3.12}$$

The distance between particles in gases is large compared to the size of the particles, so their densities are much lower than the densities of liquids and solids. Consequently, gas density is usually measured in grams per liter (g/L) rather than grams per milliliter (g/mL).

Example 3.4.5

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 6.3.12 to obtain the density.

Solution:

A The molar mass of butane (C_4H_{10}) is

$$M = (4)(12.011) + (10)(1.0079) = 58.123 \text{g/mol} \tag{3.4.16}$$

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:

$$P = 750 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 0.987 \text{ atm} \tag{3.4.17}$$

B Substituting these values into Equation 6.3.12 gives

$$\rho = \frac{58.123 \text{ g/mol} \times 0.987 \text{ atm}}{0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \times 298 \text{ K}} = 2.35 \text{ g/L} \tag{3.4.18}$$

Exercise 3.4.5

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 6.3.12 is to determine the molar mass of an unknown gas by measuring its density at a known temperature and pressure. This method is particularly useful in identifying a gas that has been produced in a reaction, and it is not difficult to carry out. A flask or glass bulb of known volume is carefully dried, evacuated, sealed, and weighed empty. It is then filled with a sample of a gas at a known temperature and pressure and reweighed. The difference in mass between the two readings is the mass of the gas. The volume of the flask is usually determined by weighing the flask when empty and when filled with a liquid of known density such as water. The use of density measurements to calculate molar masses is illustrated in Example **3.4.6**.

Example 3.4.6

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 6.3.12 for the molar mass of the gas and then calculate the density of the gas from the information given.

B. Convert all known quantities to the appropriate units for the gas constant being used. Substitute the known values into your equation and solve for the molar mass.

C. Propose a reasonable empirical formula using the atomic masses of nitrogen and oxygen and the calculated molar mass of the gas.

Solution:

A Solving Equation 6.3.12 for the molar mass gives

$$M = \frac{mRT}{PV} = \frac{dRT}{P} \tag{3.4.19}$$

Density is the mass of the gas divided by its volume:

$$\rho = \frac{m}{V} = \frac{0.289\text{g}}{0.17\text{L}} = 1.84\text{g/L} \tag{3.4.20}$$

B We must convert the other quantities to the appropriate units before inserting them into the equation:

$$T = 18 + 273 = 291K \tag{3.4.21}$$

$$P = 727\text{mmHg} \times \frac{1\text{atm}}{760\text{mmHg}} = 0.957\text{atm} \tag{3.4.22}$$

The molar mass of the unknown gas is thus

$$\rho = \frac{1.84\text{ g/L} \times 0.08206\frac{\text{L}\cdot\text{atm}}{\text{K}\cdot\text{mol}} \times 291\text{ K}}{0.957\text{ atm}} = 45.9\text{g/mol} \tag{3.4.23}$$

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:

$$M(\text{NO}) = 14 + 16 = 30\text{ g/mol} \tag{3.4.24}$$

$$M(\text{N}_2\text{O}) = (2)(14) + 16 = 44\text{ g/mol} \tag{3.4.25}$$

$$M(\text{NO}_2) = 14 + (2)(16) = 46\text{ g/mol} \tag{3.4.26}$$

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 3.4.6

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



Density and the Molar Mass of Gases: https://youtu.be/gnkGBsvUFVk

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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3.5: 6.5 Mixtures of Gases

Learning Objectives

- To determine the contribution of each component gas to the total pressure of a mixture of gases

In our use of the ideal gas law thus far, we have focused entirely on the properties of pure gases with only a single chemical species. But what happens when two or more gases are mixed? In this section, we describe how to determine the contribution of each gas present to the total pressure of the mixture.

Partial Pressures

The ideal gas law *assumes* that all gases behave identically and that their behavior is independent of attractive and repulsive forces. If volume and temperature are held constant, the ideal gas equation can be rearranged to show that the pressure of a sample of gas is directly proportional to the number of moles of gas present:

$$P = n\left(\frac{RT}{V}\right) = n \times \text{const.} \tag{3.5.1}$$

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

$$P_{tot} = P_1 + P_2 + P_3 + P_4 \ldots = \sum_{i=1}^{n} P_i \tag{3.5.2}$$

where P_{tot} is the total pressure and the other terms are the partial pressures of the individual gases (up to n component gases).

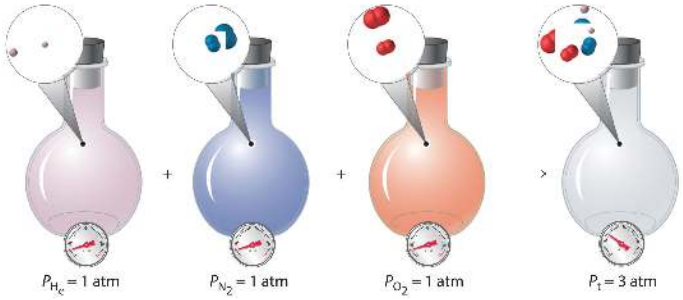


Figure **3.5.1**: Dalton's Law. The total pressure of a mixture of gases is the sum of the partial pressures of the individual gases.

For a mixture of two ideal gases, A and B, we can write an expression for the total pressure:

$$P_{tot} = P_A + P_B = n_A\left(\frac{RT}{V}\right) + n_B\left(\frac{RT}{V}\right) = (n_A + n_B)\left(\frac{RT}{V}\right) \tag{3.5.3}$$

More generally, for a mixture of n component gases, the total pressure is given by

$$P_{tot} = (P_1 + P_2 + P_3 + \cdots + P_n)\left(\frac{RT}{V}\right) \tag{3.5.4}$$

$$P_{tot} = \sum_{i=1}^{n} n_i \left(\frac{RT}{V}\right) \tag{3.5.5}$$

Equation 6.6.4 restates Equation 6.6.3 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 6.6.4 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 **3.5.1**.

Example 3.5.1

Deep-sea divers must use special gas mixtures in their tanks, rather than compressed air, to avoid serious problems, most notably a condition called "the bends." At depths of about 350 ft, divers are subject to a pressure of approximately 10 atm. A typical gas cylinder used for such depths contains 51.2 g of O_2 and 326.4 g of He and has a volume of 10.0 L. What is the partial pressure of each gas at 20.00°C, and what is the total pressure in the cylinder at this temperature?

Given: masses of components, total volume, and temperature

Asked for: partial pressures and total pressure

Strategy:

A. Calculate the number of moles of He and O_2 present.
B. Use the ideal gas law to calculate the partial pressure of each gas. Then add together the partial pressures to obtain the total pressure of the gaseous mixture.

Solution:

A The number of moles of He is

$$n_{\text{He}} = \frac{326.4\ \text{g}}{4.003\ \text{g/mol}} = 81.54\ \text{mol} \tag{3.5.6}$$

The number of moles of O_2 is

$$n_{\text{O}_2} = \frac{51.2\ \text{g}}{32.00\ \text{g/mol}} = 1.60\ \text{mol} \tag{3.5.7}$$

B We can now use the ideal gas law to calculate the partial pressure of each:

$$P_{\text{He}} = \frac{n_{\text{He}}RT}{V} = \frac{81.54\ \text{mol} \times 0.08206\ \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 293.15\ \text{K}}{10.0\ \text{L}} = 196.2\ \text{atm} \tag{3.5.8}$$

$$P_{\text{O}_2} = \frac{n_{\text{O}_2}RT}{V} = \frac{1.60\ \text{mol} \times 0.08206\ \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 293.15\ \text{K}}{10.0\ \text{L}} = 3.85\ \text{atm} \tag{3.5.9}$$

The total pressure is the sum of the two partial pressures:

$$P_{\text{tot}} = P_{\text{He}} + P_{\text{O}_2} = (196.2 + 3.85)\ \text{atm} = 200.1\ \text{atm} \tag{3.5.10}$$

Exercise 3.5.1

A cylinder of compressed natural gas has a volume of 20.0 L and contains 1813 g of methane and 336 g of ethane. Calculate the partial pressure of each gas at 22.0°C and the total pressure in the cylinder.

Answer: $P_{CH_4} = 137\ atm$; $P_{C_2H_6} = 13.4\ atm$; $P_{tot} = 151\ atm$

Mole Fractions of Gas Mixtures

The composition of a gas mixture can be described by the mole fractions of the gases present. The mole fraction (X) 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}):

$$x_A = \frac{\text{moles of A}}{\text{total moles}} = \frac{n_A}{n_{tot}} = \frac{n_A}{n_A + n_B + \cdots} \tag{3.5.11}$$

The mole fraction is a dimensionless quantity between 0 and 1. If $x_A = 1.0$, then the sample is pure A, not a mixture. If $x_A = 0$, 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

$$\frac{P_A}{P_{tot}} = \frac{n_A RT/V}{n_{tot} RT/V} = \frac{n_A}{n_{tot}} = x_A \tag{3.5.12}$$

Rearranging this equation gives

$$P_A = x_A P_{tot} \tag{3.5.13}$$

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 6.6.7, 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 3.5.2

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.

	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 6.6.7.

Solution:

The mole fraction of any gas A is given by

$$x_A = \frac{P_A}{P_{tot}} \tag{3.5.14}$$

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:

$$x_{CO_2} = \frac{48 \text{ mmHg}}{767 \text{ mmHg}} = 0.063 \tag{3.5.15}$$

The following table gives the values of x_A for the gases in the exhaled air.

Gas	Mole Fraction
N_2	0.741
O_2	0.151
H_2O	0.037
CO_2	0.063
Ar	0.010

? Exercise 3.5.2

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

$$P_{CO_2} = 86 \text{ atm}, \; P_{N_2} = 2.7 \text{ atm}$$



Dalton's Law of Partial Pressures: https://youtu.be/y5-SbspyvBA

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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3.6: Gas Volumes and Stoichiometry

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.

Introduction

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. As a chemical engineer said to one of the authors, "Gases always go where you want them to, liquids sometimes do, but solids almost never do."

Example 3.6.1

Sulfuric acid, the industrial chemical produced in greatest quantity (almost 45 million tons per year in the United States alone), is prepared by the combustion of sulfur in air to give SO_2, followed by the reaction of SO_2 with O_2 in the presence of a catalyst to give SO_3, which reacts with water to give H_2SO_4. The overall chemical equation is as follows:

$$2S_{(s)} + 3O_{2(g)} + 2H_2O_{(l)} \rightarrow 2H_2SO_{4(aq)} \tag{3.6.1}$$

What volume of O_2 (in liters) at 22°C and 745 mmHg pressure is required to produce 1.00 ton (907.18 kg) of H_2SO_4?

Given: reaction, temperature, pressure, and mass of one product

Asked for: volume of gaseous reactant

Strategy:

A Calculate the number of moles of H_2SO_4 in 1.00 ton. From the stoichiometric coefficients in the balanced chemical equation, calculate the number of moles of O_2 required.

B Use the ideal gas law to determine the volume of O_2 required under the given conditions. Be sure that all quantities are expressed in the appropriate units.

Solution:

mass of H_2SO_4 → moles H_2SO_4 → moles O_2 → liters O_2

A We begin by calculating the number of moles of H_2SO_4 in 1.00 ton:

$$\frac{907.18 \times 10^3 \text{ g } H_2SO_4}{(2 \times 1.008 + 32.06 + 4 \times 16.00) \text{ g/mol}} = 9250 \text{ mol } H_2SO_4 \tag{3.6.2}$$

We next calculate the number of moles of O_2 required:

$$9250 \text{ mol } H_2SO_4 \times \frac{3 \text{mol } O_2}{2 \text{mol } H_2SO_4} = 1.389 \times 10^4 \text{ mol } O_2 \tag{3.6.3}$$

B After converting all quantities to the appropriate units, we can use the ideal gas law to calculate the volume of O_2:

$$V = \frac{nRT}{P} = \frac{1.389 \times 10^4 \text{ mol} \times 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times (273 + 22) \text{ K}}{745 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}} = 3.43 \times 10^5 \text{ L} \tag{3.6.4}$$

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 3.6.1

In Example 5, we saw that Charles used a balloon containing approximately 31,150 L of H_2 for his initial flight in 1783. The hydrogen gas was produced by the reaction of metallic iron with dilute hydrochloric acid according to the following balanced chemical equation:

$$Fe_{(s)} + 2HCl_{(aq)} \rightarrow H_{2(g)} + FeCl_{2(aq)} \tag{3.6.5}$$

How much iron (in kilograms) was needed to produce this volume of H_2 if the temperature was 30°C and the atmospheric pressure was 745 mmHg?

Answer: 68.6 kg of Fe (approximately 150 lb)



Ideal Gas law Equation and Reaction Stoichiometry: https://youtu.be/8pPlW8MRhgI

Collecting gases over water

As shown in Figure **3.6.1**, a common laboratory method of collecting the gaseous product of a chemical reaction is to conduct it into an inverted tube or bottle filled with water, the opening of which is immersed in a larger container of water. Because the gas is less dense than liquid water, it bubbles to the top of the bottle, displacing the water. Eventually, all the water is forced out and the bottle contains only gas. If a calibrated bottle is used (i.e., one with markings to indicate the volume of the gas) and the bottle is raised or lowered until the level of the water is the same both inside and outside, then the pressure within the bottle will exactly equal the atmospheric pressure measured separately with a barometer ($P_{bar.}$).

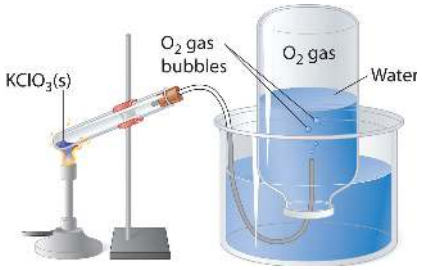


Figure **3.6.1**: An Apparatus for Collecting Gases by the Displacement of Water

Remember, however, when calculating the amount of gas formed in the reaction, the gas collected inside the bottle is *not* pure. Instead, it is a mixture of the product gas and water vapor. All liquids (including water) have a measurable amount of vapor in equilibrium with the liquid because molecules of the liquid are continuously escaping from the liquid's surface, while other molecules from the vapor phase collide with the surface and return to the liquid. The vapor thus exerts a pressure above the liquid,

which is called the liquid's ***vapor pressure***. In the case shown in Figure **3.6.1**, the bottle is therefore actually filled with a mixture of O_2 and water vapor, and the total pressure is, by **Dalton's law** of partial pressures, the sum of the pressures of the two components:

$$P_{tot} = P_{gas} + P_{H_2O} = P_{bar.} \tag{3.6.6}$$

If we want to know the pressure of the gas generated in the reaction to calculate the amount of gas formed, we must first subtract the pressure due to water vapor from the total pressure. This is done by referring to tabulated values of the vapor pressure of water as a function of temperature (Table **3.6.1**).

Table **3.6.1**: Vapor Pressure of Water at Various Temperatures

T (°C)	*P* (in mmHg)
0	4.58
15	12.79
17	14.53
19	16.48
21	18.65
23	21.07
25	23.76
30	31.82
50	92.51
70	233.8
100	760.0

As shown in Figure **3.6.2**, the vapor pressure of water increases rapidly with increasing temperature, and at the normal boiling point (100°C), the vapor pressure is exactly 1 atm. The methodology is illustrated in Example **3.6.2**. The only gases that cannot be collected using this technique are those that readily dissolve in water (e.g., NH_3, H_2S, and CO_2) and those that react rapidly with water (such as F_2 and NO_2).

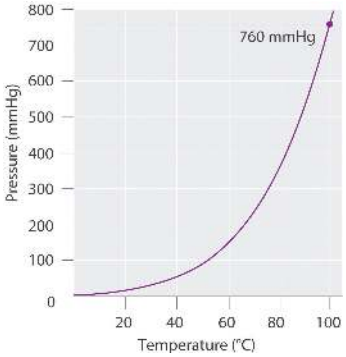


***Figure* 3.6.2:** *A Plot of the Vapor Pressure of Water versus Temperature. The vapor pressure is very low (but not zero) at 0°C and reaches 1 atm = 760 mmHg at the normal boiling point, 100°C.*

Example 3.6.2

Sodium azide (NaN_3) decomposes to form sodium metal and nitrogen gas according to the following balanced chemical equation:

$$2NaN_3 \rightarrow 2Na_{(s)} + 3N_{2\ (g)} \tag{3.6.7}$$

This reaction is used to inflate the air bags that cushion passengers during automobile collisions. The reaction is initiated in air bags by an electrical impulse and results in the rapid evolution of gas. If the N_2 gas that results from the decomposition of a 5.00 g sample of NaN_3 could be collected by displacing water from an inverted flask, as in Figure **3.6.1**, what volume of gas would be produced at 21°C and 762 mmHg?

Given: reaction, mass of compound, temperature, and pressure

Asked for: volume of nitrogen gas produced

Strategy:

A Calculate the number of moles of N_2 gas produced. From the data in Table **3.6.1**, determine the partial pressure of N_2 gas in the flask.

B Use the ideal gas law to find the volume of N_2 gas produced.

Solution:

A Because we know the mass of the reactant and the stoichiometry of the reaction, our first step is to calculate the number of moles of N_2 gas produced:

$$\frac{5.00\ \text{g NaN}_3}{(22.99 + 3 \times 14.01)\ \text{g/mol}} \times \frac{3\text{mol N}_2}{2\text{mol NaN}_3} = 0.115\ \text{mol N}_2 \tag{3.6.8}$$

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 **3.6.1** tells us that the vapor pressure of water is 18.65 mmHg at 21°C (294 K), so the partial pressure of the N_2 gas in the flask is only

$$(762 - 18.65)\ \text{mmHg} \times \frac{1\ \text{atm}}{760\ \text{atm}} = 743.4\ \text{mmHg} \times \frac{1\ \text{atm}}{760\ \text{atm}} = 0.978\ \text{atm}. \tag{3.6.9}$$

B Solving the ideal gas law for V and substituting the other quantities (in the appropriate units), we get

$$V = \frac{nRT}{P} = \frac{0.115\ \text{mol} \times 0.08206 \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 294\ \text{K}}{0.978\ \text{atm}} = 2.84\ \text{L} \tag{3.6.10}$$

? Exercise 3.6.2

A 1.00 g sample of zinc metal is added to a solution of dilute hydrochloric acid. It dissolves to produce H_2 gas according to the equation Zn(s) + 2 HCl(aq) → 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



Collecting a Product Gas over Water: https://youtu.be/zFuy3t81vjQ

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.

Conceptual Problems

1. Why are so many industrially important reactions carried out in the gas phase?
2. The volume of gas produced during a chemical reaction can be measured by collecting the gas in an inverted container filled with water. The gas forces water out of the container, and the volume of liquid displaced is a measure of the volume of gas. What additional information must be considered to determine the number of moles of gas produced? The volume of some gases cannot be measured using this method. What property of a gas precludes the use of this method?
3. Equal masses of two solid compounds (A and B) are placed in separate sealed flasks filled with air at 1 atm and heated to 50°C for 10 hours. After cooling to room temperature, the pressure in the flask containing A was 1.5 atm. In contrast, the pressure in the flask containing B was 0.87 atm. Suggest an explanation for these observations. Would the masses of samples A and B still be equal after the experiment? Why or why not?

Numerical Problems

1. 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?
    1. $SO_2(g) + O_2(g) \rightarrow SO_3(g)$ given 2.4 mol of O_2
    2. $H_2(g) + Cl_2(g) \rightarrow HCl(g)$ given 0.78 g of H_2
    3. $C_2H_6(g) + O_2(g) \rightarrow CO_2(g) + H_2O(g)$ given 1.91 mol of O_2

- 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,
    1. what mass of CO is consumed?
    2. what volume of CO at STP is consumed?
    3. how much O_2 (in liters) at STP is used?
    4. what mass of carbon is consumed?
    5. how much iron metal (in grams) is produced?
- Complete decomposition of a sample of potassium chlorate produced 1.34 g of potassium chloride and oxygen gas.
    1. What is the mass of $KClO_3$ in the original sample?
    2. What mass of oxygen is produced?
    3. What is the volume of oxygen produced at STP?
- 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.
- 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.

Answers

1.
2.

3. 1. 2.20 g $KClO_3$
   2. 0.863 g O_2
   3. 604 mL O_2
4.
5. Percent composition: 58.3% C, 4.93% H, 23.28% O, and 13.5% N; empirical formula: $C_{10}H_{10}O_3N_2$

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3.7: Kinetic Molecular Theory of Gases

Learning Objectives

- To understand the significance of the kinetic molecular theory of gases.

The laws that describe the behavior of gases were well established long before anyone had developed a coherent model of the properties of gases. In this section, we introduce a theory that describes why gases behave the way they do. The theory we introduce can also be used to derive laws such as the ideal gas law from fundamental principles and the properties of individual particles.

A Molecular Description

The kinetic molecular theory of gases explains the laws that describe the behavior of gases. Developed during the mid-19th century by several physicists, including the Austrian Ludwig Boltzmann (1844–1906), the German Rudolf Clausius (1822–1888), and the Englishman James Clerk Maxwell (1831–1879), who is also known for his contributions to electricity and magnetism, this theory is based on the properties of individual particles as defined for an ideal gas and the fundamental concepts of physics. Thus the kinetic molecular theory of gases provides a molecular explanation for observations that led to the development of the ideal gas law. The kinetic molecular theory of gases is based on the following five postulates:

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.

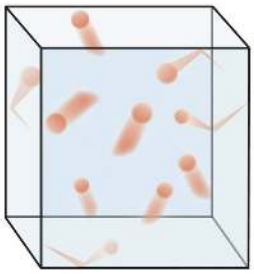


Figure **3.7.1** Visualizing molecular motion. Molecules of a gas are in constant motion and collide with one another and with the container wall.

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 Section 10.8, we explain how this theory must be modified to account for the behavior of real gases.

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 **3.7.2**).

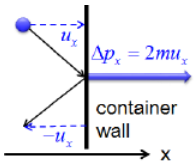


Figure **3.7.2** Momentum transfer (Impulse) from a molecule to the container wall as it bounces off the wall. u_x and Δp_x are the x component of the molecular velocity and the momentum transfered to the wall, respectively. The wall is perpendicular to x axis. Since the collisions are elastic, the molecule 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:

$$\Delta p_x = 2mu_x \tag{3.7.1}$$

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.

$$f \propto (u_x) \times \left(\frac{N}{V}\right) \tag{3.7.2}$$

The pressure the gas exerts on the wall is expressed as the product of impulse and the collision frequency.

$$P \propto (2mu_x) \times (u_x) \times \left(\frac{N}{V}\right) \propto \left(\frac{N}{V}\right) mu_x^2 \tag{3.7.3}$$

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 :

$$P = \frac{N}{V} m\overline{u_x^2} \tag{3.7.4}$$

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, $\overline{u^2} = \overline{u_x^2} + \overline{u_y^2} + \overline{u_z^2}$. 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:

$$P = \frac{1}{3}\frac{N}{V} m\overline{u^2} \tag{3.7.5}$$

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*

$$\overline{e_K} = \frac{1}{2} m\overline{u^2} = \frac{3}{2}\frac{R}{N_A} T \tag{3.7.6}$$

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:

$$N_A\overline{e_K} = \frac{1}{2} M\overline{u^2} = \frac{3}{2} RT \tag{3.7.7}$$

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:

$$u_{rms} = \sqrt{\overline{u^2}} = \sqrt{\frac{u_1^2 + u_2^2 + \cdots u_N^2}{N}} \tag{3.7.8}$$

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:

$$u_{rms} = \sqrt{\frac{3RT}{M}} \tag{3.7.9}$$

In this equation, 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).

The equation 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 (v_p) 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 v_p increases.

Note

At a given temperature, all gaseous particles have the same average kinetic energy but not the same average speed.

Example 3.7.1

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:

$$v_{av} = \frac{(1.0 + 4.0 + 4.0 + 6.0 + 6.0 + 6.0 + 8.0 + 10.0)\ \text{m/s}}{8} = 5.6\ \text{m/s} \tag{3.7.10}$$

The rms speed is the square root of the sum of the squared speeds divided by the number of particles:

$$v_{rms} = \sqrt{\frac{(1.0^2 + 4.0^2 + 4.0^2 + 6.0^2 + 6.0^2 + 6.0^2 + 8.0^2 + 10.0^2)\ \text{m}^2/\text{s}^2}{8}} = 6.2\ \text{m/s} \tag{3.7.11}$$

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.

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, as you will learn in Chapter 14. 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 **3.7.1**. 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 **3.7.1** 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.

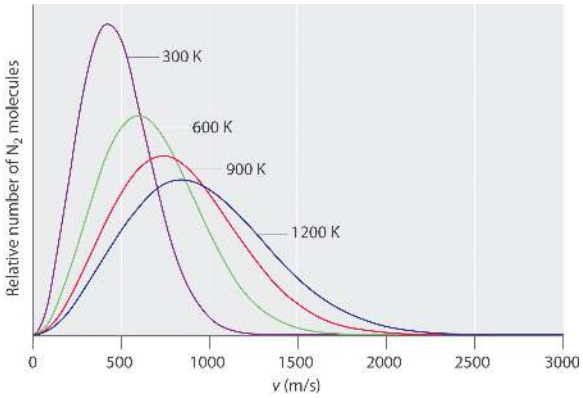


Figure **3.7.2** The Distributions of Molecular Speeds for a Sample of Nitrogen Gas at Various Temperatures. Increasing the temperature increases both the most probable speed (given at the peak of the curve) and the width of the curve.

The Relationships among Pressure, Volume, and Temperature

We now describe how the kinetic molecular theory of gases explains some of the important relationships we have discussed previously.

- **Pressure versus Volume**: At constant temperature, the kinetic energy of the molecules of a gas and hence the rms speed remain unchanged. If a given gas sample is allowed to occupy a larger volume, then the speed of the molecules does not change, but the density of the gas (number of particles per unit volume) decreases, and the average distance between the molecules increases. Hence the molecules must, on average, travel farther between collisions. They therefore collide with one another and with the walls of their containers less often, leading to a decrease in pressure. Conversely, increasing the pressure forces the molecules closer together and increases the density, until the collective impact of the collisions of the molecules with the container walls just balances the applied pressure.
- **Volume versus Temperature**: Raising the temperature of a gas increases the average kinetic energy and therefore the rms speed (and the average speed) of the gas molecules. Hence as the temperature increases, the molecules collide with the walls of their containers more frequently and with greater force. This increases the pressure, *unless* the volume increases to reduce the pressure, as we have just seen. Thus an increase in temperature must be offset by an increase in volume for the net impact (pressure) of the gas molecules on the container walls to remain unchanged.
- **Pressure of Gas Mixtures**: Postulate 3 of the kinetic molecular theory of gases states that gas molecules exert no attractive or repulsive forces on one another. If the gaseous molecules do not interact, then the presence of one gas in a gas mixture will have no effect on the pressure exerted by another, and Dalton's law of partial pressures holds.

Example 3.7.2

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

1. average kinetic energy of the N_2 molecules?
2. rms speed of the N_2 molecules?
3. average speed of the N_2 molecules?
4. impact of each N_2 molecule on the wall of the container during a collision with the wall?
5. total number of collisions per second of N_2 molecules with the walls of the entire container?
6. number of collisions per second of N_2 molecules with each square centimeter of the container wall?
7. 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:

1. Increasing the temperature increases the average kinetic energy of the N_2 molecules.
2. An increase in average kinetic energy can be due only to an increase in the rms speed of the gas particles.
3. If the rms speed of the N_2 molecules increases, the average speed also increases.
4. If, on average, the particles are moving faster, then they strike the container walls with more energy.
5. Because the particles are moving faster, they collide with the walls of the container more often per unit time.
6. 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.
7. 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 3.7.2

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

1. average kinetic energy of the He atoms?
2. rms speed of the He atoms?
3. average speed of the He atoms?
4. impact of each He atom on the wall of the container during a collision with the wall?
5. total number of collisions per second of He atoms with the walls of the entire container?
6. number of collisions per second of He atoms with each square centimeter of the container wall?
7. pressure of the He gas?

Answer: a. no change; b. no change; c. no change; d. no change; e. decreases; f. decreases; g. decreases



Kinetic-Molecular Theory of Gases: https://youtu.be/9f83XAYfXAg

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:**

$$\overline{e_K} = \frac{1}{2} m {u_{\text{rms}}}^2 = \frac{3}{2} \frac{R}{N_A} T, \tag{3.7.12}$$

- **Root mean square speed:**

$$u_{\text{rms}} = \sqrt{\frac{u_1^2 + u_2^2 + \cdots u_N^2}{N}}, \tag{3.7.13}$$

- **Kinetic molecular theory of gases:**

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}. \tag{3.7.14}$$

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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3.8: Connecting Gas Properties to Kinetic Molecular Theory

Learning Objectives

- To understand the significance of the kinetic molecular theory of gases

We now describe how the kinetic molecular theory of gases explains some of the important relationships we have discussed previously.

Diffusion and Effusion

As you have learned, the molecules of a gas are *not* stationary but in constant and random motion. If someone opens a bottle of perfume in the next room, for example, you are likely to be aware of it soon. Your sense of smell relies on molecules of the aromatic substance coming into contact with specialized olfactory cells in your nasal passages, which contain specific receptors (protein molecules) that recognize the substance. How do the molecules responsible for the aroma get from the perfume bottle to your nose? You might think that they are blown by drafts, but, in fact, molecules can move from one place to another even in a draft-free environment.

Diffusion is the gradual mixing of gases due to the motion of their component particles even in the absence of mechanical agitation such as stirring. The result is a gas mixture with uniform composition. Diffusion is also a property of the particles in liquids and liquid solutions and, to a lesser extent, of solids and solid solutions. The related process, effusion, is the escape of gaseous molecules through a small (usually microscopic) hole, such as a hole in a balloon, into an evacuated space.

The phenomenon of effusion had been known for thousands of years, but it was not until the early 19th century that quantitative experiments related the rate of effusion to molecular properties. The rate of effusion of a gaseous substance is inversely proportional to the square root of its molar mass. This relationship *is referred to as Graham's law*, after the Scottish chemist Thomas Graham (1805–1869). The ratio of the effusion rates of two gases is the square root of the inverse ratio of their molar masses*:*

$$\frac{\text{rate of effusion A}}{\text{rate of effusion B}} = \sqrt{\frac{M_B}{M_A}} \tag{3.8.1}$$



Ethylene oxide

Figure **3.8.1** for ethylene oxide and helium. 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.

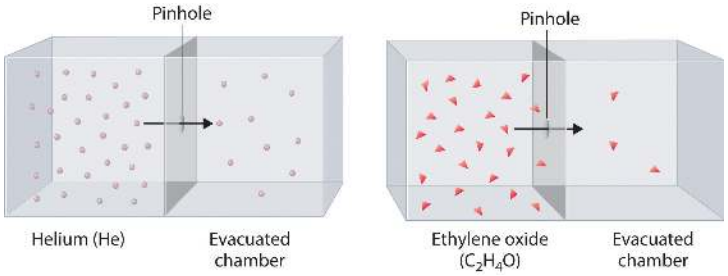


Figure **3.8.1**: The Relative Rates of Effusion of Two Gases with Different Masses. The lighter He atoms (M = 4.00 g/mol) effuse through the small hole more rapidly than the heavier ethylene oxide (C_2H_4O) molecules (M = 44.0 g/mol), as predicted by Graham's law.

Note

At a given temperature, heavier molecules move more slowly than lighter molecules.

Example 3.8.1

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 $^{235}\mathrm{U}$. Naturally occurring uranium is only 0.720% $^{235}\mathrm{U}$, whereas most of the rest (99.275%) is $^{238}\mathrm{U}$, which is not fissionable (i.e., it will not break apart to release nuclear energy) and also actually poisons the fission process. Because both isotopes of uranium have the same reactivity, they cannot be separated chemically. Instead, a process of gaseous effusion was developed using the volatile compound UF_6 (boiling point = 56°C).

1. Calculate the ratio of the rates of effusion of $^{235}UF_6$ and $^{238}UF_6$ for a single step in which UF_6 is allowed to pass through a porous barrier. (The atomic mass of ^{235}U is 235.04, and the atomic mass of ^{238}U is 238.05.)
2. If n identical successive separation steps are used, the overall separation is given by the separation in a single step (in this case, the ratio of effusion rates) raised to the nth power. How many effusion steps are needed to obtain 99.0% pure $^{235}UF_6$?

Given: isotopic content of naturally occurring uranium and atomic masses of ^{235}U and ^{238}U

Asked for: ratio of rates of effusion and number of effusion steps needed to obtain 99.0% pure $^{235}UF_6$

Strategy:

A. Calculate the molar masses of $^{235}UF_6$ and $^{238}UF_6$, and then use Graham's law to determine the ratio of the effusion rates. Use this value to determine the isotopic content of $^{235}UF_6$ after a single effusion step.
B. Divide the final purity by the initial purity to obtain a value for the number of separation steps needed to achieve the desired purity. Use a logarithmic expression to compute the number of separation steps required.

Solution:

1. The molar mass of $^{238}UF_6$ is 238.05 + (6)(18.998) = 352.04 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:

$$\frac{\text{rate } ^{235}\mathrm{UF_6}}{\text{rate } ^{238}\mathrm{UF_6}} = \sqrt{\frac{352.04\ \text{g/mol}}{349.03\ \text{g/mol}}} = 1.0043 \tag{3.8.2}$$

2.

   Thus passing UF_6 containing a mixture of the two isotopes through a single porous barrier gives an enrichment of 1.0043, so after one step the isotopic content is (0.720%)(1.0043) = 0.723% $^{235}UF_6$.

3. **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

$$1.0043^n = \frac{0.990}{0.00720} = 137.50 \tag{3.8.3}$$

4. Taking the logarithm of both sides gives

$$n \ln(1.0043) = \ln(137.50) \tag{3.8.4}$$

$$n = \frac{\ln(137.50)}{\ln(1.0043)} = 1148 \tag{3.8.5}$$

Thus at least a thousand effusion steps are necessary to obtain highly enriched ^{235}U. Figure **3.8.2** shows a small part of a system that is used to prepare enriched uranium on a large scale.



Figure **3.8.2**: 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 3.8.1

Helium consists of two isotopes: ^{3}He (natural abundance = 0.000134%) and ^{4}He (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 ^{4}He by a process of gaseous effusion.

a. Calculate the ratio of the effusion rates of ^{3}He and ^{4}He and thus the enrichment possible in a single effusion step.
b. How many effusion steps are necessary to yield 99.0% pure ^{3}He?

Answer: a. ratio of effusion rates = 1.15200; one step gives 0.000154% ^{3}He; b. 96 steps

Rates of Diffusion or Effusion

Graham's law is an empirical relationship that states that the ratio of the rates of diffusion or effusion of two gases is the square root of the inverse ratio of their molar masses. The relationship is based on the postulate that all gases at the same temperature have the same average kinetic energy. We can write the expression for the average kinetic energy of two gases with different molar masses:

$$KE = \frac{1}{2}\frac{M_\mathrm{A}}{N_A} v_{\mathrm{rms,A}}^2 = \frac{1}{2}\frac{M_\mathrm{B}}{N_A} v_{\mathrm{rms,B}}^2 \tag{3.8.6}$$

Multiplying both sides by 2 and rearranging give

$$\frac{v_{\mathrm{rms,B}}^2}{v_{\mathrm{rms,A}}^2} = \frac{M_\mathrm{A}}{M_\mathrm{B}} \tag{3.8.7}$$

Taking the square root of both sides gives

$$\frac{v_{\mathrm{rms,B}}}{v_{\mathrm{rms,A}}} = \sqrt{\frac{M_\mathrm{A}}{M_\mathrm{B}}} \tag{3.8.8}$$

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 6.8.4 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 **3.8.3** 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.

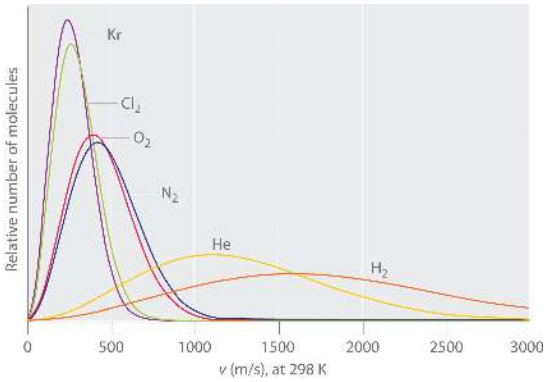


Figure **3.8.3**: The Wide Variation in Molecular Speeds Observed at 298 K for Gases with Different Molar Masses

The lightest gases have a wider distribution of speeds and the highest average speeds.

Note

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 **3.8.4**.

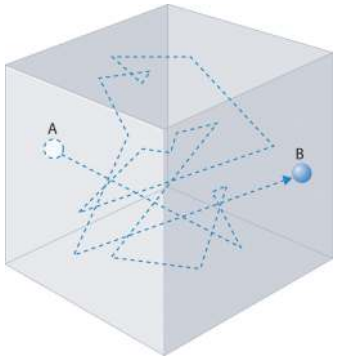


Figure **3.8.4**: The Path of a Single Particle in a Gas Sample. The frequent changes in direction are the result of collisions with other gas molecules and with the walls of the container.

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).

Note

The **denser** the gas, the **shorter** the mean free path.

Example 3.8.2

Calculate the rms speed of a sample of *cis*-2-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 6.8.5 to calculate the rms speed of the gas.

Solution:

To use Equation 6.8.4, 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

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.3145 \ \frac{\text{J}}{\text{K} \cdot \text{mol}} \times (20 + 273) \ \text{K}}{56.11 \times 10^{-3} \ \text{kg}}} = 361 \ \text{m/s} \tag{3.8.9}$$

or approximately 810 mi/h.

Exercise 3.8.2

Calculate the rms speed of a sample of radon gas at 23°C.

Answer: 1.82×10^2 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. In Section 10.8, we explore how the behavior of real gases differs from that of ideal gases.



Graham’s law of Diffusion and Effusion: https://youtu.be/9HO-qgh-iGI

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:**

$$\overline{e_K} = \frac{1}{2} m {u_{\text{rms}}}^2 = \frac{3}{2} \frac{R}{N_A} T, \tag{3.8.10}$$

- **Root mean square speed:**

$$u_{\text{rms}} = \sqrt{\frac{u_1^2 + u_2^2 + \cdots u_N^2}{N}}, \tag{3.8.11}$$

- **Kinetic molecular theory of gases**:

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}. \tag{3.8.12}$$

- **Graham's law for effusion:**

$$\frac{v_{\text{rms,B}}}{v_{\text{rms,A}}} = \sqrt{\frac{M_{\text{A}}}{M_{\text{B}}}} \tag{3.8.13}$$

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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3.9: Chapter Problems

Application Problems

Be sure you are familiar with the material in Essential Skills 5 (Section 10.9 "Essential Skills 5") before proceeding to the Application Problems. Problems marked with a ♦ involve multiple concepts.

1. ♦ Oxalic acid ($C_2H_2O_4$) is a metabolic product of many molds. Although oxalic acid is toxic to humans if ingested, many plants and vegetables contain significant amounts of oxalic acid or oxalate salts. In solution, oxalic acid can be oxidized by air via the following chemical equation:

   $H_2C_2O_4(aq) + O_2(g) \rightarrow H_2O_2(l) + 2\ CO_2(g)$

   If a plant metabolized enough oxalic acid to produce 3.2 L of CO_2 on a day when the temperature was 29°C and the pressure was 752 mmHg, how many grams of oxalic acid were converted to CO_2? Given that air is 21% oxygen, what volume of air was needed for the oxidation?

2. ♦ The decomposition of iron oxide is used to produce gas during the manufacture of porous, expanded materials. These materials have very low densities due to the swelling that occurs during the initial rapid heating. Consequently, they are used as additives to provide insulation in concrete, road building, and other construction materials. Iron oxide decomposes at 1150°C according to the following chemical equation:

   $6\ Fe_2O_3(s) \rightarrow 4\ Fe_3O_4(s) + O_2(g)$

   1. Explain how this reaction could cause materials containing Fe_2O_3 to swell on heating.
   2. If you begin with 15.4 g of Fe_2O_3, what volume of O_2 gas at STP is produced?
   3. What is the volume of the same amount of O_2 gas at 1200°C, assuming a constant pressure of 1.0 atm?
   4. If 6.3 L of gas were produced at 1200°C and 1 atm, how many kilograms of Fe_2O_3 were initially used in the reaction? How many kilograms of Fe_3O_4 are produced?

3. ♦ A 70 kg man expends 480 kcal of energy per hour shoveling snow. The oxidation of organic nutrients such as glucose during metabolism liberates approximately 3.36 kcal of energy per gram of oxygen consumed. If air is 21% oxygen, what volume of air at STP is needed to produce enough energy for the man to clear snow from a walkway that requires 35 minutes of shoveling?

4. ♦ Calcium carbonate is an important filler in the processing industry. Its many uses include a reinforcing agent for rubber and improving the whiteness and hiding power of paints. When calcium nitrate is used as a starting material in the manufacture of fertilizers, calcium carbonate is produced according to the following chemical reaction:

   $Ca(NO_3)_2 + 2\ NH_3 + CO_2 + H_2O \rightarrow CaCO_3 + 2\ NH_4NO_3$

   1. What volume of CO_2 at STP is needed to react completely with 28.0 g of calcium nitrate?
   2. What volume of ammonia at STP is needed to react with the amount of calcium nitrate?
   3. If this reaction were carried out in Denver, Colorado (pressure = 630 mmHg), what volumes of CO_2 and NH_3 at room temperature (20°C) would be needed?

5. ♦ Calcium nitrate used in the process described in Problem 4 is produced by the reaction of fluoroapatite—$Ca_5[(PO_4)_3(F)]$—with nitric acid:

   $Ca_5[(PO_4)_3(F)] + 10\ HNO_3 \rightarrow 5\ Ca(NO_3)_2 + HF + 3\ H_3PO_4\ Ca(NO_3)_2 + 2\ NH_3 + CO_2 + H_2O \rightarrow CaCO_3 + 2\ NH_4NO_3$

   1. Your lab is in Denver, Colorado, and you have a cylinder with 8.40 L of CO_2 at room temperature (20°C) and 4.75 atm pressure. What would be the volume of the CO_2 gas at 630 mmHg? How many grams of fluoroapatite could be converted to $CaCO_3$ using the two reactions and this amount of CO_2?
   2. If 3.50 L of a 0.753 M HF solution was produced during the conversion of fluoroapatite to calcium nitrate, how many grams of calcium carbonate could you produce, assuming 100% efficiency?
   3. How many liters of ammonia gas at this higher altitude and 20°C are required to convert the calcium nitrate to calcium carbonate *and* to neutralize all of the HF solution?

4. If the reaction of fluoroapatite with nitric acid takes place at 330 atm and 80°C, what volumes of NH_3 and CO_2 are needed to convert 20.5 kg of fluoroapatite to calcium carbonate?

6. Mars has an average temperature of −47°C; a surface pressure of 500 Pa; and an atmosphere that is 95% carbon dioxide, 3% nitrogen, and 2% argon by mass, with traces of other gases. What is the partial pressure (in atmospheres) of each gas in this atmosphere? A 5.0 L sample is returned to Earth and stored in a laboratory at 19°C and 1 atm. What is the volume of this sample?

7. ♦ Chlorofluorocarbons (CFCs) are inert substances that were long used as refrigerants. Because CFCs are inert, when they are released into the atmosphere they are not rapidly destroyed in the lower atmosphere. Instead, they are carried into the stratosphere, where they cause ozone depletion. A method for destroying CFC stockpiles passes the CFC through packed sodium oxalate ($Na_2C_2O_4$) powder at 270°C. The reaction for Freon-12 (CF_2Cl_2) is as follows:

   $CF_2Cl_2(g) + 2\ Na_2C_2O_4(s) \rightarrow 2\ NaF(s) + 2\ NaCl + C(s) + 4\ CO_2(g)$

   1. If this reaction produced 11.4 L of CO_2 gas at 21°C and 752 mmHg, what mass of sodium oxalate was consumed in the reaction?
   2. If you had to design a reactor to carry out the reaction at a maximum safe pressure of 10.0 atm while destroying 1.0 kg of Freon-12, what volume reactor would you need?
   3. A 2.50 L reaction vessel is charged with 20.0 atm of Freon-12 and excess sodium oxalate at 20°C. The temperature is increased to 270°C, and the pressure is monitored as the reaction progresses. What is the initial pressure at 270°C? What is the final pressure when the reaction has gone to completion?

8. ♦ The exhaust from a typical six-cylinder car contains the following average compositions of CO and CO_2 under different conditions (data reported as percent by volume; rpm = rotations per minute):

Species	Idling (1000 rpm)	Accelerating (4000 rpm)	Decelerating (800 rpm)
CO	1.0	1.2	0.60
CO_2	0.80	0.40	0.40

   1. What are the mole fractions of CO and CO_2 under each set of conditions?
   2. If the engine takes in 4.70 L of air at STP mixed with fine droplets of gasoline (C_8H_{18}) with each rotation, how many grams of gasoline are burned per minute?

9. Automobile airbags inflate by the decomposition of sodium azide (NaN_3), which produces sodium metal and nitrogen gas according to the following chemical equation:

   $2\ NaN_3 \rightarrow 2\ Na(s) + 3\ N_2(g)$

   How many grams of sodium azide are needed to inflate a 15.0 L airbag at 20°C and 760 mmHg? The density of NaN_3 is 1.847 g/cm^3. What is the volume of the gas produced compared to the solid reactant? Suggest a plausible reason to explain why skin burns can result from the inflation of an airbag during an automobile accident.

10. Under basic conditions, the reaction of hydrogen peroxide (H_2O_2) and potassium permanganate ($KMnO_4$) produces oxygen and manganese dioxide. During a laboratory exercise, you carefully weighed out your sample of $KMnO_4$. Unfortunately, however, you lost your data just before mixing the $KMnO_4$ with an H_2O_2 solution of unknown concentration. Devise a method to determine the mass of your sample of $KMnO_4$ using excess H_2O_2.

11. Carbonated beverages are pressurized with CO_2. In an attempt to produce another bubbly soda beverage, an intrepid chemist attempted to use three other gases: He, N_2, and Xe. Rank the four beverages in order of how fast the drink would go “flat” and explain your reasoning. Which beverage would have the shortest shelf life (i.e., how long will an *unopened* bottle still be good)? Explain your answer.

12. ♦ Urea is synthesized industrially by the reaction of ammonia and carbon dioxide to produce ammonium carbamate, followed by dehydration of ammonium carbamate to give urea and water. This process is shown in the following set of chemical equations:

$2\ NH_3(g) + CO_2(g) \rightarrow NH_2CO_2NH_4(s)$ $NH_2CO_2NH_4(s) \rightarrow NH_2CONH_2(s) + H_2O(g)$

1. A 50.0 L reaction vessel is charged with 2.5 atm of ammonia and 2.5 atm of CO_2 at 50°C, and the vessel is then heated to 150°C. What is the pressure in the vessel when the reaction has gone to completion? If the vessel is then cooled to 20°C, what is the pressure?
2. An aqueous solution of urea and water is drained from the reaction vessel. What is the molarity of the urea solution? Industrially, this reaction is actually carried out at pressures ranging from 130 to 260 atm and temperatures of approximately 180°C. Give a plausible reason for using these extreme conditions.

13. Explain what happens to the temperature, the volume, or the pressure of a gas during each operation and give the direction of heat flow, if any.

    1. The gas is allowed to expand from V_1 to V_2; a heat transfer occurs to maintain a constant gas temperature.
    2. The gas is allowed to expand from V_2 to V_3 with no concomitant heat transfer.
    3. The gas is compressed from V_3 to V_4; a heat transfer occurs to maintain a constant gas temperature.
    4. The gas is compressed from V_4 to V_1; no heat transfer occurs.

    These four processes constitute the cycle used in refrigeration, in which a gas such as Freon is alternately compressed and allowed to expand in the piston of a compressor. Which step eventually causes the food in a refrigerator to cool? Where does the thermal energy go that was removed in the cooling process?

Answers

1. 5.9 g oxalic acid, 7.8 L
2.
3. 278 L

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CHAPTER OVERVIEW

4: Intermolecular Forces

4.1: Intermolecular Forces

4.2: Properties of Liquids

4.3: Intermolecular Forces and the Solution Process

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4.1: Intermolecular Forces

Learning Objectives

- Describe the types of intermolecular forces possible between atoms or molecules in condensed phases (dispersion forces, dipole-dipole attractions, and hydrogen bonding)
- Identify the types of intermolecular forces experienced by specific molecules based on their structures
- Explain the relation between the intermolecular forces present within a substance and the temperatures associated with changes in its physical state

As was the case for gaseous substances, the kinetic molecular theory may be used to explain the behavior of solids and liquids. In the following description, the term *particle* will be used to refer to an atom, molecule, or ion. Note that we will use the popular phrase "intermolecular attraction" to refer to attractive forces between the particles of a substance, regardless of whether these particles are molecules, atoms, or ions.

Consider these two aspects of the molecular-level environments in solid, liquid, and gaseous matter:

- Particles in a solid are tightly packed together and often arranged in a regular pattern; in a liquid, they are close together with no regular arrangement; in a gas, they are far apart with no regular arrangement.
- Particles in a solid vibrate about fixed positions and do not generally move in relation to one another; in a liquid, they move past each other but remain in essentially constant contact; in a gas, they move independently of one another except when they collide.

The differences in the properties of a solid, liquid, or gas reflect the strengths of the attractive forces between the atoms, molecules, or ions that make up each phase. The phase in which a substance exists depends on the relative extents of its intermolecular forces (IMFs) and the kinetic energies (KE) of its molecules. IMFs are the various forces of attraction that may exist between the atoms and molecules of a substance due to electrostatic phenomena, as will be detailed in this module. These forces serve to hold particles close together, whereas the particles' KE provides the energy required to overcome the attractive forces and thus increase the distance between particles. Figure **4.1.1** illustrates how changes in physical state may be induced by changing the temperature, hence, the average KE, of a given substance.

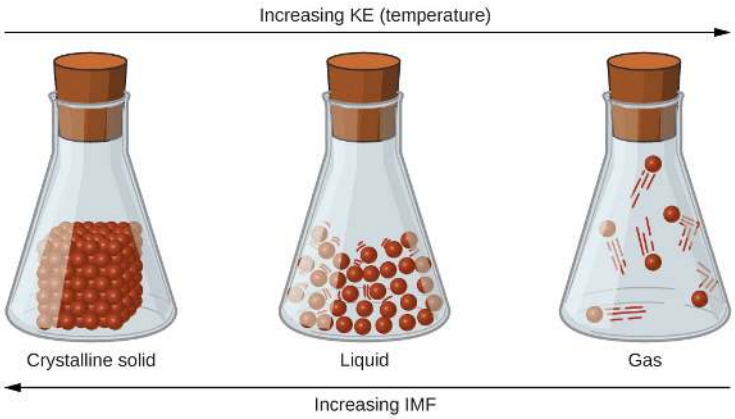


Figure **4.1.1**: Transitions between solid, liquid, and gaseous states of a substance occur when conditions of temperature or pressure favor the associated changes in intermolecular forces. (Note: The space between particles in the gas phase is much greater than shown.)

As an example of the processes depicted in this figure, consider a sample of water. When gaseous water is cooled sufficiently, the attractions between H_2O molecules will be capable of holding them together when they come into contact with each other; the gas condenses, forming liquid H_2O. For example, liquid water forms on the outside of a cold glass as the water vapor in the air is cooled by the cold glass, as seen in Figure **4.1.2**.



Figure **4.1.2**: Condensation forms when water vapor in the air is cooled enough to form liquid water, such as (a) on the outside of a cold beverage glass or (b) in the form of fog. (credit a: modification of work by Jenny Downing; credit b: modification of work by Cory Zanker)

We can also liquefy many gases by compressing them, if the temperature is not too high. The increased pressure brings the molecules of a gas closer together, such that the attractions between the molecules become strong relative to their KE. Consequently, they form liquids. Butane, C_4H_{10}, is the fuel used in disposable lighters and is a gas at standard temperature and pressure. Inside the lighter's fuel compartment, the butane is compressed to a pressure that results in its condensation to the liquid state, as shown in Figure **4.1.3**.



Figure **4.1.3**: Gaseous butane is compressed within the storage compartment of a disposable lighter, resulting in its condensation to the liquid state. (credit: modification of work by "Sam-Cat"/Flickr)

Finally, if the temperature of a liquid becomes sufficiently low, or the pressure on the liquid becomes sufficiently high, the molecules of the liquid no longer have enough KE to overcome the IMF between them, and a solid forms. A more thorough discussion of these and other changes of state, or phase transitions, is provided in a later module of this chapter.

4.1.1: Forces between Molecules

Under appropriate conditions, the attractions between all gas molecules will cause them to form liquids or solids. This is due to intermolecular forces, not *intra*molecular forces. *Intra*molecular forces are those *within* the molecule that keep the molecule together, for example, the bonds between the atoms. *Inter*molecular forces are the attractions *between* molecules, which determine many of the physical properties of a substance. Figure **4.1.4** illustrates these different molecular forces. The strengths of these attractive forces vary widely, though usually the IMFs between small molecules are weak compared to the intramolecular forces that bond atoms together within a molecule. For example, to overcome the IMFs in one mole of liquid HCl and convert it into

gaseous HCl requires only about 17 kilojoules. However, to break the covalent bonds between the hydrogen and chlorine atoms in one mole of HCl requires about 25 times more energy—430 kilojoules.

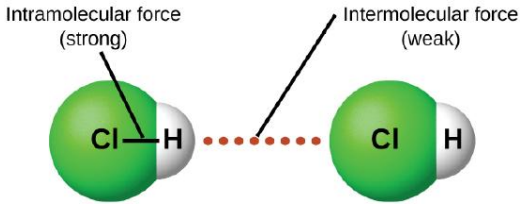


Figure **4.1.4**: Intramolecular forces keep a molecule intact. Intermolecular forces hold multiple molecules together and determine many of a substance's properties.

All of the attractive forces between neutral atoms and molecules are known as van der Waals forces, although they are usually referred to more informally as intermolecular attraction. We will consider the various types of IMFs in the next three sections of this module.

4.1.2: Dispersion Forces

One of the three van der Waals forces is present in all condensed phases, regardless of the nature of the atoms or molecules composing the substance. This attractive force is called the London dispersion force in honor of German-born American physicist Fritz London who, in 1928, first explained it. This force is often referred to as simply the dispersion force. Because the electrons of an atom or molecule are in constant motion (or, alternatively, the electron's location is subject to quantum-mechanical variability), at any moment in time, an atom or molecule can develop a temporary, instantaneous dipole if its electrons are distributed asymmetrically. The presence of this dipole can, in turn, distort the electrons of a neighboring atom or molecule, producing an induced dipole. These two rapidly fluctuating, temporary dipoles thus result in a relatively weak electrostatic attraction between the species—a so-called dispersion force like that illustrated in Figure **4.1.5**.

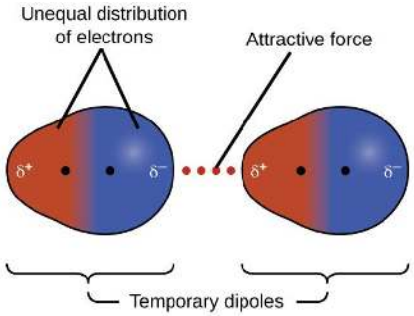


Figure **4.1.5**: Dispersion forces result from the formation of temporary dipoles, as illustrated here for two nonpolar diatomic molecules.

Dispersion forces that develop between atoms in different molecules can attract the two molecules to each other. The forces are relatively weak, however, and become significant only when the molecules are very close. Larger and heavier atoms and molecules exhibit stronger dispersion forces than do smaller and lighter atoms and molecules. F_2 and Cl_2 are gases at room temperature (reflecting weaker attractive forces); Br_2 is a liquid, and I_2 is a solid (reflecting stronger attractive forces). Trends in observed melting and boiling points for the halogens clearly demonstrate this effect, as seen in Table **4.1.1**.

Table **4.1.1**: Melting and Boiling Points of the Halogens

Halogen	Molar Mass	Atomic Radius	Melting Point	Boiling Point
fluorine, F_2	38 g/mol	72 pm	53 K	85 K
chlorine, Cl_2	71 g/mol	99 pm	172 K	238 K
bromine, Br_2	160 g/mol	114 pm	266 K	332 K
iodine, I_2	254 g/mol	133 pm	387 K	457 K
astatine, At_2	420 g/mol	150 pm	575 K	610 K

The increase in melting and boiling points with increasing atomic/molecular size may be rationalized by considering how the strength of dispersion forces is affected by the electronic structure of the atoms or molecules in the substance. In a larger atom, the valence electrons are, on average, farther from the nuclei than in a smaller atom. Thus, they are less tightly held and can more easily form the temporary dipoles that produce the attraction. The measure of how easy or difficult it is for another electrostatic charge (for example, a nearby ion or polar molecule) to distort a molecule's charge distribution (its electron cloud) is known as polarizability. A molecule that has a charge cloud that is easily distorted is said to be very polarizable and will have large dispersion forces; one with a charge cloud that is difficult to distort is not very polarizable and will have small dispersion forces.

Example 4.1.1: London Forces and Their Effects

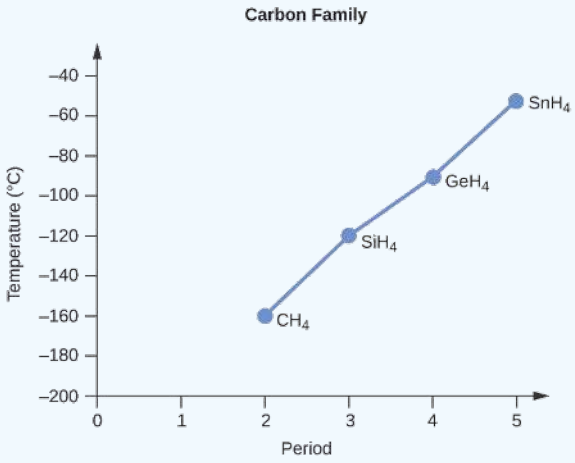
Order the following compounds of a group 14 element and hydrogen from lowest to highest boiling point: CH_4, SiH_4, GeH_4, and SnH_4. Explain your reasoning.

Solution

Applying the skills acquired in the chapter on chemical bonding and molecular geometry, all of these compounds are predicted to be nonpolar, so they may experience only dispersion forces: the smaller the molecule, the less polarizable and the weaker the dispersion forces; the larger the molecule, the larger the dispersion forces. The molar masses of CH_4, SiH_4, GeH_4, and SnH_4 are approximately 16 g/mol, 32 g/mol, 77 g/mol, and 123 g/mol, respectively. Therefore, CH_4 is expected to have the lowest boiling point and SnH_4 the highest boiling point. The ordering from lowest to highest boiling point is expected to be

$$CH_4 < SiH_4 < GeH_4 < SnH_4$$

A graph of the actual boiling points of these compounds versus the period of the group 14 elements shows this prediction to be correct:



Exercise 4.1.1

Order the following hydrocarbons from lowest to highest boiling point: C_2H_6, C_3H_8, and C_4H_{10}.

Answer

All of these compounds are nonpolar and only have London dispersion forces: the larger the molecule, the larger the dispersion forces and the higher the boiling point. The ordering from lowest to highest boiling point is therefore

$$C_2H_6 < C_3H_8 < C_4H_{10}.$$

The shapes of molecules also affect the magnitudes of the dispersion forces between them. For example, boiling points for the isomers *n*-pentane, isopentane, and neopentane (shown in Figure **4.1.6**) are 36 °C, 27 °C, and 9.5 °C, respectively. Even though these compounds are composed of molecules with the same chemical formula, C_5H_{12}, the difference in boiling points suggests that dispersion forces in the liquid phase are different, being greatest for *n*-pentane and least for neopentane. The elongated shape of *n*-

pentane provides a greater surface area available for contact between molecules, resulting in correspondingly stronger dispersion forces. The more compact shape of isopentane offers a smaller surface area available for intermolecular contact and, therefore, weaker dispersion forces. Neopentane molecules are the most compact of the three, offering the least available surface area for intermolecular contact and, hence, the weakest dispersion forces. This behavior is analogous to the connections that may be formed between strips of VELCRO brand fasteners: the greater the area of the strip's contact, the stronger the connection.

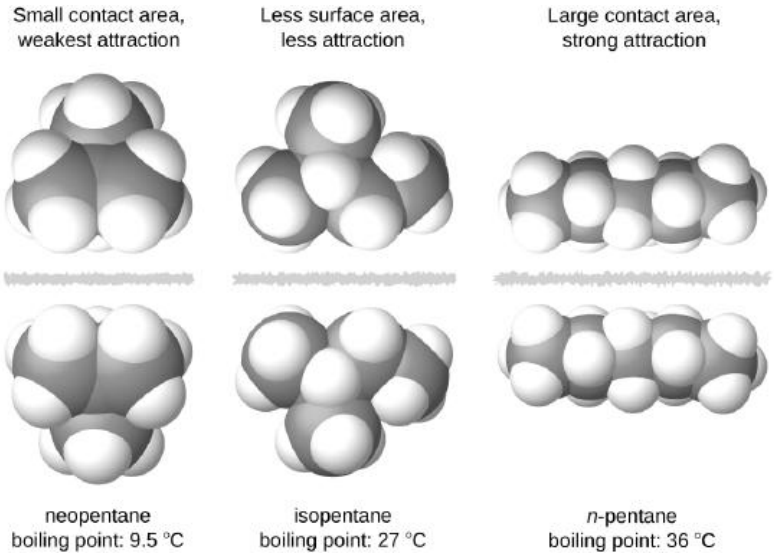


Figure **4.1.6**: The strength of the dispersion forces increases with the contact area between molecules, as demonstrated by the boiling points of these pentane isomers.

Applications: Geckos and Intermolecular Forces

Geckos have an amazing ability to adhere to most surfaces. They can quickly run up smooth walls and across ceilings that have no toe-holds, and they do this without having suction cups or a sticky substance on their toes. And while a gecko can lift its feet easily as it walks along a surface, if you attempt to pick it up, it sticks to the surface. How are geckos (as well as spiders and some other insects) able to do this? Although this phenomenon has been investigated for hundreds of years, scientists only recently uncovered the details of the process that allows geckos' feet to behave this way.

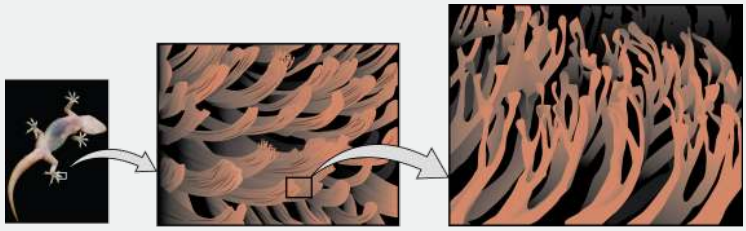


Figure **4.1.7**: Geckos' toes contain large numbers of tiny hairs (setae), which branch into many triangular tips (spatulae). Geckos adhere to surfaces because of van der Waals attractions between the surface and a gecko's millions of spatulae. By changing how the spatulae contact the surface, geckos can turn their stickiness "on" and "off." (credit photo: modification of work by "JC*+A!"/Flickr)

Geckos' toes are covered with hundreds of thousands of tiny hairs known as *setae*, with each seta, in turn, branching into hundreds of tiny, flat, triangular tips called *spatulae*. The huge numbers of spatulae on its setae provide a gecko, shown in Figure **4.1.7**, with a large total surface area for sticking to a surface. In 2000, Kellar Autumn, who leads a multi-institutional gecko research team, found that geckos adhered equally well to both polar silicon dioxide and nonpolar gallium arsenide. This proved that geckos stick to surfaces because of dispersion forces—weak intermolecular attractions arising from temporary, synchronized charge distributions between adjacent molecules. Although dispersion forces are very weak, the total attraction over millions of spatulae is large enough to support many times the gecko's weight.

In 2014, two scientists developed a model to explain how geckos can rapidly transition from “sticky” to “non-sticky.” Alex Greaney and Congcong Hu at Oregon State University described how geckos can achieve this by changing the angle between their spatulae and the surface. Geckos’ feet, which are normally nonsticky, become sticky when a small shear force is applied. By curling and uncurling their toes, geckos can alternate between sticking and unsticking from a surface, and thus easily move across it. Further investigations may eventually lead to the development of better adhesives and other applications.



Watch this video to learn more about Kellar Autumn’s research that determined that van der Waals forces are responsible for a gecko’s ability to cling and climb.

4.1.3: Dipole-Dipole Attractions

Recall from the chapter on chemical bonding and molecular geometry that *polar* molecules have a partial positive charge on one side and a partial negative charge on the other side of the molecule—a separation of charge called a *dipole*. Consider a polar molecule such as hydrogen chloride, HCl. In the HCl molecule, the more electronegative Cl atom bears the partial negative charge, whereas the less electronegative H atom bears the partial positive charge. An attractive force between HCl molecules results from the attraction between the positive end of one HCl molecule and the negative end of another. This attractive force is called a dipole-dipole attraction—the electrostatic force between the partially positive end of one polar molecule and the partially negative end of another, as illustrated in Figure **4.1.8**.

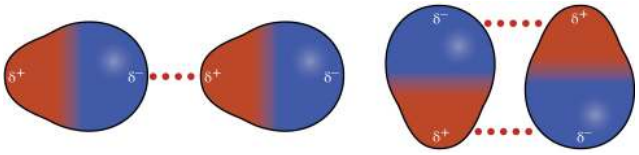


Figure **4.1.8**: This image shows two arrangements of polar molecules, such as HCl, that allow an attraction between the partial negative end of one molecule and the partial positive end of another.

The effect of a dipole-dipole attraction is apparent when we compare the properties of HCl molecules to nonpolar F_2 molecules. Both HCl and F_2 consist of the same number of atoms and have approximately the same molecular mass. At a temperature of 150 K, molecules of both substances would have the same average KE. However, the dipole-dipole attractions between HCl molecules are sufficient to cause them to “stick together” to form a liquid, whereas the relatively weaker dispersion forces between nonpolar F_2 molecules are not, and so this substance is gaseous at this temperature. The higher normal boiling point of HCl (188 K) compared to F_2 (85 K) is a reflection of the greater strength of dipole-dipole attractions between HCl molecules, compared to the attractions between nonpolar F_2 molecules. We will often use values such as boiling or freezing points, or enthalpies of vaporization or fusion, as indicators of the relative strengths of IMFs of attraction present within different substances.

✔ Example **4.1.2**: Dipole-Dipole Forces and Their Effects

Predict which will have the higher boiling point: N_2 or CO. Explain your reasoning.

Solution

CO and N_2 are both diatomic molecules with masses of about 28 amu, so they experience similar London dispersion forces. Because CO is a polar molecule, it experiences dipole-dipole attractions. Because N_2 is nonpolar, its molecules cannot exhibit dipole-dipole attractions. The dipole-dipole attractions between CO molecules are comparably stronger than the dispersion forces between nonpolar N_2 molecules, so CO is expected to have the higher boiling point.

A common method for preparing oxygen is the decomposition

? Exercise 4.1.2

Predict which will have the higher boiling point: **ICl** or **Br_2**. Explain your reasoning.

Answer

ICl. ICl and Br_2 have similar masses (~160 amu) and therefore experience similar London dispersion forces. ICl is polar and thus also exhibits dipole-dipole attractions; Br_2 is nonpolar and does not. The relatively stronger dipole-dipole attractions require more energy to overcome, so ICl will have the higher boiling point.

4.1.4: Hydrogen Bonding

Nitrosyl fluoride (ONF, molecular mass 49 amu) is a gas at room temperature. Water (H_2O, molecular mass 18 amu) is a liquid, even though it has a lower molecular mass. We clearly cannot attribute this difference between the two compounds to dispersion forces. Both molecules have about the same shape and ONF is the heavier and larger molecule. It is, therefore, expected to experience more significant dispersion forces. Additionally, we cannot attribute this difference in boiling points to differences in the dipole moments of the molecules. Both molecules are polar and exhibit comparable dipole moments. The large difference between the boiling points is due to a particularly strong dipole-dipole attraction that may occur when a molecule contains a hydrogen atom bonded to a fluorine, oxygen, or nitrogen atom (the three most electronegative elements). The very large difference in electronegativity between the H atom (2.1) and the atom to which it is bonded (4.0 for an F atom, 3.5 for an O atom, or 3.0 for a N atom), combined with the very small size of a H atom and the relatively small sizes of F, O, or N atoms, leads to *highly concentrated partial charges* with these atoms. Molecules with F-H, O-H, or N-H moieties are very strongly attracted to similar moieties in nearby molecules, a particularly strong type of dipole-dipole attraction called hydrogen bonding. Examples of hydrogen bonds include HF···HF, H_2O···HOH, and H_3N···HNH_2, in which the hydrogen bonds are denoted by dots. Figure **4.1.9** illustrates hydrogen bonding between water molecules.

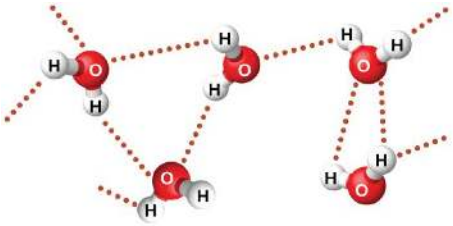


Figure **4.1.9**: Water molecules participate in multiple hydrogen-bonding interactions with nearby water molecules.

Despite use of the word “bond,” keep in mind that hydrogen bonds are *intermolecular* attractive forces, not *intramolecular* attractive forces (covalent bonds). Hydrogen bonds are much weaker than covalent bonds, only about 5 to 10% as strong, but are generally much stronger than other dipole-dipole attractions and dispersion forces.

Hydrogen bonds have a pronounced effect on the properties of condensed phases (liquids and solids). For example, consider the trends in boiling points for the binary hydrides of group 15 (NH_3, PH_3, AsH_3, and SbH_3), group 16 hydrides (H_2O, H_2S, H_2Se, and H_2Te), and group 17 hydrides (HF, HCl, HBr, and HI). The boiling points of the heaviest three hydrides for each group are plotted in Figure **4.1.10**. As we progress down any of these groups, the polarities of the molecules decrease slightly, whereas the sizes of the molecules increase substantially. The effect of increasingly stronger dispersion forces dominates that of increasingly weaker dipole-dipole attractions, and the boiling points are observed to increase steadily. For the group 15, 16, and 17 hydrides, the boiling points for each class of compounds increase with increasing molecular mass for elements in periods 3, 4, and 5.

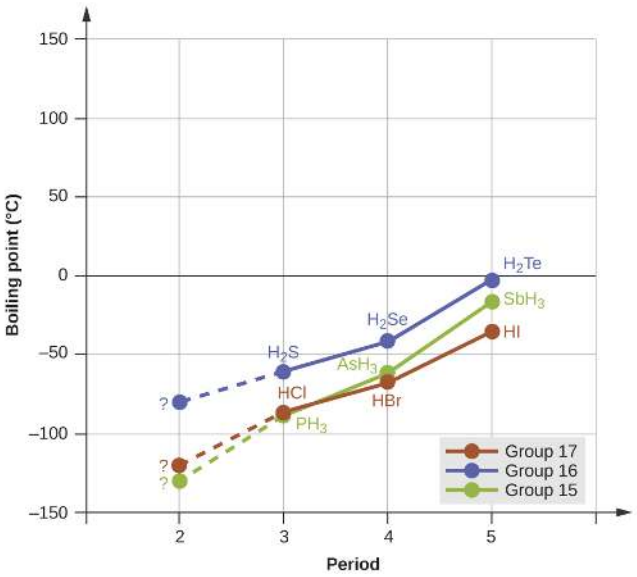


Figure 4.1.10: In comparison to periods 3−5, the binary hydrides of period 2 elements in groups 17, 16 and 15 (F, O and N, respectively) exhibit anomalously high boiling points due to hydrogen bonding.

If we use this trend to predict the boiling points for the lightest hydride for each group, we would expect NH_3 to boil at about −120 °C, H_2O to boil at about −80 °C, and HF to boil at about −110 °C. However, when we measure the boiling points for these compounds, we find that they are dramatically higher than the trends would predict, as shown in Figure 4.1.10. The stark contrast between our naïve predictions and reality provides compelling evidence for the strength of hydrogen bonding.

✔ Example 4.1.3: Effect of Hydrogen Bonding on Boiling Points

Consider the compounds dimethylether (CH_3OCH_3), ethanol (CH_3CH_2OH), and propane ($CH_3CH_2CH_3$). Their boiling points, not necessarily in order, are −42.1 °C, −24.8 °C, and 78.4 °C. Match each compound with its boiling point. Explain your reasoning.

Solution

The VSEPR-predicted shapes of CH_3OCH_3, CH_3CH_2OH, and $CH_3CH_2CH_3$ are similar, as are their molar masses (46 g/mol, 46 g/mol, and 44 g/mol, respectively), so they will exhibit similar dispersion forces. Since $CH_3CH_2CH_3$ is nonpolar, it may exhibit *only* dispersion forces. Because CH_3OCH_3 is polar, it will also experience dipole-dipole attractions. Finally, CH_3CH_2OH has an −OH group, and so it will experience the uniquely strong dipole-dipole attraction known as hydrogen bonding. So the ordering in terms of strength of IMFs, and thus boiling points, is $CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CH_2OH$. The boiling point of propane is −42.1 °C, the boiling point of dimethylether is −24.8 °C, and the boiling point of ethanol is 78.5 °C.

? Exercise 4.1.2

Ethane (CH_3CH_3) has a melting point of −183 °C and a boiling point of −89 °C. Predict the melting and boiling points for methylamine (CH_3NH_2). Explain your reasoning.

Answer

The melting point and boiling point for methylamine are predicted to be significantly greater than those of ethane. CH_3CH_3 and CH_3NH_2 are similar in size and mass, but methylamine possesses an −NH group and therefore may exhibit hydrogen bonding. This greatly increases its IMFs, and therefore its melting and boiling points. It is difficult to predict values, but the known values are a melting point of −93 °C and a boiling point of −6 °C.

4.1.5: Hydrogen Bonding and DNA

Deoxyribonucleic acid (DNA) is found in every living organism and contains the genetic information that determines the organism's characteristics, provides the blueprint for making the proteins necessary for life, and serves as a template to pass this information on to the organism's offspring. A DNA molecule consists of two (anti-)parallel chains of repeating nucleotides, which form its well-known double helical structure, as shown in Figure 4.1.10.

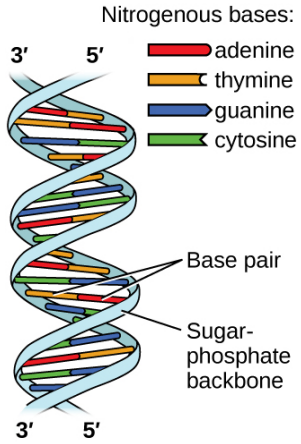


Figure 4.1.11: Two separate DNA molecules form a double-stranded helix in which the molecules are held together via hydrogen bonding. (credit: modification of work by Jerome Walker, Dennis Myts)

Each nucleotide contains a (deoxyribose) sugar bound to a phosphate group on one side, and one of four nitrogenous bases on the other. Two of the bases, cytosine (C) and thymine (T), are single-ringed structures known as pyrimidines. The other two, adenine (A) and guanine (G), are double-ringed structures called purines. These bases form complementary base pairs consisting of one purine and one pyrimidine, with adenine pairing with thymine, and cytosine with guanine. Each base pair is held together by hydrogen bonding. A and T share two hydrogen bonds, C and G share three, and both pairings have a similar shape and structure Figure 4.1.12

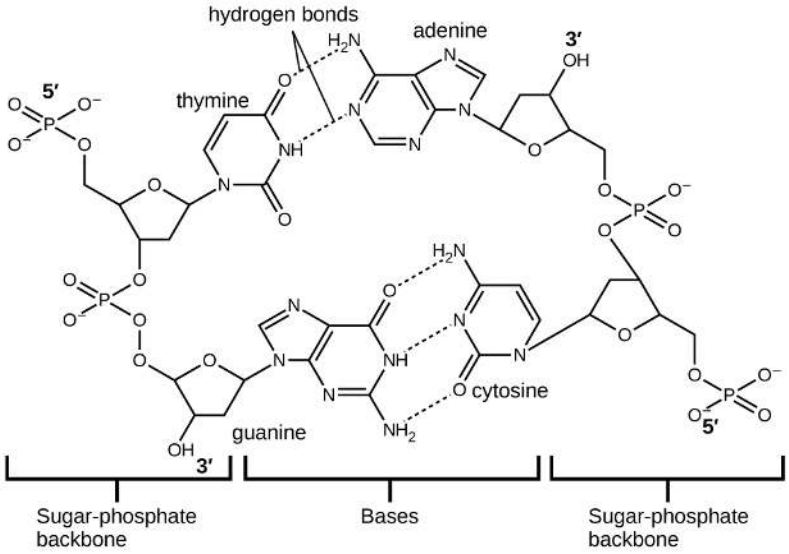


Figure 4.1.12: The geometries of the base molecules result in maximum hydrogen bonding between adenine and thymine (AT) and between guanine and cytosine (GC), so-called "complementary base pairs."

The cumulative effect of millions of hydrogen bonds effectively holds the two strands of DNA together. Importantly, the two strands of DNA can relatively easily "unzip" down the middle since hydrogen bonds are relatively weak compared to the covalent bonds that hold the atoms of the individual DNA molecules together. This allows both strands to function as a template for replication.

Summary

The physical properties of condensed matter (liquids and solids) can be explained in terms of the kinetic molecular theory. In a liquid, intermolecular attractive forces hold the molecules in contact, although they still have sufficient kinetic energy to move past each other. Intermolecular attractive forces, collectively referred to as van der Waals forces, are responsible for the behavior of liquids and solids and are electrostatic in nature. Dipole-dipole attractions result from the electrostatic attraction of the partial negative end of one dipolar molecule for the partial positive end of another. The temporary dipole that results from the motion of the electrons in an atom can induce a dipole in an adjacent atom and give rise to the London dispersion force. London forces increase with increasing molecular size. Hydrogen bonds are a special type of dipole-dipole attraction that results when hydrogen is bonded to one of the three most electronegative elements: F, O, or N.

Glossary

dipole-dipole attraction
: intermolecular attraction between two permanent dipoles

dispersion force
: (also, London dispersion force) attraction between two rapidly fluctuating, temporary dipoles; significant only when particles are very close together

hydrogen bonding
: occurs when exceptionally strong dipoles attract; bonding that exists when hydrogen is bonded to one of the three most electronegative elements: F, O, or N

induced dipole
: temporary dipole formed when the electrons of an atom or molecule are distorted by the instantaneous dipole of a neighboring atom or molecule

instantaneous dipole
: temporary dipole that occurs for a brief moment in time when the electrons of an atom or molecule are distributed asymmetrically

intermolecular force
: noncovalent attractive force between atoms, molecules, and/or ions

polarizability
: measure of the ability of a charge to distort a molecule’s charge distribution (electron cloud)

van der Waals force
: attractive or repulsive force between molecules, including dipole-dipole, dipole-induced dipole, and London dispersion forces; does not include forces due to covalent or ionic bonding, or the attraction between ions and molecules

Contributors and Attributions

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4.2: Properties of Liquids

Learning Objectives

- Distinguish between adhesive and cohesive forces
- Define viscosity, surface tension, and capillary rise
- Describe the roles of intermolecular attractive forces in each of these properties/phenomena

When you pour a glass of water, or fill a car with gasoline, you observe that water and gasoline flow freely. But when you pour syrup on pancakes or add oil to a car engine, you note that syrup and motor oil do not flow as readily. The viscosity of a liquid is a measure of its resistance to flow. Water, gasoline, and other liquids that flow freely have a low viscosity. Honey, syrup, motor oil, and other liquids that do not flow freely, like those shown in Figure **4.2.1**, have higher viscosities. We can measure viscosity by measuring the rate at which a metal ball falls through a liquid (the ball falls more slowly through a more viscous liquid) or by measuring the rate at which a liquid flows through a narrow tube (more viscous liquids flow more slowly).



Figure **4.2.1**: (a) Honey and (b) motor oil are examples of liquids with high viscosities; they flow slowly. (credit a: modification of work by Scott Bauer; credit b: modification of work by David Nagy)

Two photographs are shown and labeled “a” and “b.” Photo a shows a jar of honey with a dipper drizzling it onto a biscuit. More biscuits are shown in a basket in the background. Photo b shows the engine of a car and a person adding motor oil to the engine.

The IMFs between the molecules of a liquid, the size and shape of the molecules, and the temperature determine how easily a liquid flows. As Table **4.2.1** shows, the more structurally complex are the molecules in a liquid and the stronger the IMFs between them, the more difficult it is for them to move past each other and the greater is the viscosity of the liquid. As the temperature increases, the molecules move more rapidly and their kinetic energies are better able to overcome the forces that hold them together; thus, the viscosity of the liquid decreases.

Table **4.2.1**: Viscosities of Common Substances at 25 °C

Substance	Formula	Viscosity (mPa·s)
water	H_2O	0.890
mercury	Hg	1.526
ethanol	C_2H_5OH	1.074
octane	C_8H_{18}	0.508
ethylene glycol	$CH_2(OH)CH_2(OH)$	16.1
honey	variable	~2,000–10,000
motor oil	variable	~50–500

The various IMFs between identical molecules of a substance are examples of cohesive forces. The molecules within a liquid are surrounded by other molecules and are attracted equally in all directions by the cohesive forces within the liquid. However, the molecules on the surface of a liquid are attracted only by about one-half as many molecules. Because of the unbalanced molecular

attractions on the surface molecules, liquids contract to form a shape that minimizes the number of molecules on the surface—that is, the shape with the minimum surface area. A small drop of liquid tends to assume a spherical shape, as shown in Figure **4.2.2**, because in a sphere, the ratio of surface area to volume is at a minimum. Larger drops are more greatly affected by gravity, air resistance, surface interactions, and so on, and as a result, are less spherical.

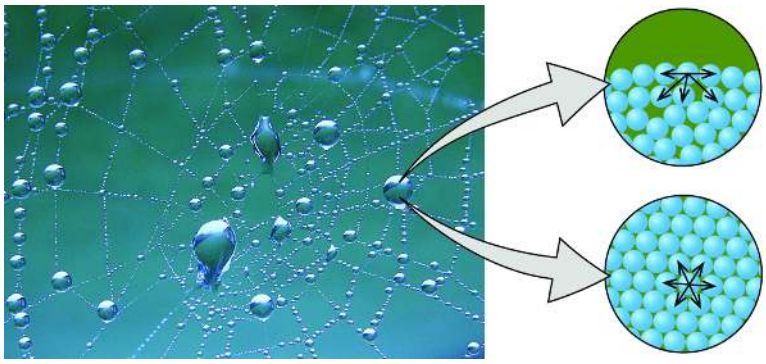


Figure **4.2.2**: Attractive forces result in a spherical water drop that minimizes surface area; cohesive forces hold the sphere together; adhesive forces keep the drop attached to the web. (credit photo: modification of work by "OliBac"/Flickr)

A photo of a spider's web with droplets of water attached to it is shown. Two images are shown the right of the photo and arrows lead from the photo to the images. The upper image shows twenty eight blue spheres stacked one atop the other in the bottom of a circular background. Five arrows are drawn pointing to the sides and downward from the sphere in the top middle of the drawing. The lower image shows another circular background of the same size as the first, but this time the blue spheres fill the image and are packed closely together. A sphere in the middle has six arrows pointing in all directions away from it.

Surface tension is defined as the energy required to increase the surface area of a liquid, or the force required to increase the length of a liquid surface by a given amount. This property results from the cohesive forces between molecules at the surface of a liquid, and it causes the surface of a liquid to behave like a stretched rubber membrane. Surface tensions of several liquids are presented in Table **4.2.2**.

Table **4.2.2**: Surface Tensions of Common Substances at 25 °C

Substance	Formula	Surface Tension (mN/m)
water	H_2O	71.99
mercury	Hg	458.48
ethanol	C_2H_5OH	21.97
octane	C_8H_{18}	21.14
ethylene glycol	$CH_2(OH)CH_2(OH)$	47.99

Among common liquids, water exhibits a distinctly high surface tension due to strong hydrogen bonding between its molecules. As a result of this high surface tension, the surface of water represents a relatively "tough skin" that can withstand considerable force without breaking. A steel needle carefully placed on water will float. Some insects, like the one shown in Figure **4.2.3**, even though they are denser than water, move on its surface because they are supported by the surface tension.

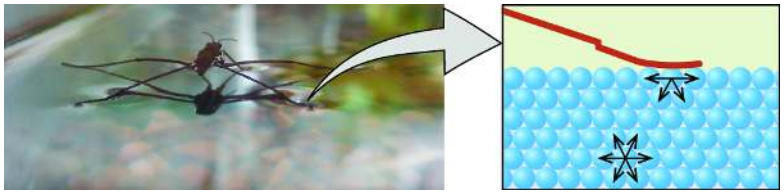


Figure **4.2.3**: Surface tension (right) prevents this insect, a "water strider," from sinking into the water.

A photo and a diagram as shown and a right-facing arrow leads from the photo to the image. The photo shows an insect standing on the surface of a sample of water. The image shows a square background that is two thirds covered in blue spheres that are closely packet together. A brown line starts at the upper left corner of the background and rests on top of the first row of spheres. The sphere directly under this low point of the line has four arrows drawn on it that face to both sides and downward. A sphere in the bottom center of the image has six arrows drawn on it that all face outward in different directions.

The IMFs of attraction between two *different* molecules are called adhesive forces. Consider what happens when water comes into contact with some surface. If the adhesive forces between water molecules and the molecules of the surface are weak compared to the cohesive forces between the water molecules, the water does not "wet" the surface. For example, water does not wet waxed surfaces or many plastics such as polyethylene. Water forms drops on these surfaces because the cohesive forces within the drops are greater than the adhesive forces between the water and the plastic. Water spreads out on glass because the adhesive force between water and glass is greater than the cohesive forces within the water. When water is confined in a glass tube, its meniscus (surface) has a concave shape because the water wets the glass and creeps up the side of the tube. On the other hand, the cohesive forces between mercury atoms are much greater than the adhesive forces between mercury and glass. Mercury therefore does not wet glass, and it forms a convex meniscus when confined in a tube because the cohesive forces within the mercury tend to draw it into a drop (Figure **4.2.4**).

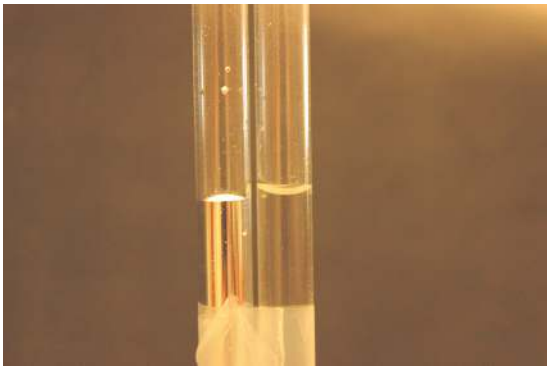


Figure **4.2.4**: Differences in the relative strengths of cohesive and adhesive forces result in different meniscus shapes for mercury (left) and water (right) in glass tubes. (credit: Mark Ott)

This figure shows two test tubes. The test tube on the left contains mercury with a meniscus that rounds up. The test tube on the right contains water with a meniscus that rounds down.

If you place one end of a paper towel in spilled wine, as shown in Figure **4.2.5**, the liquid wicks up the paper towel. A similar process occurs in a cloth towel when you use it to dry off after a shower. These are examples of capillary action—when a liquid flows within a porous material due to the attraction of the liquid molecules to the surface of the material and to other liquid molecules. The adhesive forces between the liquid and the porous material, combined with the cohesive forces within the liquid, may be strong enough to move the liquid upward against gravity.

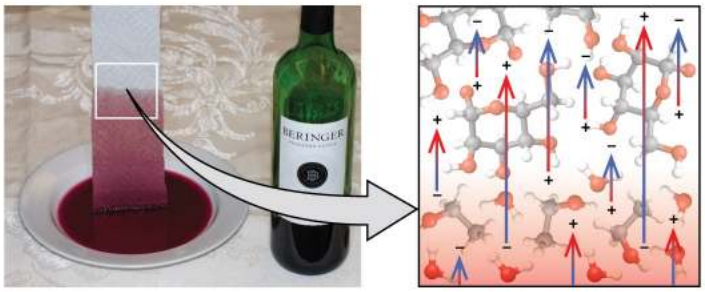


Figure **4.2.5**: Wine wicks up a paper towel (left) because of the strong attractions of water (and ethanol) molecules to the −OH groups on the towel's cellulose fibers and the strong attractions of water molecules to other water (and ethanol) molecules (right). (credit photo: modification of work by Mark Blaser)

A photo and a diagram are shown. In the photo, a paper towel is dipped into a bowl full of a red liquid sitting on a countertop. The red liquid is traveling up the lower part of the paper towel, and this section of the photo has a square drawn around it. A right-facing arrow leads from this square to the image. The image is square and has a background of two types of molecules, mixed together. The first type of molecule is composed of two bonded black spheres, one of which is single bonded to three white spheres and one of which is single bonded to two white spheres and a red sphere that is itself bonded to a white sphere. The other type of molecule is composed of six black spheres bonded together in a row and bonded to other red and white spheres. Six upward-facing arrows are drawn on top of this background. They have positive signs on their lower ends and negative signs on their heads. Four upward-facing arrows are drawn with their signs reversed.

Towels soak up liquids like water because the fibers of a towel are made of molecules that are attracted to water molecules. Most cloth towels are made of cotton, and paper towels are generally made from paper pulp. Both consist of long molecules of cellulose

that contain many −OH groups. Water molecules are attracted to these −OH groups and form hydrogen bonds with them, which draws the H_2O molecules up the cellulose molecules. The water molecules are also attracted to each other, so large amounts of water are drawn up the cellulose fibers.

Capillary action can also occur when one end of a small diameter tube is immersed in a liquid, as illustrated in Figure **4.2.6**. If the liquid molecules are strongly attracted to the tube molecules, the liquid creeps up the inside of the tube until the weight of the liquid and the adhesive forces are in balance. The smaller the diameter of the tube is, the higher the liquid climbs. It is partly by capillary action occurring in plant cells called xylem that water and dissolved nutrients are brought from the soil up through the roots and into a plant. Capillary action is the basis for thin layer chromatography, a laboratory technique commonly used to separate small quantities of mixtures. You depend on a constant supply of tears to keep your eyes lubricated and on capillary action to pump tear fluid away.

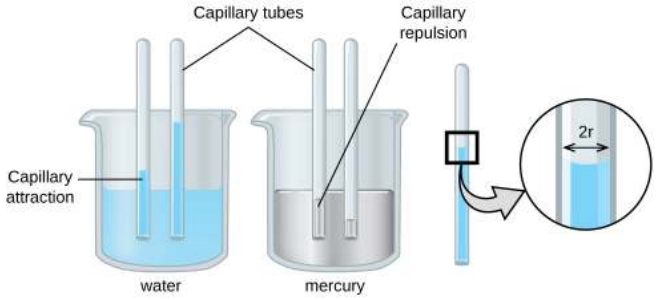


Figure **4.2.6**: Depending upon the relative strengths of adhesive and cohesive forces, a liquid may rise (such as water) or fall (such as mercury) in a glass capillary tube. The extent of the rise (or fall) is directly proportional to the surface tension of the liquid and inversely proportional to the density of the liquid and the radius of the tube.

An image of two beakers and a tube is shown. The first beaker, drawn on the left and labeled “Water,” is drawn half-full of a blue liquid. Two tubes are placed vertically in the beaker and inserted into the liquid. The liquid is shown higher in the tubes than in the beaker and is labeled “Capillary attraction.” The second beaker, drawn in the middle and labeled “Mercury,” is drawn half-full of a gray liquid. Two tubes are placed vertically in the beaker and inserted into the liquid. The liquid is shown lower in the tubes than in the beaker and is labeled “Capillary repulsion.” Lines point to the vertical tubes and label them “Capillary tubes.” A separate drawing of one of the vertical tubes from the first beaker is shown on the right. A right-facing arrow leads from the liquid in the tube to a square call-out box that shows a close-up view of the liquid’s surface. The distance across the tube is labeled “2 r” in this image.

The height to which a liquid will rise in a capillary tube is determined by several factors as shown in the following equation:

$$h = \frac{2T\cos\theta}{r\rho g} \tag{4.2.1}$$

where

- h is the height of the liquid inside the capillary tube relative to the surface of the liquid outside the tube,
- T is the surface tension of the liquid,
- θ is the contact angle between the liquid and the tube,
- r is the radius of the tube, ρ is the density of the liquid, and
- g is the acceleration due to gravity, 9.8 m/s^2.

When the tube is made of a material to which the liquid molecules are strongly attracted, they will spread out completely on the surface, which corresponds to a contact angle of 0°. This is the situation for water rising in a glass tube.

Example 4.2.1: Capillary Rise

At 25 °C, how high will water rise in a glass capillary tube with an inner diameter of 0.25 mm?

For water, T = 71.99 mN/m and ρ = 1.0 g/cm^3.

Solution

The liquid will rise to a height h given by Equation 4.2.1 :

$$h = \frac{2T\cos\theta}{r\rho g}$$

The Newton is defined as a kg m/s^2, and so the provided surface tension is equivalent to 0.07199 kg/s^2. The provided density must be converted into units that will cancel appropriately: ρ = 1000 kg/m^3. The diameter of the tube in meters is 0.00025 m, so the radius is 0.000125 m. For a glass tube immersed in water, the contact angle is θ = 0°, so cos θ = 1. Finally, acceleration due to gravity on the earth is g = 9.8 m/s^2. Substituting these values into the equation, and cancelling units, we have:

$$h = \frac{2(0.07199\ \text{kg/s}^2)}{(0.000125\ \text{m})(1000\ \text{kg/m}^3)(9.8\ \text{m/s}^2)} = 0.12\ \text{m} = 12\ \text{cm}$$

? Exercise 4.2.1

Water rises in a glass capillary tube to a height of 8.4 cm. What is the diameter of the capillary tube?

Answer

diameter = 0.36 mm

Applications: Capillary Action is Used to Draw Blood

Many medical tests require drawing a small amount of blood, for example to determine the amount of glucose in someone with diabetes or the hematocrit level in an athlete. This procedure can be easily done because of capillary action, the ability of a liquid to flow up a small tube against gravity, as shown in Figure **4.2.7**. When your finger is pricked, a drop of blood forms and holds together due to surface tension—the unbalanced intermolecular attractions at the surface of the drop. Then, when the open end of a narrow-diameter glass tube touches the drop of blood, the adhesive forces between the molecules in the blood and those at the glass surface draw the blood up the tube. How far the blood goes up the tube depends on the diameter of the tube (and the type of fluid). A small tube has a relatively large surface area for a given volume of blood, which results in larger (relative) attractive forces, allowing the blood to be drawn farther up the tube. The liquid itself is held together by its own cohesive forces. When the weight of the liquid in the tube generates a downward force equal to the upward force associated with capillary action, the liquid stops rising.



Figure **4.2.7**:: Blood is collected for medical analysis by capillary action, which draws blood into a small diameter glass tube. (credit: modification of work by Centers for Disease Control and Prevention)

A photograph shows a person’s hand being held by a person wearing medical gloves. A thin glass tube is pressed against the persons finger and blood is moving up the tube.

4.2.1: Key Concepts and Summary

The intermolecular forces between molecules in the liquid state vary depending upon their chemical identities and result in corresponding variations in various physical properties. Cohesive forces between like molecules are responsible for a liquid’s viscosity (resistance to flow) and surface tension (elasticity of a liquid surface). Adhesive forces between the molecules of a liquid and different molecules composing a surface in contact with the liquid are responsible for phenomena such as surface wetting and capillary rise.

4.2.2: Key Equations

- $h = \frac{2T\cos\theta}{r\rho g}$

Glossary

adhesive force

force of attraction between molecules of different chemical identities

capillary action

flow of liquid within a porous material due to the attraction of the liquid molecules to the surface of the material and to other liquid molecules

cohesive force

force of attraction between identical molecules

surface tension

energy required to increase the area, or length, of a liquid surface by a given amount

viscosity

measure of a liquid’s resistance to flow

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4.3: Intermolecular Forces and the Solution Process

Learning Objectives

- To understand the relationship between solubility and molecular structure.
- To demonstrate how the strength of intramolecular bonding determines the solubility of a solute in a given solvent.

The interactions that determine the solubility of a substance in a liquid depend largely on the chemical nature of the solute (such as whether it is ionic or molecular) rather than on its physical state (solid, liquid, or gas). We will first describe the general case of forming a solution of a molecular species in a liquid solvent and then describe the formation of a solution of an ionic compound.

The Role of Enthalpy in Solution Formation

Energy is required to overcome the intermolecular interactions in a solute, which can be supplied only by the new interactions that occur in the solution, when each solute particle is surrounded by particles of the solvent in a process called **solvation**, or hydration when the solvent is water. Thus all of the solute–solute interactions and many of the solvent–solvent interactions must be disrupted for a solution to form. In this section, we describe the role of enthalpy in this process.

Because enthalpy is a state function, we can use a thermochemical cycle to analyze the energetics of solution formation. The process occurs in three discrete steps, indicated by ΔH_1, ΔH_2, and ΔH_3 in Figure **4.3.1**. The overall enthalpy change in the formation of the solution (ΔH_{soln}) is the sum of the enthalpy changes in the three steps:

$$\Delta H_{soln} = \Delta H_1 + \Delta H_2 + \Delta H_3 \tag{4.3.1}$$

When a solvent is added to a solution, steps 1 and 2 are both endothermic because energy is required to overcome the intermolecular interactions in the solvent (ΔH_1) and the solute (ΔH_2). Because ΔH is positive for both steps 1 and 2, the solute–solvent interactions (ΔH_3) must be stronger than the solute–solute and solvent–solvent interactions they replace in order for the dissolution process to be exothermic ($\Delta H_{soln} < 0$). When the solute is an ionic solid, ΔH_2 corresponds to the lattice energy that must be overcome to form a solution. The higher the charge of the ions in an ionic solid, the higher the lattice energy. Consequently, solids that have very high lattice energies, such as MgO (−3791 kJ/mol), are generally insoluble in all solvents.

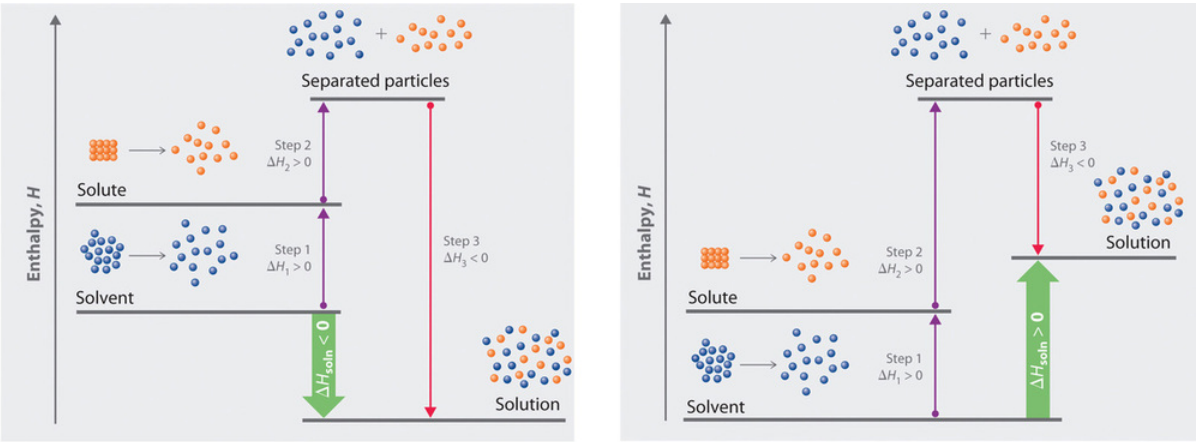


Figure **4.3.1**: Enthalpy Changes That Accompany the Formation of a Solution. Solvation can be an exothermic or endothermic process depending on the nature of the solute and solvent. In both cases, step 1, separation of the solvent particles, is energetically uphill ($\Delta H_1 > 0$), as is step 2, separation of the solute particles ($\Delta H_2 > 0$). In contrast, energy is released in step 3 ($\Delta H_3 < 0$) because of interactions between the solute and solvent. (a) When ΔH_3 is larger in magnitude than the sum of ΔH_1 and ΔH_2, the overall process is exothermic ($\Delta H_{soln} < 0$), as shown in the thermochemical cycle. (b) When ΔH_3 is smaller in magnitude than the sum of ΔH_1 and ΔH_2, the overall process is endothermic ($\Delta H_{soln} > 0$).

A positive value for ΔH_{soln} does not mean that a solution will not form. Whether a given process, including formation of a solution, occurs spontaneously depends on whether the total energy of the system is lowered as a result. Enthalpy is only one of the contributing factors. A high ΔH_{soln} is usually an indication that the substance is not very soluble. Instant cold packs used to treat

athletic injuries, for example, take advantage of the large positive ΔH_{soln} of ammonium nitrate during dissolution (+25.7 kJ/mol), which produces temperatures less than 0°C (Figure **4.3.2**).



Figure **4.3.2**: Commercial Cold Packs for Treating Injuries. These packs contain solid NH_4NO_3 and water in separate compartments. When the seal between the compartments is broken, the NH_4NO_3 dissolves in the water. Because ΔH_{soln} for NH_4NO_3 is much greater than zero, heat is absorbed by the cold pack during the dissolution process, producing local temperatures less than 0°C.

Solutions of Molecular Substances in Liquids

The London dispersion forces, dipole–dipole interactions, and hydrogen bonds that hold molecules to other molecules are generally weak. Even so, energy is required to disrupt these interactions. Unless some of that energy is recovered in the formation of new, favorable solute–solvent interactions, the increase in entropy on solution formation is not enough for a solution to form.

For solutions of gases in liquids, we can safely ignore the energy required to separate the solute molecules ($\Delta H_2 = 0$) because the molecules are already separated. Thus we need to consider only the energy required to separate the solvent molecules (ΔH_1) and the energy released by new solute–solvent interactions (ΔH_3). Nonpolar gases such as N_2, O_2, and Ar have no dipole moment and cannot engage in dipole–dipole interactions or hydrogen bonding. Consequently, the only way they can interact with a solvent is by means of London dispersion forces, which may be weaker than the solvent–solvent interactions in a polar solvent. It is not surprising, then, that nonpolar gases are most soluble in nonpolar solvents. In this case, ΔH_1 and ΔH_3 are both small and of similar magnitude. In contrast, for a solution of a nonpolar gas in a polar solvent, ΔH_1 is far greater than ΔH_3. As a result, nonpolar gases are less soluble in polar solvents than in nonpolar solvents. For example, the concentration of N_2 in a saturated solution of N_2 in water, a polar solvent, is only $7.07 \times 10^{-4}\ M$ compared with $4.5 \times 10^{-3}\ M$ for a saturated solution of N_2 in benzene, a nonpolar solvent.

The solubilities of nonpolar gases in water generally increase as the molecular mass of the gas increases, as shown in Table **4.3.1**. This is precisely the trend expected: as the gas molecules become larger, the strength of the solvent–solute interactions due to London dispersion forces increases, approaching the strength of the solvent–solvent interactions.

Table **4.3.1**: Solubilities of Selected Gases in Water at 20°C and 1 atm Pressure

Gas	Solubility (M) × 10^{-4}
He	3.90
Ne	4.65
Ar	15.2
Kr	27.9
Xe	50.2
H_2	8.06
N_2	7.07
CO	10.6
O_2	13.9
N_2O	281
CH_4	15.5

Virtually all common organic liquids, whether polar or not, are miscible. The strengths of the intermolecular attractions are comparable; thus the enthalpy of solution is expected to be small ($\Delta H_{soln} \approx 0$), and the increase in entropy drives the formation of a solution. If the predominant intermolecular interactions in two liquids are very different from one another, however, they may be immiscible. For example, organic liquids such as benzene, hexane, CCl_4, and CS_2 (S=C=S) are nonpolar and have no ability to act as hydrogen bond donors or acceptors with hydrogen-bonding solvents such as H_2O, HF, and NH_3; hence they are immiscible in these solvents. When shaken with water, they form separate phases or layers separated by an interface (Figure **4.3.3**), the region between the two layers. Just because two liquids are immiscible, however, does not mean that they are completely insoluble in each other. For example, 188 mg of benzene dissolves in 100 mL of water at 23.5°C. Adding more benzene results in the separation of an upper layer consisting of benzene with a small amount of dissolved water (the solubility of water in benzene is only 178 mg/100 mL of benzene).



Figure **4.3.3**: Immiscible Liquids. Separatory funnel demonstrating the separation of oil and colored water. from Wikipedia

The solubilities of simple alcohols in water are given in Table **4.3.2**.

Table **4.3.2**: Solubilities of Straight-Chain Organic Alcohols in Water at 20°C

Alcohol	Solubility (mol/100 g of H_2O)
methanol	completely miscible
ethanol	completely miscible
n-propanol	completely miscible
n-butanol	0.11
n-pentanol	0.030
n-hexanol	0.0058
n-heptanol	0.0008

Only the three lightest alcohols (methanol, ethanol, and n-propanol) are completely miscible with water. As the molecular mass of the alcohol increases, so does the proportion of hydrocarbon in the molecule. Correspondingly, the importance of hydrogen bonding and dipole–dipole interactions in the pure alcohol decreases, while the importance of London dispersion forces increases, which leads to progressively fewer favorable electrostatic interactions with water. Organic liquids such as acetone, ethanol, and tetrahydrofuran are sufficiently polar to be completely miscible with water yet sufficiently nonpolar to be completely miscible with all organic solvents.



Tetrahydrofuran (THF)

The same principles govern the solubilities of molecular solids in liquids. For example, elemental sulfur is a solid consisting of cyclic S_8 molecules that have no dipole moment. Because the S_8 rings in solid sulfur are held to other rings by London dispersion forces, elemental sulfur is insoluble in water. It is, however, soluble in nonpolar solvents that have comparable London dispersion forces, such as CS_2 (23 g/100 mL). In contrast, glucose contains five –OH groups that can form hydrogen bonds. Consequently, glucose is very soluble in water (91 g/120 mL of water) but essentially insoluble in nonpolar solvents such as benzene. The structure of one isomer of glucose is shown here.



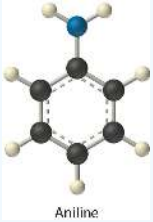
D-Glucose

Low-molecular-mass hydrocarbons with highly electronegative and polarizable halogen atoms, such as chloroform ($CHCl_3$) and methylene chloride (CH_2Cl_2), have both significant dipole moments and relatively strong London dispersion forces. These hydrocarbons are therefore powerful solvents for a wide range of polar and nonpolar compounds. Naphthalene, which is nonpolar, and phenol (C_6H_5OH), which is polar, are very soluble in chloroform. In contrast, the solubility of ionic compounds is largely determined not by the polarity of the solvent but rather by its dielectric constant, a measure of its ability to separate ions in solution, as you will soon see.

Example 4.3.1

Identify the most important solute–solvent interactions in each solution.

a. iodine in benzene
b. aniline ($C_6H_5NH_2$) in dichloromethane (CH_2Cl_2)


Aniline

c. iodine in water

Given: components of solutions

Asked for: predominant solute–solvent interactions

Strategy:

Identify all possible intermolecular interactions for both the solute and the solvent: London dispersion forces, dipole–dipole interactions, or hydrogen bonding. Determine which is likely to be the most important factor in solution formation.

Solution

a. Benzene and $I2$ are both nonpolar molecules. The only possible attractive forces are London dispersion forces.
b. Aniline is a polar molecule with an $-NH_2$ group, which can act as a hydrogen bond donor. Dichloromethane is also polar, but it has no obvious hydrogen bond acceptor. Therefore, the most important interactions between aniline and CH_2Cl_2 are likely to be London interactions.
c. Water is a highly polar molecule that engages in extensive hydrogen bonding, whereas I_2 is a nonpolar molecule that cannot act as a hydrogen bond donor or acceptor. The slight solubility of I_2 in water ($1.3 \times 10^{-3}\ mol/L$ at 25°C) is due to London dispersion forces.

Exercise 4.3.1

Identify the most important interactions in each solution:

a. ethylene glycol ($HOCH_2CH_2OH$) in acetone
b. acetonitrile ($CH_3C{\equiv}N$) in acetone
c. n-hexane in benzene

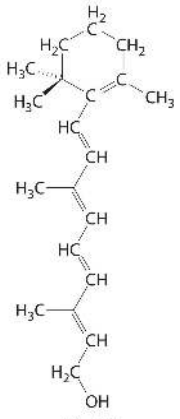
Answer:

a. hydrogen bonding
b. London interactions
c. London dispersion forces

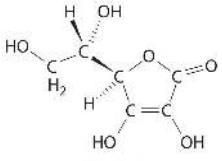
Hydrophilic and Hydrophobic Solutes

A solute can be classified as hydrophilic (literally, “water loving”), meaning that it has an electrostatic attraction to water, or hydrophobic (“water fearing”), meaning that it repels water. A hydrophilic substance is polar and often contains O–H or N–H groups that can form hydrogen bonds to water. For example, glucose with its five O–H groups is hydrophilic. In contrast, a hydrophobic substance may be polar but usually contains C–H bonds that do not interact favorably with water, as is the case with naphthalene and n-octane. Hydrophilic substances tend to be very soluble in water and other strongly polar solvents, whereas hydrophobic substances are essentially insoluble in water and soluble in nonpolar solvents such as benzene and cyclohexane.

The difference between hydrophilic and hydrophobic substances has substantial consequences in biological systems. For example, vitamins can be classified as either fat soluble or water soluble. Fat-soluble vitamins, such as vitamin A, are mostly nonpolar, hydrophobic molecules. As a result, they tend to be absorbed into fatty tissues and stored there. In contrast, water-soluble vitamins, such as vitamin C, are polar, hydrophilic molecules that circulate in the blood and intracellular fluids, which are primarily aqueous. Water-soluble vitamins are therefore excreted much more rapidly from the body and must be replenished in our daily diet. A comparison of the chemical structures of vitamin A and vitamin C quickly reveals why one is hydrophobic and the other hydrophilic.



Vitamin A
(*trans*-Retinol)

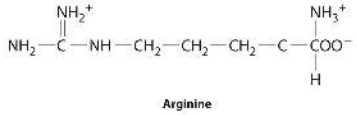


Vitamin C
(L-Ascorbic acid)

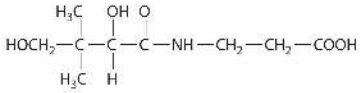
Because water-soluble vitamins are rapidly excreted, the risk of consuming them in excess is relatively small. Eating a dozen oranges a day is likely to make you tired of oranges long before you suffer any ill effects due to their high vitamin C content. In contrast, fat-soluble vitamins constitute a significant health hazard when consumed in large amounts. For example, the livers of polar bears and other large animals that live in cold climates contain large amounts of vitamin A, which have occasionally proven fatal to humans who have eaten them.

Example 4.3.2

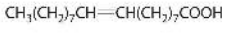
The following substances are essential components of the human diet:



Arginine



Pantothenic acid



Oleic acid

Using what you know of hydrophilic and hydrophobic solutes, classify each as water soluble or fat soluble and predict which are likely to be required in the diet on a daily basis.

a. arginine
b. pantothenic acid
c. oleic acid

Given: chemical structures

Asked for: classification as water soluble or fat soluble; dietary requirement

Strategy:

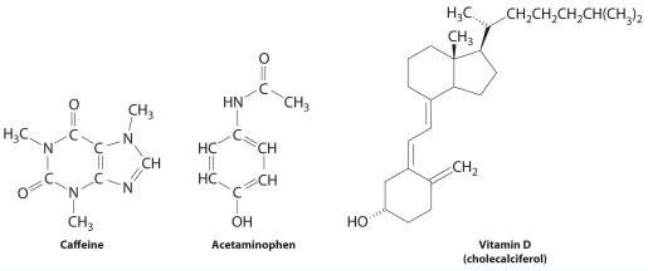
Based on the structure of each compound, decide whether it is hydrophilic or hydrophobic. If it is hydrophilic, it is likely to be required on a daily basis.

Solution:

a. Arginine is a highly polar molecule with two positively charged groups and one negatively charged group, all of which can form hydrogen bonds with water. As a result, it is hydrophilic and required in our daily diet.
b. Although pantothenic acid contains a hydrophobic hydrocarbon portion, it also contains several polar functional groups ($-OH$ and $-CO_2H$) that should interact strongly with water. It is therefore likely to be water soluble and required in the diet. (In fact, pantothenic acid is almost always a component of multiple-vitamin tablets.)
c. Oleic acid is a hydrophobic molecule with a single polar group at one end. It should be fat soluble and not required daily.

? Exercise 4.3.2

These compounds are consumed by humans: caffeine, acetaminophen, and vitamin D. Identify each as primarily hydrophilic (water soluble) or hydrophobic (fat soluble), and predict whether each is likely to be excreted from the body rapidly or slowly.



Answer: Caffeine and acetaminophen are water soluble and rapidly excreted, whereas vitamin D is fat soluble and slowly excreted

Solid Solutions

Solutions are not limited to gases and liquids; solid solutions also exist. For example, amalgams, which are usually solids, are solutions of metals in liquid mercury. Because most metals are soluble in mercury, amalgams are used in gold mining, dentistry, and many other applications. A major difficulty when mining gold is separating very small particles of pure gold from tons of crushed rock. One way to accomplish this is to agitate a suspension of the crushed rock with liquid mercury, which dissolves the gold (as well as any metallic silver that might be present). The very dense liquid gold–mercury amalgam is then isolated and the mercury distilled away.

An alloy is a solid or liquid solution that consists of one or more elements in a metallic matrix. A solid alloy has a single homogeneous phase in which the crystal structure of the solvent remains unchanged by the presence of the solute. Thus the microstructure of the alloy is uniform throughout the sample. Examples are substitutional and interstitial alloys such as brass or solder. Liquid alloys include sodium/potassium and gold/mercury. In contrast, a partial alloy solution has two or more phases that can be homogeneous in the distribution of the components, but the microstructures of the two phases are not the same. As a liquid solution of lead and tin is cooled, for example, different crystalline phases form at different cooling temperatures. Alloys usually have properties that differ from those of the component elements.

Network solids such as diamond, graphite, and $ceSiO_2$ are insoluble in all solvents with which they do not react chemically. The covalent bonds that hold the network or lattice together are simply too strong to be broken under normal conditions. They are certainly much stronger than any conceivable combination of intermolecular interactions that might occur in solution. Most metals are insoluble in virtually all solvents for the same reason: the delocalized metallic bonding is much stronger than any favorable metal atom–solvent interactions. Many metals react with solutions such as aqueous acids or bases to produce a solution. However, in these instances the metal undergoes a chemical transformation that cannot be reversed by simply removing the solvent.

Solids with very strong intermolecular bonding tend to be insoluble.

Solubilities of Ionic Substances in Liquids

Ionic substances are generally most soluble in polar solvents; the higher the lattice energy, the more polar the solvent must be to overcome the lattice energy and dissolve the substance. Because of its high polarity, water is the most common solvent for ionic compounds. Many ionic compounds are soluble in other polar solvents, however, such as liquid ammonia, liquid hydrogen fluoride, and methanol. Because all these solvents consist of molecules that have relatively large dipole moments, they can interact favorably with the dissolved ions.

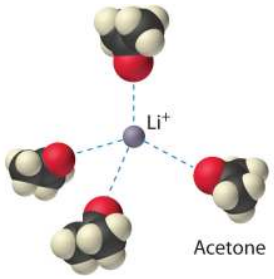


Figure **4.3.4**: Ion–Dipole Interactions in the Solvation of Li+ Ions by Acetone, a Polar Solvent

The interaction of water with Na+ and Cl− ions in an aqueous solution of **NaCl** was illustrated in Figure 4.3. The ion–dipole interactions between Li+ ions and acetone molecules in a solution of LiCl in acetone are shown in Figure **4.3.4**. The energetically favorable Li+–acetone interactions make ΔH_3 in Figure 13.1 sufficiently negative to overcome the positive ΔH_1 and ΔH_2. Because the dipole moment of acetone (2.88 D), and thus its polarity, is actually larger than that of water (1.85 D), one might even expect that LiCl would be more soluble in acetone than in water. In fact, the opposite is true: 83 g of LiCl dissolve in 100 mL of water at 20°C, but only about 4.1 g of LiCl dissolve in 100 mL of acetone. This apparent contradiction arises from the fact that the dipole moment is a property of a single molecule in the gas phase. A more useful measure of the ability of a solvent to dissolve ionic compounds is its dielectric constant (ε), which is the ability of a bulk substance to decrease the electrostatic forces between two charged particles. By definition, the dielectric constant of a vacuum is 1. In essence, a solvent with a high dielectric constant causes the charged particles to behave as if they have been moved farther apart. At 25°C, the dielectric constant of water is 80.1, one of the highest known, and that of acetone is only 21.0. Hence water is better able to decrease the electrostatic attraction between Li+ and Cl− ions, so LiCl is more soluble in water than in acetone. This behavior is in contrast to that of molecular substances, for which polarity is the dominant factor governing solubility.

A solvent's dielectric constant is the most useful measure of its ability to dissolve ionic compounds. A solvent's polarity is the dominant factor in dissolving molecular substances.

Summary

The solubility of a substance is the maximum amount of a solute that can dissolve in a given quantity of solvent; it depends on the chemical nature of both the solute and the solvent and on the temperature and pressure. The solubility of a substance in a liquid is determined by intermolecular interactions, which also determine whether two liquids are miscible. Solutes can be classified as hydrophilic (water loving) or hydrophobic (water fearing). Vitamins with hydrophilic structures are water soluble, whereas those with hydrophobic structures are fat soluble. Many metals dissolve in liquid mercury to form amalgams. Covalent network solids and most metals are insoluble in nearly all solvents. The solubility of ionic compounds is largely determined by the dielectric constant (ε) of the solvent, a measure of its ability to decrease the electrostatic forces between charged particles. Solutions of many ionic compounds in organic solvents can be dissolved using crown ethers, cyclic polyethers large enough to accommodate a metal ion in the center, or cryptands, compounds that completely surround a cation.

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CHAPTER OVERVIEW

5: Solids

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General Chemistry

The great distances between atoms and molecules in a gaseous phase, and the corresponding absence of any significant interactions between them, allows for simple descriptions of many physical properties that are the same for all gases, regardless of their chemical identities. As described in the final module of the chapter on gases, this situation changes at high pressures and low temperatures—conditions that permit the atoms and molecules to interact to a much greater extent. In the liquid and solid states, these interactions are of considerable strength and play an important role in determining a number of physical properties that *do* depend on the chemical identity of the substance. In this chapter, the nature of these interactions and their effects on various physical properties of liquid and solid phases will be examined.

5.1: Prelude to Liquids and Solids

5.2: Carbon and Silicon- Network Atomic Solids

5.3: The Solid State of Matter

5.4: Lattice Structures in Crystalline Solids

5.5: Bonding in Metals and Semiconductors

5.E: Liquids and Solids (Exercises)

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5.1: Prelude to Liquids and Solids

The great distances between atoms and molecules in a gaseous phase, and the corresponding absence of any significant interactions between them, allows for simple descriptions of many physical properties that are the same for all gases, regardless of their chemical identities. As described in the final module of the chapter on gases, this situation changes at high pressures and low temperatures—conditions that permit the atoms and molecules to interact to a much greater extent.



Figure **5.1.1**: Solid carbon dioxide (“dry ice”, left) sublimes vigorously when placed in a liquid (right), cooling the liquid and generating a fog of condensed water vapor above the cylinder. (credit: modification of work by Paul Flowers)

This figure shows pieces of a white substance which appear to be sublimating. To the right of these pieces are three graduated cylinders. Each cylinder holds a different color liquid, and above the liquid, the cylinders are filled with a fog-like substance. This fog-like substance swirls out of the top and around the outside of the cylinders.

In the liquid and solid states, these interactions are of considerable strength and play an important role in determining a number of physical properties that *do* depend on the chemical identity of the substance. In this chapter, the nature of these interactions and their effects on various physical properties of liquid and solid phases will be examined.

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5.2: Carbon and Silicon- Network Atomic Solids

Learning Objectives

- To understand the correlation between bonding and the properties of solids.
- To classify solids as ionic, molecular, covalent (network), or metallic, where the general order of increasing strength of interactions.

Crystalline solids fall into one of four categories. All four categories involve packing discrete molecules or atoms into a lattice or repeating array, though *network solids* are a special case. The categories are distinguished by the nature of the interactions holding the discrete molecules or atoms together. Based on the nature of the forces that hold the component atoms, molecules, or ions together, solids may be formally classified as ionic, molecular, covalent (network), or metallic. The variation in the relative strengths of these four types of interactions correlates nicely with their wide variation in properties.

Table **5.2.1**: Solids may be formally classified as ionic, molecular, covalent (network), or metallic

Type of Solid	Interaction	Properties	Examples
Ionic	Ionic	High Melting Point, Brittle, Hard	NaCl, MgO
Molecular	Hydrogen Bonding, Dipole-Dipole, London Dispersion	Low Melting Point, Nonconducting	H_2, CO_2
Metallic	Metallic Bonding	Variable Hardness and Melting Point (depending upon strength of metallic bonding), Conducting	Fe, Mg
Network	Covalent Bonding	High Melting Point, Hard, Nonconducting	C (diamond), SiO_2 (quartz)

In ionic and molecular solids, there are no chemical bonds between the molecules, atoms, or ions. The solid consists of discrete chemical species held together by intermolecular forces that are **electrostatic** or **Coulombic** in nature. This behavior is most obvious for an ionic solid such as $NaCl$, where the positively charged Na^+ ions are attracted to the negatively charged Cl^- ions. Even in the absence of ions, however, electrostatic forces are operational. For polar molecules such as CH_2Cl_2, the positively charged region of one molecular is attracted to the negatively charged region of another molecule (dipole-dipole interactions). For a nonpolar molecule such as CO_2, which has no permanent dipole moment, the random motion of electrons gives rise to temporary polarity (a temporary dipole moment). Electrostatic attractions between two temporarily polarized molecules are called London Dispersion Forces.

Hydrogen bonding is a term describing an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X–H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation. (See the IUPAC Provisional Recommendation on the definition of a hydrogen bond.) Dots are employed to indicate the presence of a hydrogen bond: X–H•••Y. The attractive interaction in a hydrogen bond typically has a strong electrostatic contribution, but dispersion forces and weak covalent bonding are also present.

In metallic solids and network solids, however, chemical bonds hold the individual chemical subunits together. The crystal is essential a single, macroscopic molecule with continuous chemical bonding throughout the entire structure. In metallic solids, the valence electrons are no longer exclusively associated with a single atom. Instead these electrons exist in molecular orbitals that are delocalized over many atoms, producing an electronic band structure. The metallic crystal essentially consists of a set of metal cations in a sea of electrons. This type of chemical bonding is called metallic bonding.

Ionic Solids

You learned previously that an ionic solid consists of positively and negatively charged ions held together by electrostatic forces. The strength of the attractive forces depends on the charge and size of the ions that compose the lattice and determines many of the physical properties of the crystal.

The **lattice energy** (i.e., the energy required to separate 1 mol of a crystalline ionic solid into its component ions in the gas phase) is directly proportional to the product of the ionic charges and inversely proportional to the sum of the radii of the ions. For example, NaF and CaO both crystallize in the face-centered cubic (fcc) sodium chloride structure, and the sizes of their component ions are about the same: Na^+ (102 pm) versus Ca^{2+} (100 pm), and F^- (133 pm) versus O^{2-} (140 pm). Because of the higher charge on the ions in CaO, however, the lattice energy of CaO is almost four times greater than that of NaF (3401 kJ/mol versus 923 kJ/mol). The forces that hold Ca and O together in CaO are much stronger than those that hold Na and F together in NaF, so the heat of fusion of CaO is almost twice that of NaF (59 kJ/mol versus 33.4 kJ/mol), and the melting point of CaO is 2927°C versus 996°C for NaF. In both cases, however, the values are large; that is, simple ionic compounds have high melting points and are relatively hard (and brittle) solids.

Molecular Solids

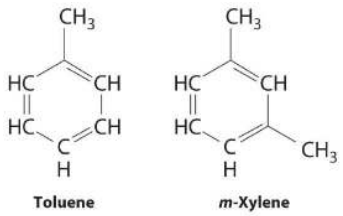
Molecular solids consist of atoms or molecules held to each other by dipole–dipole interactions, London dispersion forces, or hydrogen bonds, or any combination of these. The arrangement of the molecules in solid benzene is as follows:



The structure of solid benzene. In solid benzene, the molecules are not arranged with their planes parallel to one another but at 90° angles. (CC BY-NC-SA; Anonymous by request).

Because the intermolecular interactions in a molecular solid are relatively weak compared with ionic and covalent bonds, molecular solids tend to be soft, low melting, and easily vaporized (ΔH_{fus} and ΔH_{vap} are low). For similar substances, the strength of the London dispersion forces increases smoothly with increasing molecular mass. For example, the melting points of benzene (C_6H_6), naphthalene ($C_{10}H_8$), and anthracene ($C_{14}H_{10}$), with one, two, and three fused aromatic rings, are 5.5°C, 80.2°C, and 215°C, respectively. The enthalpies of fusion also increase smoothly within the series: benzene (9.95 kJ/mol) < naphthalene (19.1 kJ/mol) < anthracene (28.8 kJ/mol). If the molecules have shapes that cannot pack together efficiently in the crystal, however, then the melting points and the enthalpies of fusion tend to be unexpectedly low because the molecules are unable to arrange themselves to optimize intermolecular interactions. Thus toluene ($C_6H_5CH_3$) and m-xylene [m-$C_6H_4(CH_3)_2$] have melting points of −95°C and −48°C, respectively, which are significantly lower than the melting point of the lighter but more symmetrical analog, benzene.

Self-healing rubber is an example of a molecular solid with the potential for significant commercial applications. The material can stretch, but when snapped into pieces it can bond back together again through reestablishment of its hydrogen-bonding network without showing any sign of weakness. Among other applications, it is being studied for its use in adhesives and bicycle tires that will self-heal.



Toluene and m-xylene. The methyl groups attached to the phenyl ring in toluene and m-xylene prevent the rings from packing together as in solid benzene. (CC BY-NC-SA; Anonymous by request).

Covalent Network Solids

Covalent solids are formed by networks or chains of atoms or molecules held together by covalent bonds. A perfect single crystal of a covalent solid is therefore a single giant molecule. For example, the structure of diamond, shown in part (a) in Figure **5.2.1**, consists of sp3 hybridized carbon atoms, each bonded to four other carbon atoms in a tetrahedral array to create a giant network. The carbon atoms form six-membered rings.

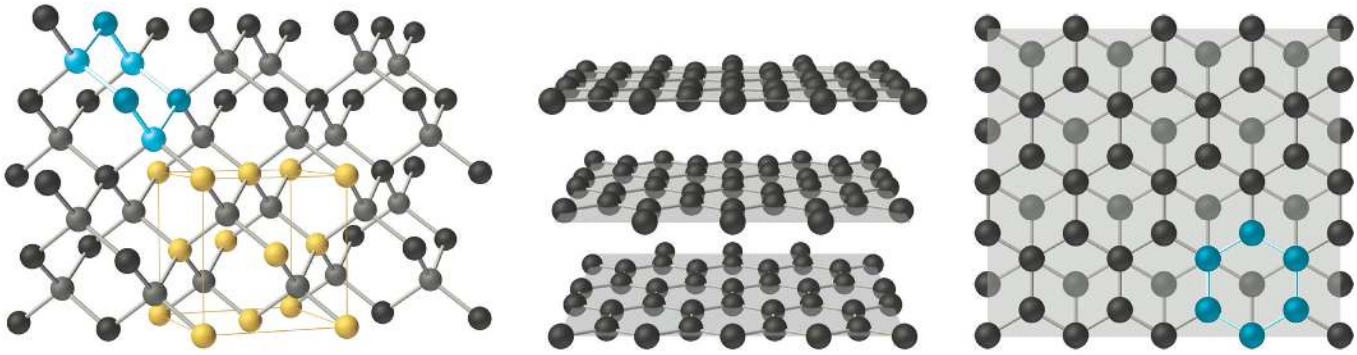


Figure **5.2.1**: The Structures of Diamond and Graphite. (a) Diamond consists of sp3 hybridized carbon atoms, each bonded to four other carbon atoms. The tetrahedral array forms a giant network in which carbon atoms form six-membered rings. This is easier to see in the rotating cube shown in Figure **5.2.2** below. (b) These side (left) and top (right) views of the graphite structure show the layers of fused six-membered rings and the arrangement of atoms in alternate layers of graphite. The rings in alternate layers are staggered, such that every other carbon atom in one layer lies directly under (and above) the center of a six-membered ring in an adjacent layer. (CC BY-NC-SA; Anonymous by request).

The unit cell of diamond can be described as an fcc array of carbon atoms with four additional carbon atoms inserted into four of the tetrahedral holes. It thus has the zinc blende structure described in Section 12.3, except that in zinc blende the atoms that compose the fcc array are sulfur and the atoms in the tetrahedral holes are zinc. Elemental silicon has the same structure, as does silicon carbide (SiC), which has alternating C and Si atoms. The structure of crystalline quartz (SiO_2), shown in Section 12.1, can be viewed as being derived from the structure of silicon by inserting an oxygen atom between each pair of silicon atoms.

All compounds with the diamond and related structures are hard, high-melting-point solids that are not easily deformed. Instead, they tend to shatter when subjected to large stresses, and they usually do not conduct electricity very well. In fact, diamond (melting point = 3500°C at 63.5 atm) is one of the hardest substances known, and silicon carbide (melting point = 2986°C) is used commercially as an abrasive in sandpaper and grinding wheels. It is difficult to deform or melt these and related compounds because strong covalent (C–C or Si–Si) or polar covalent (Si–C or Si–O) bonds must be broken, which requires a large input of energy.

Other covalent solids have very different structures. For example, graphite, the other common allotrope of carbon, has the structure shown in part (b) in Figure **5.2.1**. It contains planar networks of six-membered rings of sp2 hybridized carbon atoms in which each carbon is bonded to three others. This leaves a single electron in an unhybridized 2pz orbital that can be used to form C=C double bonds, resulting in a ring with alternating double and single bonds. Because of its resonance structures, the bonding in graphite is best viewed as consisting of a network of C–C single bonds with one-third of a π bond holding the carbons together, similar to the bonding in benzene.

To completely describe the bonding in graphite, we need a molecular orbital approach similar to the one used for benzene in Chapter 9. In fact, the C–C distance in graphite (141.5 pm) is slightly longer than the distance in benzene (139.5 pm), consistent with a net carbon–carbon bond order of 1.33. In graphite, the two-dimensional planes of carbon atoms are stacked to form a three-dimensional solid; only London dispersion forces hold the layers together. As a result, graphite exhibits properties typical of both covalent and molecular solids. Due to strong covalent bonding within the layers, graphite has a very high melting point, as expected for a covalent solid (it actually sublimes at about 3915°C). It is also very soft; the layers can easily slide past one another because of the weak interlayer interactions. Consequently, graphite is used as a lubricant and as the “lead” in pencils; the friction between graphite and a piece of paper is sufficient to leave a thin layer of carbon on the paper. Graphite is unusual among covalent solids in that its electrical conductivity is very high parallel to the planes of carbon atoms because of delocalized C–C π bonding. Finally, graphite is black because it contains an immense number of alternating double bonds, which results in a very small energy

difference between the individual molecular orbitals. Thus light of virtually all wavelengths is absorbed. Diamond, on the other hand, is colorless when pure because it has no delocalized electrons. Table **5.2.2** compares the strengths of the intermolecular and intramolecular interactions for three covalent solids, showing the comparative weakness of the interlayer interactions.

Table **5.2.2**: A Comparison of Intermolecular (ΔH_{sub}) and Intramolecular Interactions

Substance	ΔH_{sub} (kJ/mol)	Average Bond Energy (kJ/mol)
phosphorus (s)	58.98	201
sulfur (s)	64.22	226
iodine (s)	62.42	149

Carbon: An example of an Covalent Network Solid

In network solids, conventional chemical bonds hold the chemical subunits together. The bonding between chemical subunits, however, is identical to that within the subunits, resulting in a continuous network of chemical bonds. One common examples of network solids are diamond (a form of pure carbon) Carbon exists as a pure element at room temperature in three different forms: graphite (the most stable form), diamond, and fullerene.

Diamonds

The structure of diamond is shown at the right in a "ball-and-stick" format. The balls represent the carbon atoms and the sticks represent a covalent bond. Be aware that in the "ball-and-stick" representation the size of the balls do not accurately represent the size of carbon atoms. In addition, a single stick is drawn to represent a covalent bond irrespective of whether the bond is a single, double, or triple bond or requires resonance structures to represent. In the diamond structure, all bonds are single covalent bonds (σ bonds). The "space-filling" format is an alternate representation that displays atoms as spheres with a radius equal to the van der Waals radius, thus providing a better sense of the size of the atoms.

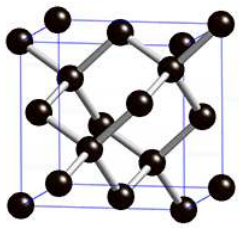


Figure **5.2.2**: Rotating model of diamond cubic. (CC0; H.K.D.H. Bhadeshia via Wikipedia)

Notice that diamond is a network solid. The entire solid is an "endless" repetition of carbon atoms bonded to each other by covalent bonds. (In the display at the right, the structure is truncated to fit in the display area.)

Questions to consider

- What is the bonding geometry around each carbon?
- What is the hybridization of carbon in diamond?
- The diamond structure consists of a repeating series of rings. How many carbon atoms are in a ring?
- Diamond are renowned for its hardness. Explain why this property is expected on the basis of the structure of diamond.

Graphite

The most stable form of carbon is graphite. Graphite consists of sheets of carbon atoms covalently bonded together. These sheets are then stacked to form graphite. Figure **5.2.3** shows a ball-and-stick representation of graphite with sheets that extended "indefinitely" in the xy plane, but the structure has been truncated for display purposed. Graphite may also be regarded as a

network solid, even though there is no bonding in the z direction. Each layer, however, is an "endless" bonded network of carbon atoms.

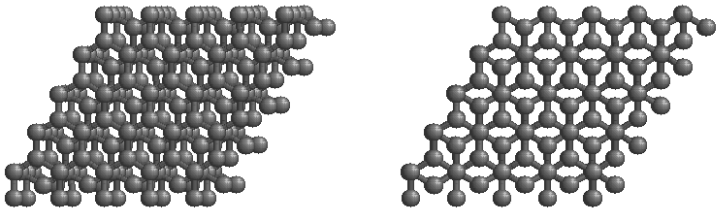


Figure **5.2.3**: Animation of a rotating graphite structure. This is a stereogram and can be viewed in 3D if a viewer's eyes are crossed slightly to overlap the two panels. Images used with permission from Wikipedia.

Questions to consider

- What is the bonding geometry around each carbon?
- What is the hybridization of carbon in graphite?
- The a layer of the graphite structure consists of a repeating series of rings. How many carbon atoms are in a ring?
- What force holds the carbon sheets together in graphite?
- Graphite is very slippery and is often used in lubricants. Explain why this property is expected on the basis of the structure of graphite.
- The slipperiness of graphite is enhanced by the introduction of impurities. Where would such impurities be located and why would they make graphite a better lubricant?

Fullerenes

Until the mid 1980's, pure carbon was thought to exist in two forms: graphite and diamond. The discovery of C_{60} molecules in interstellar dust in 1985 added a third form to this list. The existence of C_{60}, which resembles a soccer ball, had been hypothesized by theoreticians for many years. In the late 1980's synthetic methods were developed for the synthesis of C_{60}, and the ready availability of this form of carbon led to extensive research into its properties.

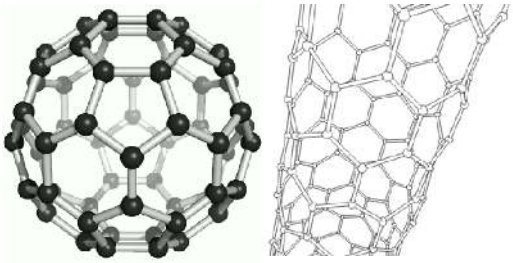


Figure **5.2.4**: Example of fullerenes: a buckyball (C_{60} on left and an extended bucktube. Images used with permission from Wikipedia.

The C_{60} molecule (Figure **5.2.4**; left), is called buckminsterfullerene, though the shorter name fullerene is often used. The name is a tribute to the American architect R. Buckminster Fuller, who is famous for designing and constructing geodesic domes which bear a close similarity to the structure of C_{60}. As is evident from the display, C_{60} is a sphere composed of six-member and five-member carbon rings. These balls are sometimes fondly referred to as "Bucky balls". It should be noted that fullerenes are an entire class of pure carbon compounds rather than a single compound. A distorted sphere containing more than 60 carbon atoms have also been found, and it is also possible to create long tubes (Figure **5.2.4**; right). All of these substances are pure carbon.

Questions to Consider

- What is the bonding geometry around each carbon? (Note that this geometry is distorted in C_{60}.)
- What is the hybridization of carbon in fullerene?
- A single crystal of C60 falls into which class of crystalline solids?
- It has been hypothesized that C60 would make a good lubricant. Why might C60 make a good lubricant?

Metallic Solids

Metallic solids such as crystals of copper, aluminum, and iron are formed by metal atoms Figure 5.2.5. The structure of metallic crystals is often described as a uniform distribution of atomic nuclei within a “sea” of delocalized electrons. The atoms within such a metallic solid are held together by a unique force known as *metallic bonding* that gives rise to many useful and varied bulk properties. All exhibit high thermal and electrical conductivity, metallic luster, and malleability. Many are very hard and quite strong. Because of their malleability (the ability to deform under pressure or hammering), they do not shatter and, therefore, make useful construction materials.

Metals are characterized by their ability to reflect light, called luster, their high electrical and thermal conductivity, their high heat capacity, and their malleability and ductility. Every lattice point in a pure metallic element is occupied by an atom of the same metal. The packing efficiency in metallic crystals tends to be high, so the resulting metallic solids are dense, with each atom having as many as 12 nearest neighbors.

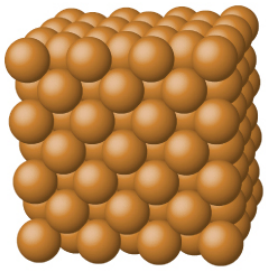


Figure 5.2.5: Copper is a metallic solid. (CC BY 4.0; OpenStax).

Bonding in metallic solids is quite different from the bonding in the other kinds of solids we have discussed. Because all the atoms are the same, there can be no ionic bonding, yet metals always contain too few electrons or valence orbitals to form covalent bonds with each of their neighbors. Instead, the valence electrons are delocalized throughout the crystal, providing a strong cohesive force that holds the metal atoms together.

> *Valence electrons in a metallic solid are delocalized, providing a strong cohesive force that holds the atoms together.*

The strength of metallic bonds varies dramatically. For example, cesium melts at 28.4°C, and mercury is a liquid at room temperature, whereas tungsten melts at 3680°C. Metallic bonds tend to be weakest for elements that have nearly empty (as in Cs) or nearly full (Hg) valence subshells, and strongest for elements with approximately half-filled valence shells (as in W). As a result, the melting points of the metals increase to a maximum around group 6 and then decrease again from left to right across the d block. Other properties related to the strength of metallic bonds, such as enthalpies of fusion, boiling points, and hardness, have similar periodic trends.

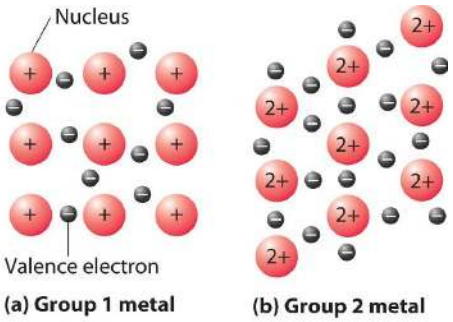


Figure 5.2.6: The Electron-Sea Model of Bonding in Metals. Fixed, positively charged metal nuclei from group 1 (a) or group 2 (b) are surrounded by a “sea” of mobile valence electrons. Because a group 2 metal has twice the number of valence electrons as a group 1 metal, it should have a higher melting point.

A somewhat oversimplified way to describe the bonding in a metallic crystal is to depict the crystal as consisting of positively charged nuclei in an electron sea (Figure 5.2.6). In this model, the valence electrons are not tightly bound to any one atom but are distributed uniformly throughout the structure. Very little energy is needed to remove electrons from a solid metal because they are

not bound to a single nucleus. When an electrical potential is applied, the electrons can migrate through the solid toward the positive electrode, thus producing high electrical conductivity. The ease with which metals can be deformed under pressure is attributed to the ability of the metal ions to change positions within the electron sea without breaking any specific bonds. The transfer of energy through the solid by successive collisions between the metal ions also explains the high thermal conductivity of metals. This model does not, however, explain many of the other properties of metals, such as their metallic luster and the observed trends in bond strength as reflected in melting points or enthalpies of fusion. Some general properties of the four major classes of solids are summarized in Table 5.2.2.

Table 5.2.2: Properties of the Major Classes of Solids

Ionic Solids	Molecular Solids	Covalent Solids	Metallic Solids
poor conductors of heat and electricity	poor conductors of heat and electricity	poor conductors of heat and electricity*	good conductors of heat and electricity
relatively high melting point	low melting point	high melting point	melting points depend strongly on electron configuration
hard but brittle; shatter under stress	soft	very hard and brittle	easily deformed under stress; ductile and malleable
relatively dense	low density	low density	usually high density
dull surface	dull surface	dull surface	lustrous

*Many exceptions exist. For example, graphite has a relatively high electrical conductivity within the carbon planes, and diamond has the highest thermal conductivity of any known substance.

The general order of increasing strength of interactions in a solid is:

$$\textit{molecular solids} < \textit{ionic solids} \approx \textit{metallic solids} < \textit{covalent solids}$$

Example 5.2.1

Classify Ge, RbI, $C_6(CH_3)_6$, and Zn as ionic, molecular, covalent, or metallic solids and arrange them in order of increasing melting points.

Given: compounds

Asked for: classification and order of melting points

Strategy:

A. Locate the component element(s) in the periodic table. Based on their positions, predict whether each solid is ionic, molecular, covalent, or metallic.
B. Arrange the solids in order of increasing melting points based on your classification, beginning with molecular solids.

Solution:

A Germanium lies in the p block just under Si, along the diagonal line of semimetallic elements, which suggests that elemental Ge is likely to have the same structure as Si (the diamond structure). Thus Ge is probably a covalent solid. RbI contains a metal from group 1 and a nonmetal from group 17, so it is an ionic solid containing Rb^+ and I^- ions. The compound C6(CH3)6 is a hydrocarbon (hexamethylbenzene), which consists of isolated molecules that stack to form a molecular solid with no covalent bonds between them. Zn is a d-block element, so it is a metallic solid.

B Arranging these substances in order of increasing melting points is straightforward, with one exception. We expect $C_6(CH_3)_6$ to have the lowest melting point and Ge to have the highest melting point, with RbI somewhere in between. The melting points of metals, however, are difficult to predict based on the models presented thus far. Because Zn has a filled valence shell, it should not have a particularly high melting point, so a reasonable guess is $C_6(CH_3)_6$ < Zn ~ RbI < Ge. The actual melting points are $C_6(CH_3)_6$, 166°C; Zn, 419°C; RbI, 642°C; and Ge, 938°C. This agrees with our prediction.

? Exercise 5.2.1

Classify C_{60}, $BaBr_2$, GaAs, and AgZn as ionic, covalent, molecular, or metallic solids and then arrange them in order of increasing melting points.

Answer

C_{60} (molecular) < AgZn (metallic) ~ $BaBr_2$ (ionic) < GaAs (covalent). The actual melting points are C60, about 300°C; AgZn, about 700°C; $BaBr_2$, 856°C; and GaAs, 1238°C.

Summary

The major types of solids are ionic, molecular, covalent, and metallic. Ionic solids consist of positively and negatively charged ions held together by electrostatic forces; the strength of the bonding is reflected in the lattice energy. Ionic solids tend to have high melting points and are rather hard. Molecular solids are held together by relatively weak forces, such as dipole–dipole interactions, hydrogen bonds, and London dispersion forces. As a result, they tend to be rather soft and have low melting points, which depend on their molecular structure. Covalent solids consist of two- or three-dimensional networks of atoms held together by covalent bonds; they tend to be very hard and have high melting points. Metallic solids have unusual properties: in addition to having high thermal and electrical conductivity and being malleable and ductile, they exhibit luster, a shiny surface that reflects light. An alloy is a mixture of metals that has bulk metallic properties different from those of its constituent elements. Alloys can be formed by substituting one metal atom for another of similar size in the lattice (substitutional alloys), by inserting smaller atoms into holes in the metal lattice (interstitial alloys), or by a combination of both. Although the elemental composition of most alloys can vary over wide ranges, certain metals combine in only fixed proportions to form intermetallic compounds with unique properties.

Contributors and Attributions

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5.3: The Solid State of Matter

Learning Objectives

- Define and describe the bonding and properties of ionic, molecular, metallic, and covalent network crystalline solids
- Describe the main types of crystalline solids: ionic solids, metallic solids, covalent network solids, and molecular solids
- Explain the ways in which crystal defects can occur in a solid

When most liquids are cooled, they eventually freeze and form crystalline solids, solids in which the atoms, ions, or molecules are arranged in a definite repeating pattern. It is also possible for a liquid to freeze before its molecules become arranged in an orderly pattern. The resulting materials are called amorphous solids or noncrystalline solids (or, sometimes, glasses). The particles of such solids lack an ordered internal structure and are randomly arranged (Figure **5.3.1**).

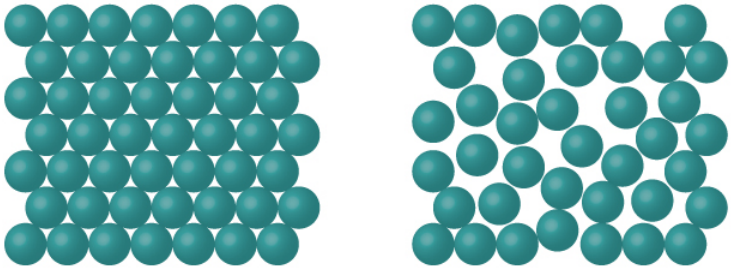


Figure **5.3.1**: The entities of a solid phase may be arranged in a regular, repeating pattern (crystalline solids) or randomly (amorphous).

The crystalline arrangement shows many circles drawn in rows and stacked together tightly. The amorphous arrangement shows many circles spread slightly apart and in no organized pattern.

Metals and ionic compounds typically form ordered, crystalline solids. Substances that consist of large molecules, or a mixture of molecules whose movements are more restricted, often form amorphous solids. For examples, candle waxes are amorphous solids composed of large hydrocarbon molecules. Some substances, such as boron oxide (Figure **5.3.2**), can form either crystalline or amorphous solids, depending on the conditions under which it is produced. Also, amorphous solids may undergo a transition to the crystalline state under appropriate conditions.

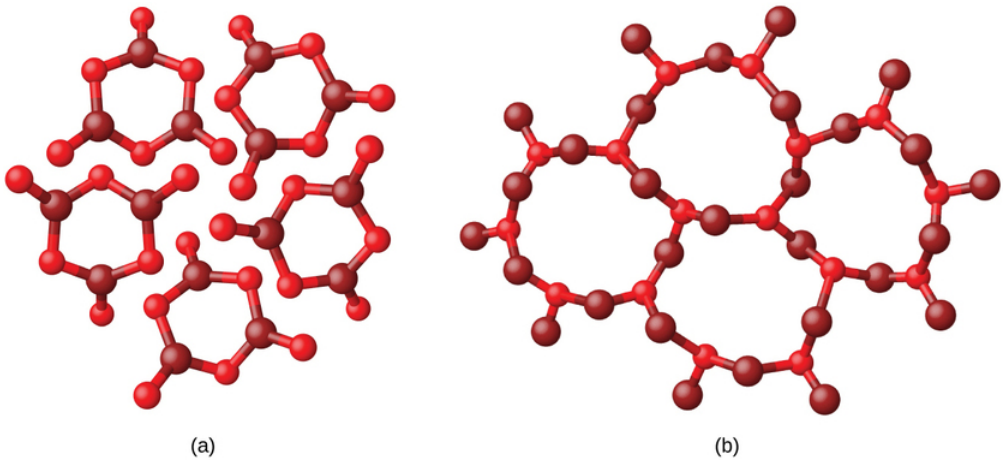


Figure **5.3.2**: (a) Diboron trioxide, B_2O_3, is normally found as a white, amorphous solid (a glass), which has a high degree of disorder in its structure. (b) By careful, extended heating, it can be converted into a crystalline form of B_2O_3, which has a very ordered arrangement.

The first structure of diboron trioxide shows five identical and separated hexagonal rings. The second structure of diboron trioxide shows a more interconnected structure with four large rings forming a more stable structure.

Crystalline solids are generally classified according the nature of the forces that hold its particles together. These forces are primarily responsible for the physical properties exhibited by the bulk solids. The following sections provide descriptions of the major types of crystalline solids: ionic, metallic, covalent network, and molecular.

5.3.1: Ionic Solids

Ionic solids, such as sodium chloride and nickel oxide, are composed of positive and negative ions that are held together by electrostatic attractions, which can be quite strong (Figure **5.3.3**). Many ionic crystals also have high melting points. This is due to the very strong attractions between the ions—in ionic compounds, the attractions between full charges are (much) larger than those between the partial charges in polar molecular compounds. This will be looked at in more detail in a later discussion of lattice energies. Although they are hard, they also tend to be brittle, and they shatter rather than bend. Ionic solids do not conduct electricity; however, they do conduct when molten or dissolved because their ions are free to move. Many simple compounds formed by the reaction of a metallic element with a nonmetallic element are ionic.

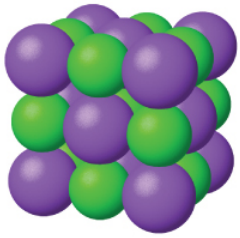


Figure **5.3.3**: Sodium chloride is an ionic solid.

A cube composed of purple and green spheres is shown. The cube has dimensions of three by three spheres. The purple spheres are slightly larger than the green spheres.

5.3.2: Metallic Solids

Metallic solids such as crystals of copper, aluminum, and iron are formed by metal atoms Figure **5.3.4**. The structure of metallic crystals is often described as a uniform distribution of atomic nuclei within a “sea” of delocalized electrons. The atoms within such a metallic solid are held together by a unique force known as *metallic bonding* that gives rise to many useful and varied bulk properties. All exhibit high thermal and electrical conductivity, metallic luster, and malleability. Many are very hard and quite strong. Because of their malleability (the ability to deform under pressure or hammering), they do not shatter and, therefore, make useful construction materials. The melting points of the metals vary widely. Mercury is a liquid at room temperature, and the alkali metals melt below 200 °C. Several post-transition metals also have low melting points, whereas the transition metals melt at temperatures above 1000 °C. These differences reflect differences in strengths of metallic bonding among the metals.

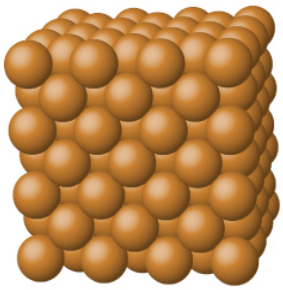


Figure **5.3.4**: Copper is a metallic solid.

5.3.3: Covalent Network Solids

Covalent network solids include crystals of diamond, silicon, some other nonmetals, and some covalent compounds such as silicon dioxide (sand) and silicon carbide (carborundum, the abrasive on sandpaper). Many minerals have networks of covalent bonds. The atoms in these solids are held together by a network of covalent bonds, as shown in Figure **5.3.5**. To break or to melt a covalent network solid, covalent bonds must be broken. Because covalent bonds are relatively strong, covalent network solids are typically characterized by hardness, strength, and high melting points. For example, diamond is one of the hardest substances known and melts above 3500 °C.

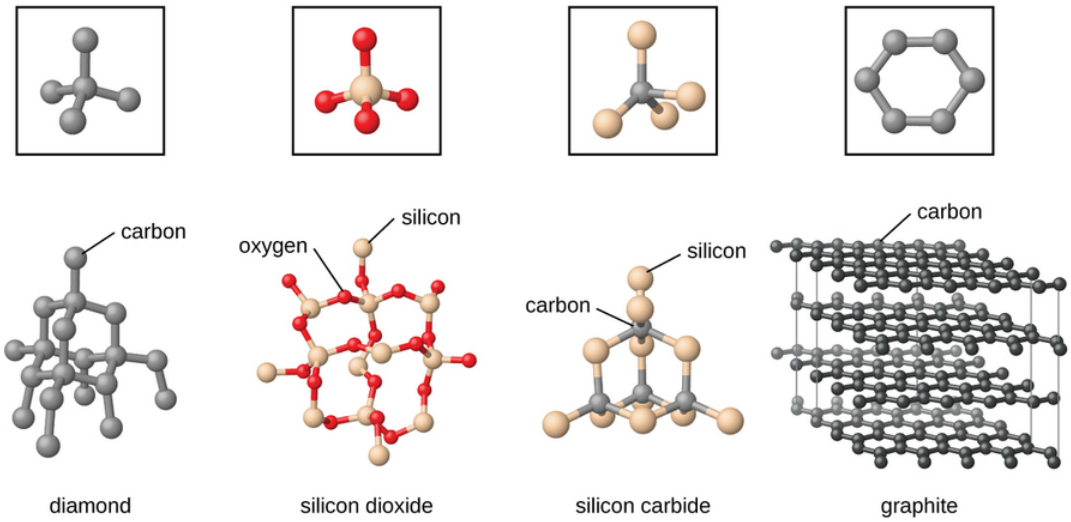


Figure **5.3.5**. A covalent crystal contains a three-dimensional network of covalent bonds, as illustrated by the structures of diamond, silicon dioxide, silicon carbide, and graphite. Graphite is an exceptional example, composed of planar sheets of covalent crystals that are held together in layers by noncovalent forces. Unlike typical covalent solids, graphite is very soft and electrically conductive.

The complex three dimensional structure of diamond, silicon dioxide, silicon carbide and graphite is shown along with a a smaller repeating unit of the structure shown above each structure.

5.3.4: Molecular Solids

Molecular solids, such as ice, sucrose (table sugar), and iodine, as shown in Figure **5.3.6**, are composed of neutral molecules. The strengths of the attractive forces between the units present in different crystals vary widely, as indicated by the melting points of the crystals. Small symmetrical molecules (nonpolar molecules), such as H_2, N_2, O_2, and F_2, have weak attractive forces and form molecular solids with very low melting points (below −200 °C). Substances consisting of larger, nonpolar molecules have larger attractive forces and melt at higher temperatures. Molecular solids composed of molecules with permanent dipole moments (polar molecules) melt at still higher temperatures. Examples include ice (melting point, 0 °C) and table sugar (melting point, 185 °C).

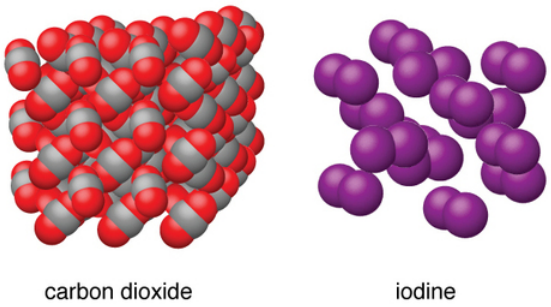


Figure **5.3.6**: Carbon dioxide (CO_2) consists of small, nonpolar molecules and forms a molecular solid with a melting point of −78 °C. Iodine (I_2) consists of larger, nonpolar molecules and forms a molecular solid that melts at 114 °C.

On the left, many red and grey molecules are densely stacked in a 3-D drawing to represent carbon dioxide. On the right, purple molecules are scattered randomly to represent iodine.

5.3.5: Properties of Solids

A crystalline solid, like those listed in Table **5.3.1** has a precise melting temperature because each atom or molecule of the same type is held in place with the same forces or energy. Thus, the attractions between the units that make up the crystal all have the same strength and all require the same amount of energy to be broken. The gradual softening of an amorphous material differs dramatically from the distinct melting of a crystalline solid. This results from the structural nonequivalence of the molecules in the amorphous solid. Some forces are weaker than others, and when an amorphous material is heated, the weakest intermolecular attractions break first. As the temperature is increased further, the stronger attractions are broken. Thus amorphous materials soften over a range of temperatures.

Table **5.3.1**: Types of Crystalline Solids and Their Properties

Type of Solid	Type of Particles	Type of Attractions	Properties	Examples
ionic	ions	ionic bonds	hard, brittle, conducts electricity as a liquid but not as a solid, high to very high melting points	NaCl, Al_2O_3
metallic	atoms of electropositive elements	metallic bonds	shiny, malleable, ductile, conducts heat and electricity well, variable hardness and melting temperature	Cu, Fe, Ti, Pb, U
covalent network	atoms of electronegative elements	covalent bonds	very hard, not conductive, very high melting points	C (diamond), SiO_2, SiC
molecular	molecules (or atoms)	IMFs	variable hardness, variable brittleness, not conductive, low melting points	H_2O, CO_2, I_2, $C_{12}H_{22}O_{11}$

Graphene: Material of the Future

Carbon is an essential element in our world. The unique properties of carbon atoms allow the existence of carbon-based life forms such as ourselves. Carbon forms a huge variety of substances that we use on a daily basis, including those shown in Figure **5.3.7**. You may be familiar with diamond and graphite, the two most common *allotropes* of carbon. (Allotropes are different structural forms of the same element.) Diamond is one of the hardest-known substances, whereas graphite is soft enough to be used as pencil lead. These very different properties stem from the different arrangements of the carbon atoms in the different allotropes.

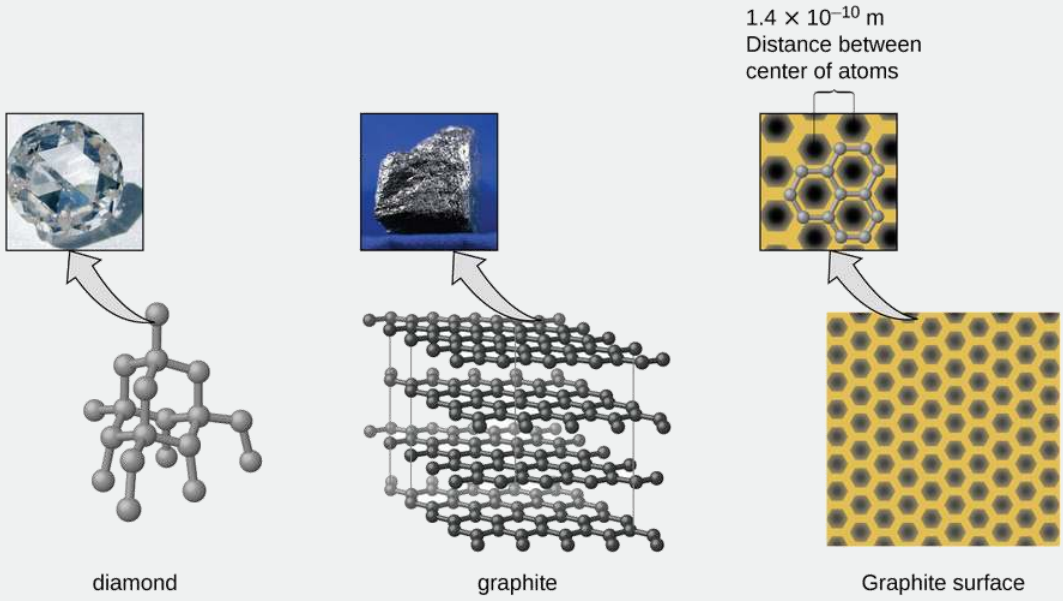


Figure **5.3.7**: Diamond is extremely hard because of the strong bonding between carbon atoms in all directions. Graphite (in pencil lead) rubs off onto paper due to the weak attractions between the carbon layers. An image of a graphite surface shows the distance between the centers of adjacent carbon atoms. (credit left photo: modification of work by Steve Jurvetson; credit middle photo: modification of work by United States Geological Survey)

A close up of a piece of diamond shows a three dimensional sturcture of a complex network of well bonded carbon atoms. A close up of a graphite shows several layers of carbon sheets. Each sheet is composed of a repeated and connected hexagonal structure of carbon atoms. The third diagram shows that the distance between the center of atoms is 1.4 times 10 to the power of negative 10 meters.

You may be less familiar with a recently discovered form of carbon: graphene. Graphene was first isolated in 2004 by using tape to peel off thinner and thinner layers from graphite. It is essentially a single sheet (one atom thick) of graphite. Graphene, illustrated in Figure **5.3.8**, is not only strong and lightweight, but it is also an excellent conductor of electricity and heat. These properties may prove very useful in a wide range of applications, such as vastly improved computer chips and circuits, better batteries and solar cells, and stronger and lighter structural materials. The 2010 Nobel Prize in Physics was awarded to Andre Geim and Konstantin Novoselov for their pioneering work with graphene.

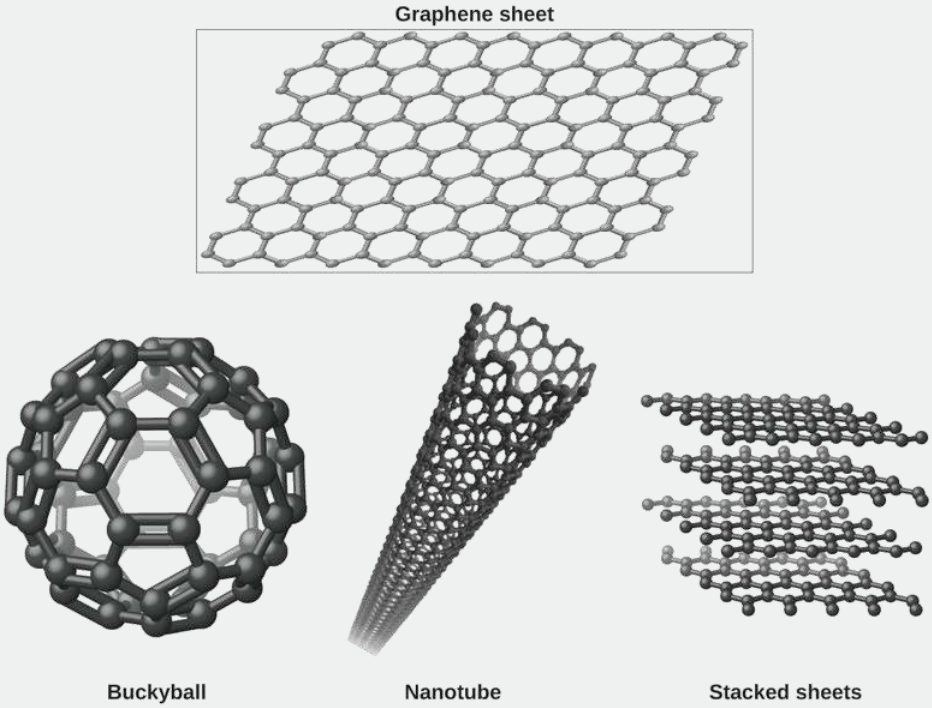


Figure **5.3.8**: Graphene sheets can be formed into buckyballs, nanotubes, and stacked layers.

A sheet of interconnected hexagonal rings is shown at the top. Below it, a bukcyball is shown which is a sphere is composed of hexagonal rings. In the lower middle image, a nanotube is shown that is made by rolling a graphene sheet into a tube. In the lower right image, stacked sheets made up of four horizontal sheets composed of joined, hexagonal rings is shown.

5.3.6: Crystal Defects

In a crystalline solid, the atoms, ions, or molecules are arranged in a definite repeating pattern, but occasional defects may occur in the pattern. Several types of defects are known, as illustrated in Figure **5.3.9**. Vacancies are defects that occur when positions that should contain atoms or ions are vacant. Less commonly, some atoms or ions in a crystal may occupy positions, called interstitial sites, located between the regular positions for atoms. Other distortions are found in impure crystals, as, for example, when the cations, anions, or molecules of the impurity are too large to fit into the regular positions without distorting the structure. Trace amounts of impurities are sometimes added to a crystal (a process known as *doping)* in order to create defects in the structure that yield desirable changes in its properties. For example, silicon crystals are doped with varying amounts of different elements to yield suitable electrical properties for their use in the manufacture of semiconductors and computer chips.

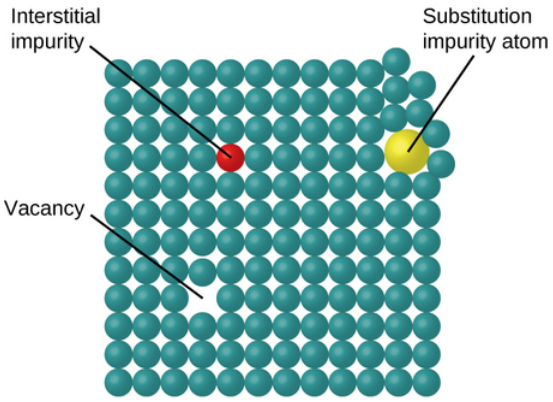


Figure **5.3.9**: Types of crystal defects include vacancies, interstitial atoms, and substitutions impurities.

Summary

Some substances form crystalline solids consisting of particles in a very organized structure; others form amorphous (noncrystalline) solids with an internal structure that is not ordered. The main types of crystalline solids are ionic solids, metallic

solids, covalent network solids, and molecular solids. The properties of the different kinds of crystalline solids are due to the types of particles of which they consist, the arrangements of the particles, and the strengths of the attractions between them. Because their particles experience identical attractions, crystalline solids have distinct melting temperatures; the particles in amorphous solids experience a range of interactions, so they soften gradually and melt over a range of temperatures. Some crystalline solids have defects in the definite repeating pattern of their particles. These defects (which include vacancies, atoms or ions not in the regular positions, and impurities) change physical properties such as electrical conductivity, which is exploited in the silicon crystals used to manufacture computer chips.

Glossary

amorphous solid

(also, noncrystalline solid) solid in which the particles lack an ordered internal structure

covalent network solid

solid whose particles are held together by covalent bonds

crystalline solid

solid in which the particles are arranged in a definite repeating pattern

interstitial sites

spaces between the regular particle positions in any array of atoms or ions

ionic solid

solid composed of positive and negative ions held together by strong electrostatic attractions

metallic solid

solid composed of metal atoms

molecular solid

solid composed of neutral molecules held together by intermolecular forces of attraction

vacancy

defect that occurs when a position that should contain an atom or ion is vacant

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5.4: Lattice Structures in Crystalline Solids

Learning Objectives

- Describe the arrangement of atoms and ions in crystalline structures
- Compute ionic radii using unit cell dimensions
- Explain the use of X-ray diffraction measurements in determining crystalline structures

Over 90% of naturally occurring and man-made solids are crystalline. Most solids form with a regular arrangement of their particles because the overall attractive interactions between particles are maximized, and the total intermolecular energy is minimized, when the particles pack in the most efficient manner. The regular arrangement at an atomic level is often reflected at a macroscopic level. In this module, we will explore some of the details about the structures of metallic and ionic crystalline solids, and learn how these structures are determined experimentally.

5.4.1: The Structures of Metals

We will begin our discussion of crystalline solids by considering elemental metals, which are relatively simple because each contains only one type of atom. A pure metal is a crystalline solid with metal atoms packed closely together in a repeating pattern. Some of the properties of metals in general, such as their malleability and ductility, are largely due to having identical atoms arranged in a regular pattern. The different properties of one metal compared to another partially depend on the sizes of their atoms and the specifics of their spatial arrangements. We will explore the similarities and differences of four of the most common metal crystal geometries in the sections that follow.

5.4.2: Unit Cells of Metals

The structure of a crystalline solid, whether a metal or not, is best described by considering its simplest repeating unit, which is referred to as its unit cell. The unit cell consists of lattice points that represent the locations of atoms or ions. The entire structure then consists of this unit cell repeating in three dimensions, as illustrated in Figure **5.4.1**.

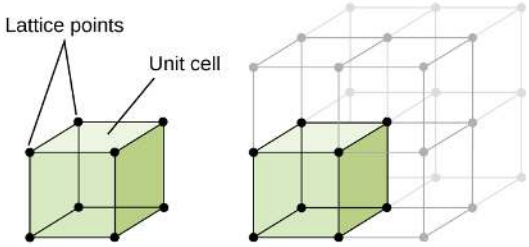


Figure **5.4.1**: A unit cell shows the locations of lattice points repeating in all directions.

A diagram of two images is shown. In the first image, a cube with a sphere at each corner is shown. The cube is labeled “Unit cell” and the spheres at the corners are labeled “Lattice points.” The second image shows the same cube, but this time it is one cube amongst eight that make up a larger cube. The original cube is shaded a color while the other cubes are not.

Let us begin our investigation of crystal lattice structure and unit cells with the most straightforward structure and the most basic unit cell. To visualize this, imagine taking a large number of identical spheres, such as tennis balls, and arranging them uniformly in a container. The simplest way to do this would be to make layers in which the spheres in one layer are directly above those in the layer below, as illustrated in Figure **5.4.2**. This arrangement is called simple cubic structure, and the unit cell is called the simple cubic unit cell or primitive cubic unit cell.

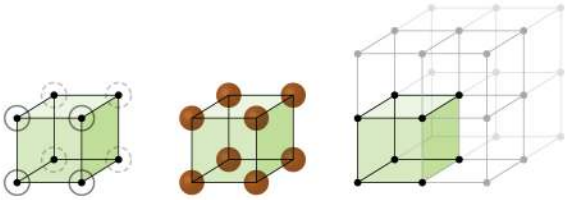


Figure 5.4.2: .When metal atoms are arranged with spheres in one layer directly above or below spheres in another layer, the lattice structure is called simple cubic. Note that the spheres are in contact.

A diagram of three images is shown. In the first image, a cube with a sphere at each corner is shown. The spheres at the corners are circled. The second image shows the same cube, but this time the spheres at the corners are larger and shaded in. In the third image, the cube is one cube amongst eight that make up a larger cube. The original cube is shaded a color while the other cubes are not.

In a simple cubic structure, the spheres are not packed as closely as they could be, and they only "fill" about 52% of the volume of the container. This is a relatively inefficient arrangement, and only one metal (polonium, Po) crystallizes in a simple cubic structure. As shown in Figure 5.4.3, a solid with this type of arrangement consists of planes (or layers) in which each atom contacts only the four nearest neighbors in its layer; one atom directly above it in the layer above; and one atom directly below it in the layer below. The number of other particles that each particle in a crystalline solid contacts is known as its coordination number. For a polonium atom in a simple cubic array, the coordination number is, therefore, six.

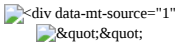


Figure 5.4.3: An atom in a simple cubic lattice structure contacts six other atoms, so it has a coordination number of six.

In a simple cubic lattice, the unit cell that repeats in all directions is a cube defined by the centers of eight atoms, as shown in Figure 5.4.4. Atoms at adjacent corners of this unit cell contact each other, so the edge length of this cell is equal to two atomic radii, or one atomic diameter. A cubic unit cell contains only the parts of these atoms that are within it. Since an atom at a corner of a simple cubic unit cell is contained by a total of eight unit cells, only one-eighth of that atom is within a specific unit cell. And since each simple cubic unit cell has one atom at each of its eight "corners," there is $8 \times \frac{1}{8} = 1$ atom within one simple cubic unit cell.

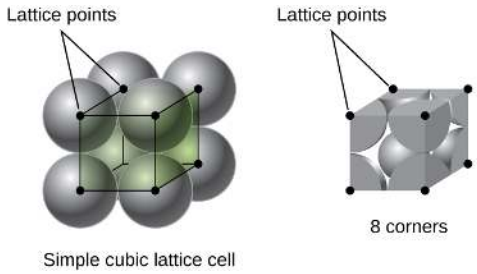


Figure 5.4.4: A simple cubic lattice unit cell contains one-eighth of an atom at each of its eight corners, so it contains one atom total.

A diagram of two images is shown. In the first image, eight spheres are stacked together to form a cube and dots at the center of each sphere are connected to form a cube shape. The dots are labeled "Lattice points" while a label under the image reads "Simple cubic lattice cell." The second image shows the portion of each sphere that lie inside the cube. The corners of the cube are shown with small circles labeled "Lattice points" and the phrase "8 corners" is written below the image.

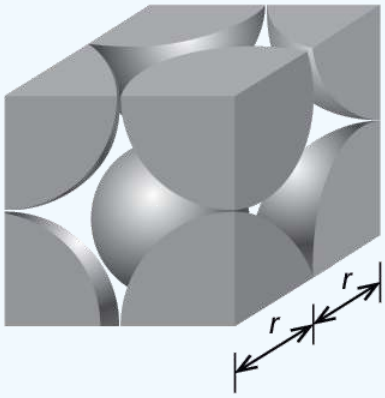
✔ Example 5.4.1: Calculating Atomic Radius and Density for Metals (Part 1)

The edge length of the unit cell of alpha polonium is 336 pm.

a. Determine the radius of a polonium atom.
b. Determine the density of alpha polonium.

Solution

Alpha polonium crystallizes in a simple cubic unit cell:



(a) Two adjacent Po atoms contact each other, so the edge length of this cell is equal to two Po atomic radii: $l = 2r$. Therefore, the radius of Po is

$$r = \frac{l}{2} = \frac{336\ \text{pm}}{2} = 168\ \text{pm}$$

(b) Density is given by

$$\text{density} = \frac{\text{mass}}{\text{volume}}.$$

The density of polonium can be found by determining the density of its unit cell (the mass contained within a unit cell divided by the volume of the unit cell). Since a Po unit cell contains one-eighth of a Po atom at each of its eight corners, a unit cell contains one Po atom.

The mass of a Po unit cell can be found by:

$$1\ \text{Po unit cell} \times \frac{1\ \text{Po atom}}{1\ \text{Po unit cell}} \times \frac{1\ \text{mol Po}}{6.022 \times 10^{23}\ \text{Po atoms}} \times \frac{208.998\ \text{g}}{1\ \text{mol Po}} = 3.47 \times 10^{-22}\ \text{g}$$

The volume of a Po unit cell can be found by:

$$V = l^3 = (336 \times 10^{-10}\ \text{cm})^3 = 3.79 \times 10^{-23}\ \text{cm}^3$$

(Note that the edge length was converted from pm to cm to get the usual volume units for density.)

Therefore, the density of

$$\text{Po} = \frac{3.471 \times 10^{-22}\ \text{g}}{3.79 \times 10^{-23}\ \text{cm}^3} = 9.16\ \text{g/cm}^3$$

? Exercise 5.4.1

The edge length of the unit cell for nickel is 0.3524 nm. The density of Ni is 8.90 g/cm^3. Does nickel crystallize in a simple cubic structure? Explain.

Answer

No. If Ni were simple cubic, its density would be given by:

$$1\ \text{Ni atom} \times \frac{1\ \text{mol Ni}}{6.022 \times 10^{23}\ \text{Ni atoms}} \times \frac{58.693\ \text{g}}{1\ \text{mol Ni}} = 9.746 \times 10^{-23}\ \text{g}$$

$$V = l^3 = (3.524 \times 10^{-8}\ \text{cm})^3 = 4.376 \times 10^{-23}\ \text{cm}^3$$

Then the density of Ni would be

$$(= \frac{9.746 \times 10^{-23}\ \text{g}}{4.376 \times 10^{-23}\ \text{cm}^3} = 2.23\ \text{g/cm}^3$$

Since the actual density of Ni is not close to this, Ni does not form a simple cubic structure.

Most metal crystals are one of the four major types of unit cells. For now, we will focus on the three cubic unit cells: simple cubic (which we have already seen), body-centered cubic unit cell, and face-centered cubic unit cell—all of which are illustrated in Figure 5.4.5. (Note that there are actually seven different lattice systems, some of which have more than one type of lattice, for a total of 14 different types of unit cells. We leave the more complicated geometries for later in this module.)

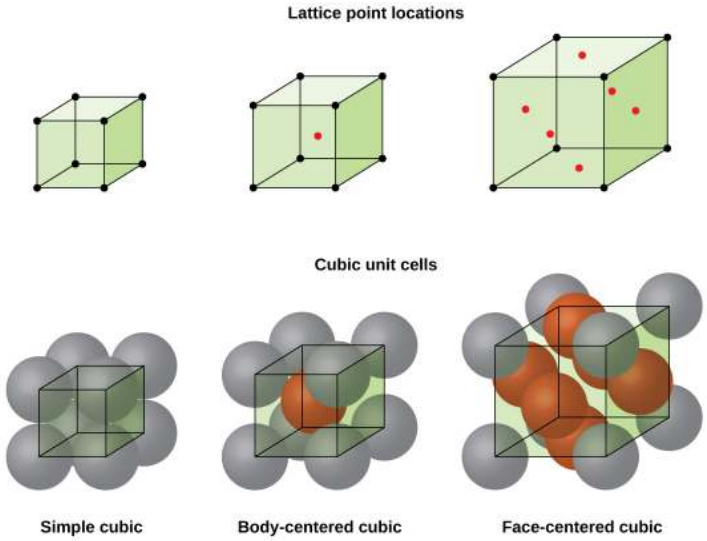


Figure 5.4.5: Cubic unit cells of metals show (in the upper figures) the locations of lattice points and (in the lower figures) metal atoms located in the unit cell.

Three pairs of images are shown. The first three images are in a row and are labeled “Lattice point locations” while the second three images are in a row labeled “Cubic unit cells.” The first image in the top row shows a cube with black dots at each corner while the first image in the second row is composed of eight spheres that are stacked together to form a cube and dots at the center of each sphere are connected to form a cube shape. The name under this image reads “Simple cubic.” The second image in the top row shows a cube with black dots at each corner and a red dot in the center while the second image in the second row is composed of eight spheres that are stacked together to form a cube with one sphere in the center of the cube and dots at the center of each corner sphere connected to form a cube shape. The name under this image reads “Body-centered cubic.” The third image in the top row shows a cube with black dots at each corner and red dots in the center of each face while the third image in the second row is composed of eight spheres that are stacked together to form a cube with six more spheres located in the center of each face of the cube. Dots at the center of each corner sphere are connected to form a cube shape. The name under this image reads “Face-centered cubic.”

Some metals crystallize in an arrangement that has a cubic unit cell with atoms at all of the corners and an atom in the center, as shown in Figure 5.4.6. This is called a body-centered cubic (BCC) solid. Atoms in the corners of a BCC unit cell do not contact each other but contact the atom in the center. A BCC unit cell contains two atoms: one-eighth of an atom at each of the eight corners ($8 \times \frac{1}{8} = 1$ atom from the corners) plus one atom from the center. Any atom in this structure touches four atoms in the layer above it and four atoms in the layer below it. Thus, an atom in a BCC structure has a coordination number of eight.

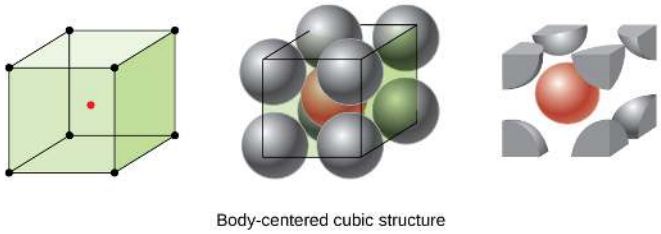


Figure 5.4.6: In a body-centered cubic structure, atoms in a specific layer do not touch each other. Each atom touches four atoms in the layer above it and four atoms in the layer below it.

Three images are shown. The first image shows a cube with black dots at each corner and a red dot in the center while the second image is composed of eight spheres that are stacked together to form a cube with one sphere in the center of the cube and dots at the center of each corner sphere connected to form a cube shape. The name under this image reads “Body-centered cubic structure.” The third image is the same as the second, but only shows the portions of the spheres that lie inside the cube shape.

Atoms in BCC arrangements are much more efficiently packed than in a simple cubic structure, occupying about 68% of the total volume. Isomorphous metals with a BCC structure include K, Ba, Cr, Mo, W, and Fe at room temperature. (Elements or compounds that crystallize with the same structure are said to be isomorphous.)

Many other metals, such as aluminum, copper, and lead, crystallize in an arrangement that has a cubic unit cell with atoms at all of the corners and at the centers of each face, as illustrated in Figure **5.4.7**. This arrangement is called a face-centered cubic (FCC) solid. A FCC unit cell contains four atoms: one-eighth of an atom at each of the eight corners ($8 \times \frac{1}{8} = 1$ atom from the corners) and one-half of an atom on each of the six faces ($6 \times \frac{1}{2} = 3$ atoms from the faces). The atoms at the corners touch the atoms in the centers of the adjacent faces along the face diagonals of the cube. Because the atoms are on identical lattice points, they have identical environments.

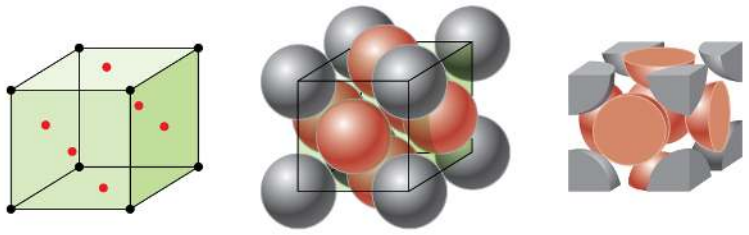


Figure **5.4.7**:A face-centered cubic solid has atoms at the corners and, as the name implies, at the centers of the faces of its unit cells.

Three images are shown. The first image shows a cube with black dots at each corner and red dots in the center of each face of the cube while the second image is composed of eight spheres that are stacked together to form a cube with six more spheres, one located on each face of the structure. Dots at the center of each corner sphere are connected to form a cube shape. The name under this image reads “Face-centered cubic structure.” The third image is the same as the second, but only shows the portions of the spheres that lie inside the cube shape.

Atoms in an FCC arrangement are packed as closely together as possible, with atoms occupying 74% of the volume. This structure is also called cubic closest packing (CCP). In CCP, there are three repeating layers of hexagonally arranged atoms. Each atom contacts six atoms in its own layer, three in the layer above, and three in the layer below. In this arrangement, each atom touches 12 near neighbors, and therefore has a coordination number of 12. The fact that FCC and CCP arrangements are equivalent may not be immediately obvious, but why they are actually the same structure is illustrated in Figure **5.4.8**.

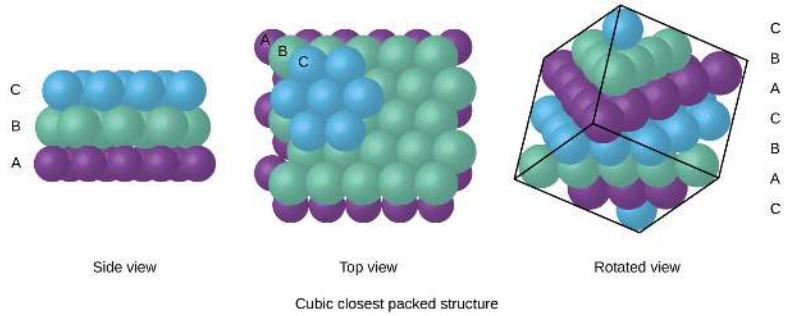


Figure **5.4.8**: A CCP arrangement consists of three repeating layers (ABCABC…) of hexagonally arranged atoms. Atoms in a CCP structure have a coordination number of 12 because they contact six atoms in their layer, plus three atoms in the layer above and three atoms in the layer below. By rotating our perspective, we can see that a CCP structure has a unit cell with a face containing an atom from layer A at one corner, atoms from layer B across a diagonal (at two corners and in the middle of the face), and an atom from layer C at the remaining corner. This is the same as a face-centered cubic arrangement.

Three images are shown. In the first image, a side view shows a layer of blue spheres, labeled “C” stacked on top of, and sitting in between the gaps in a second layer that is composed of green spheres, labeled “B,” which are sitting atop a purple layer of spheres labeled “A.” A label below this image reads “Side view.” The second image shows a top view of the same layers of spheres, where the top layer is “C,” the second layer is “B” and the lowest layer is “C.” This image is labeled “Top view” and written under this is the phrase “Cubic closest packed structure.” The third image shows an upper view of the side of a cube composed of two sets of the repeating layers shown in the other images. The layers are arranged “C, B, A, C, B, A, C” and the phrase written under this image reads “Rotated view.”

Because closer packing maximizes the overall attractions between atoms and minimizes the total intermolecular energy, the atoms in most metals pack in this manner. We find two types of closest packing in simple metallic crystalline structures: CCP, which we have already encountered, and hexagonal closest packing (HCP) shown in Figure **5.4.9**. Both consist of repeating layers of hexagonally arranged atoms. In both types, a second layer (B) is placed on the first layer (A) so that each atom in the second layer is in contact with three atoms in the first layer. The third layer is positioned in one of two ways. In HCP, atoms in the third layer are directly above atoms in the first layer (i.e., the third layer is also type A), and the stacking consists of alternating type A and type B close-packed layers (i.e., ABABAB⋯). In CCP, atoms in the third layer are not above atoms in either of the first two layers (i.e., the third layer is type C), and the stacking consists of alternating type A, type B, and type C close-packed layers (i.e., ABCABCABC⋯). About two–thirds of all metals crystallize in closest-packed arrays with coordination numbers of 12. Metals that crystallize in an HCP structure include Cd, Co, Li, Mg, Na, and Zn, and metals that crystallize in a CCP structure include Ag, Al, Ca, Cu, Ni, Pb, and Pt.

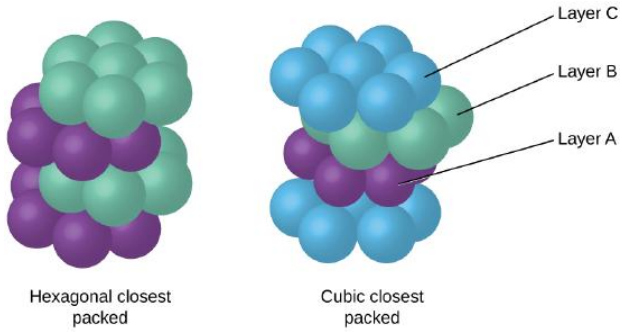


Figure **5.4.9**: In both types of closest packing, atoms are packed as compactly as possible. Hexagonal closest packing consists of two alternating layers (ABABAB…). Cubic closest packing consists of three alternating layers (ABCABCABC…).

Two images are shown. The first image, labeled “Hexagonal closest packed,” shows seven green spheres arranged in a circular sheet lying atop another sheet that is the same except the spheres are purple. The second sheet is offset just a bit so that the spheres of the top sheet lie in the grooves of the second sheet. Two more alternating green and purple layers of spheres lie below the first pair. The second image shows seven blue spheres, labeled “Layer C,” arranged in a circular sheet laying atop another sheet, labeled “Layer B” that is the same except the spheres are green. The second sheet is offset just a bit so that the spheres of the top sheet lie in the grooves of the second sheet. Two more alternating purple and then blue layers of spheres lie below the first pair. The purple layer is labeled “Layer A” and the phrase written below this image reads “Cubic closest packed.”

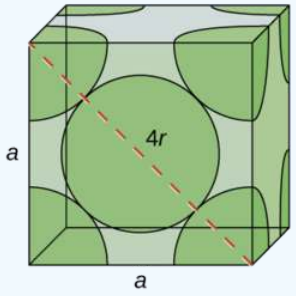
✔ Example 5.4.2: Calculating Atomic Radius and Density for Metals (Part 2)

Calcium crystallizes in a face-centered cubic structure. The edge length of its unit cell is 558.8 pm.

a. What is the atomic radius of Ca in this structure?
b. Calculate the density of Ca.

Solution

(a) In an FCC structure, Ca atoms contact each other across the diagonal of the face, so the length of the diagonal is equal to four Ca atomic radii (d = 4*r*).



Two adjacent edges and the diagonal of the face form a right triangle, with the length of each side equal to 558.8 pm and the length of the hypotenuse equal to four Ca atomic radii:

$$a^2 + a^2 = d^2$$

$$(558.8\ \text{pm})^2 + (558.5\ \text{pm})^2 = (4r)^2$$

Solving this gives

$$r = \sqrt{\frac{(558.8\ \text{pm})^2 + (558.5\ \text{pm})^2}{16}} = 197.6\ \text{pmg for a Ca radius.}$$

(b) Density is given by $\textbf{density} = \frac{\textbf{mass}}{\textbf{volume}}$. The density of calcium can be found by determining the density of its unit cell: for example, the mass contained within a unit cell divided by the volume of the unit cell. A face-centered Ca unit cell has one-eighth of an atom at each of the eight corners ($8 \times \frac{1}{8} = 1$atom) and one-half of an atom on each of the six faces $6 \times \frac{1}{2} = 3$ atoms), for a total of four atoms in the unit cell.

The mass of the unit cell can be found by:

$$1\ \text{Ca unit cell} \times \frac{4\ \text{Ca atoms}}{1\ \text{Ca unit cell}} \times \frac{1\ \text{mol Ca}}{6.022 \times 10^{23}\ \text{Ca atoms}} \times \frac{40.078\ \text{g}}{1\ \text{mol Ca}} = 2.662 \times 10^{-22}\ \text{g}$$

The volume of a Ca unit cell can be found by:

$$V = a^3 = (558.8 \times 10^{-10}\ \text{cm})^3 = 1.745 \times 10^{-22}\ \text{cm}^3$$

(Note that the edge length was converted from pm to cm to get the usual volume units for density.)

Then, the density of polonium:

$$\text{Po} = \frac{2.662 \times 10^{-22}\ \text{g}}{1.745 \times 10^{-22}\ \text{cm}^3} = 1.53\ \text{g/cm}^3$$

Exercise 5.4.2

Silver crystallizes in an FCC structure. The edge length of its unit cell is 409 pm.

a. What is the atomic radius of Ag in this structure?
b. Calculate the density of Ag.

Answer a

144 pm

Answer b

10.5 g/cm^3

In general, a unit cell is defined by the lengths of three axes (*a*, *b*, and *c*) and the angles (α, β, and γ) between them, as illustrated in Figure **5.4.10**. The axes are defined as being the lengths between points in the space lattice. Consequently, unit cell axes join points with identical environments.

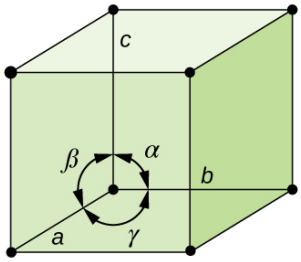


Figure 5.4.10: A unit cell is defined by the lengths of its three axes (a, b, and c) and the angles (α, β, and γ) between the axes.

A cube is shown where each corner has a black dot drawn on it. A circle in the bottom of the cube is composed of three double-ended arrows. The left top of this circle is labeled “alpha,” the top right is labeled “beta” and the bottom is labeled “gamma.” The bottom left corner of the cube is labeled “a” while the bottom of the back face is labeled “b” and the top, back, left corner is labeled “c.”

There are seven different lattice systems, some of which have more than one type of lattice, for a total of fourteen different unit cells, which have the shapes shown in Figure 5.4.11.

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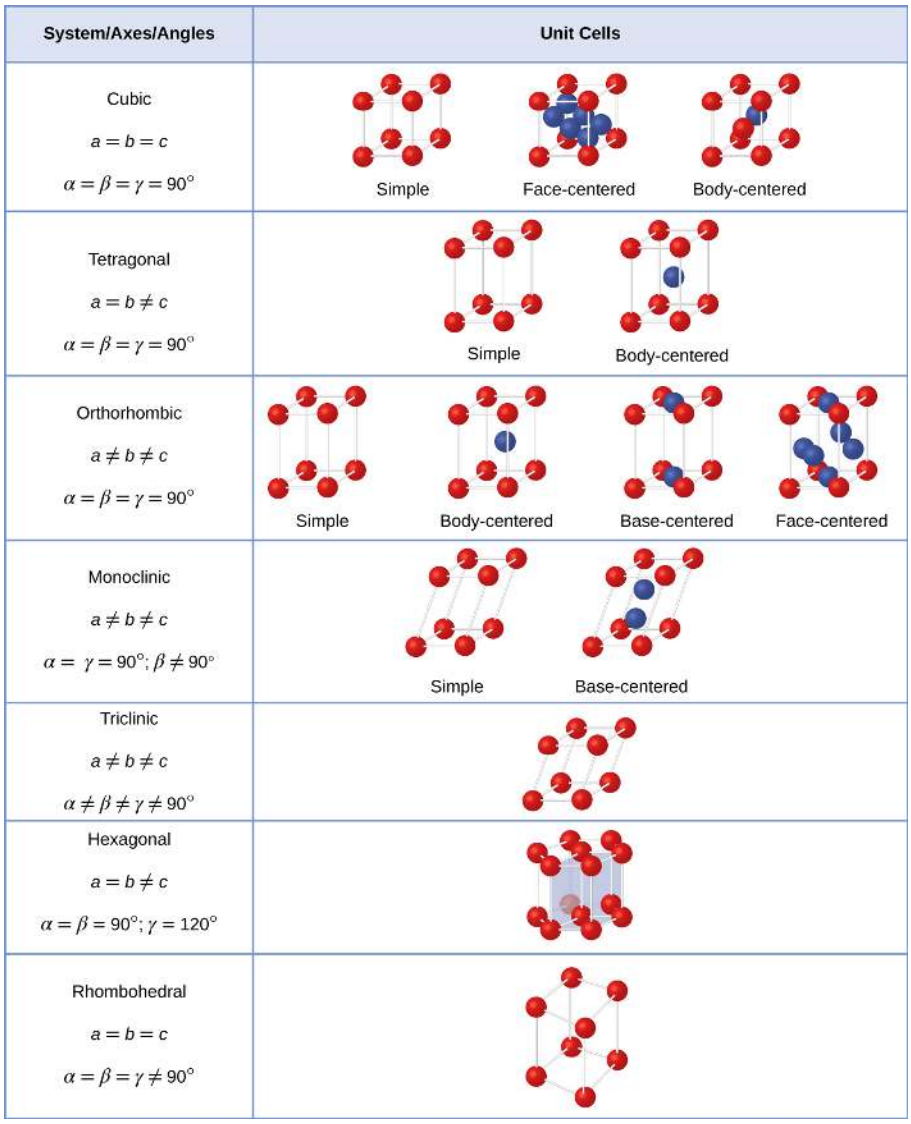


Figure **5.4.11**:There are seven different lattice systems and 14 different unit cells.

A table is composed of two columns and eight rows. The header row reads “System / Axes / Angles” and “Unit Cells .” The first column reads “Cubic, a equals b equals c, alpha equals beta equals gamma equals 90 degrees,” “Tetragonal, a equals b does not equal c, alpha equals beta equals gamma equals 90 degrees,” “Orthorhombic, a does not equal b does not equal c, alpha equals beta equals gamma equals 90 degrees,” “Monoclinic, a does not equal b does not equal c, alpha equals gamma equals 90 degrees, beta does not equal 90 degrees,” “Triclinic, a does not equal b does not equal c, alpha does not equal beta does not equal gamma does not equal 90 degrees,” “Hexagonal, a equals b does not equal c, alpha equals beta equals 90 degrees, gamma equals 120 degrees,” “Rhombohedral, a equals b equals c, alpha equals beta equals gamma does not equal 90 degrees.” The second column is composed of diagrams. The first set of diagrams in the first cell show a cube with spheres at each corner labeled “Simple,” a cube with spheres in each corner and on each face labeled “Face-centered” and a cube with spheres in each corner and one in the center labeled “Body-centered.” The second set of diagrams in the second cell show a vertical rectangle with spheres at each corner labeled “Simple” and a vertical rectangle with spheres in each corner and one in the center labeled “Body-centered.” The third set of diagrams in the third cell show a vertical rectangle with spheres at each corner labeled “Simple,” a vertical rectangle with spheres in each corner and one in the center labeled “Body-centered,” a vertical rectangle with spheres in each corner and one on the top and bottom faces labeled “Base-centered,” and a vertical rectangle with spheres in each corner and one on each face labeled “Face-centered.” The fourth set of diagrams in the fourth cell show a vertical rectangle with spheres at each corner that is slanted to one side labeled “Simple” and a vertical rectangle with spheres in each corner that is slanted to one side and has two spheres in the center is labeled “Body-centered.” The fifth diagrams in the fifth cell show a cube that is slanted with spheres at each corner while the sixth diagram in the sixth cell shows a pair of hexagonal rings that are connected together to form a six-sided shape with spheres at each corner. The seventh diagram in the seventh cell shows a rectangle that is slanted with spheres at each corner.

5.4.3: The Structures of Ionic Crystals

Ionic crystals consist of two or more different kinds of ions that usually have different sizes. The packing of these ions into a crystal structure is more complex than the packing of metal atoms that are the same size. Most monatomic ions behave as charged spheres, and their attraction for ions of opposite charge is the same in every direction. Consequently, stable structures for ionic compounds result (1) when ions of one charge are surrounded by as many ions as possible of the opposite charge and (2) when the cations and anions are in contact with each other. Structures are determined by two principal factors: the relative sizes of the ions and the ratio of the numbers of positive and negative ions in the compound.

In simple ionic structures, we usually find the anions, which are normally larger than the cations, arranged in a closest-packed array. (As seen previously, additional electrons attracted to the same nucleus make anions larger and fewer electrons attracted to the same nucleus make cations smaller when compared to the atoms from which they are formed.) The smaller cations commonly occupy one of two types of holes (or interstices) remaining between the anions. The smaller of the holes is found between three anions in one plane and one anion in an adjacent plane. The four anions surrounding this hole are arranged at the corners of a tetrahedron, so the hole is called a tetrahedral hole. The larger type of hole is found at the center of six anions (three in one layer and three in an adjacent layer) located at the corners of an octahedron; this is called an octahedral hole. Figure **5.4.12** illustrates both of these types of holes.

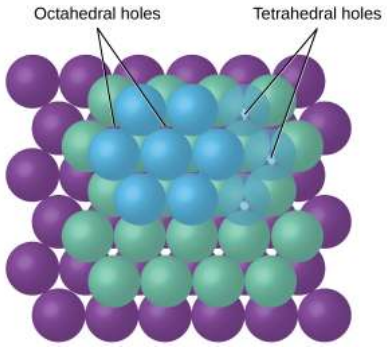


Figure **5.4.12**: Cations may occupy two types of holes between anions: octahedral holes or tetrahedral holes.

An image shows a top-view of a layer of blue spheres arranged in a sheet lying atop another sheet that is the same except the spheres are green. The second sheet is offset just a bit so that the spheres of the top sheet lie in the grooves of the second sheet. A third sheet composed of purple spheres lies at the bottom. The spaces created between the spheres in each layer are labeled “Octahedral holes” and “Tetrahedral holes.”

Depending on the relative sizes of the cations and anions, the cations of an ionic compound may occupy tetrahedral or octahedral holes, as illustrated in Figure **5.4.13**. Relatively small cations occupy tetrahedral holes, and larger cations occupy octahedral holes. If the cations are too large to fit into the octahedral holes, the anions may adopt a more open structure, such as a simple cubic array. The larger cations can then occupy the larger cubic holes made possible by the more open spacing.

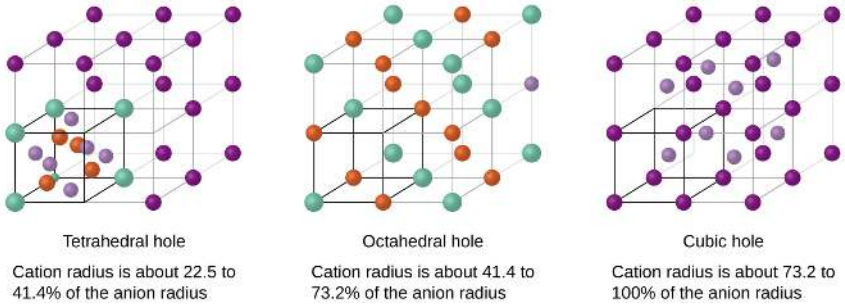


Figure 5.4.13:A cation's size and the shape of the hole occupied by the compound are directly related.

A diagram of three images is shown. In the first image, eight stacked cubes, with purple spheres at each corner, that make up one large cube are shown. The bottom left cube is different. It has green spheres at each corner and has four orange and six light purple spheres located on the faces of the cube. Labels below this structure read "Tetrahedral hole" and "Cation radius is about 22.5 to 41.4 percent of the anion radius. In the second image, eight stacked cubes, with alternating orange and green spheres at each corner, make up one large cube that is shown. The bottom left cube has darker lines that connect the spheres together. Labels below this structure read "Octahedral hole" and "Cation radius is about 41.4 to 73.2 percent of the anion radius. In the third image, eight stacked cubes, with purple spheres at each corner and light purple spheres on their interior faces, make up one large cube that is shown. Labels below this structure read "Cubic hole" and "Cation radius is about 73.2 to 100 percent of the anion radius."

There are two tetrahedral holes for each anion in either an HCP or CCP array of anions. A compound that crystallizes in a closest-packed array of anions with cations in the tetrahedral holes can have a maximum cation:anion ratio of 2:1; all of the tetrahedral holes are filled at this ratio. Examples include Li_2O, Na_2O, Li_2S, and Na_2S. Compounds with a ratio of less than 2:1 may also crystallize in a closest-packed array of anions with cations in the tetrahedral holes, if the ionic sizes fit. In these compounds, however, some of the tetrahedral holes remain vacant.

✔ Example 5.4.3: Occupancy of Tetrahedral Holes

Zinc sulfide is an important industrial source of zinc and is also used as a white pigment in paint. Zinc sulfide crystallizes with zinc ions occupying one-half of the tetrahedral holes in a closest-packed array of sulfide ions. What is the formula of zinc sulfide?

Solution

Because there are two tetrahedral holes per anion (sulfide ion) and one-half of these holes are occupied by zinc ions, there must be $\frac{1}{2} \times 2$, or 1, zinc ion per sulfide ion. Thus, the formula is ZnS.

? Exercise 5.4.3: Lithium selenide

Lithium selenide can be described as a closest-packed array of selenide ions with lithium ions in all of the tetrahedral holes. What it the formula of lithium selenide?

Answer

Li_2Se

The ratio of octahedral holes to anions in either an HCP or CCP structure is 1:1. Thus, compounds with cations in octahedral holes in a closest-packed array of anions can have a maximum cation:anion ratio of 1:1. In NiO, MnS, NaCl, and KH, for example, all of the octahedral holes are filled. Ratios of less than 1:1 are observed when some of the octahedral holes remain empty.

✔ Example 5.4.4: Stoichiometry of Ionic Compounds Sapphire

Aluminum oxide crystallizes with aluminum ions in two-thirds of the octahedral holes in a closest-packed array of oxide ions. What is the formula of aluminum oxide?

Solution

Because there is one octahedral hole per anion (oxide ion) and only two-thirds of these holes are occupied, the ratio of aluminum to oxygen must be $\frac{2}{3}$:1, which would give $\mathbf{Al_{2/3}O}$. The simplest whole number ratio is 2:3, so the formula is Al_2O_3.

? Exercise 5.4.4

The white pigment titanium oxide crystallizes with titanium ions in one-half of the octahedral holes in a closest-packed array of oxide ions. What is the formula of titanium oxide?

Answer

$\mathbf{TiO_2}$

In a simple cubic array of anions, there is one cubic hole that can be occupied by a cation for each anion in the array. In CsCl, and in other compounds with the same structure, all of the cubic holes are occupied. Half of the cubic holes are occupied in SrH_2, UO_2, $SrCl_2$, and CaF_2.

Different types of ionic compounds often crystallize in the same structure when the relative sizes of their ions and their stoichiometries (the two principal features that determine structure) are similar.

5.4.4: Unit Cells of Ionic Compounds

Many ionic compounds crystallize with cubic unit cells, and we will use these compounds to describe the general features of ionic structures. When an ionic compound is composed of cations and anions of similar size in a 1:1 ratio, it typically forms a simple cubic structure. Cesium chloride, CsCl, (Figure **5.4.14**) is an example of this, with Cs^+ and Cl^- having radii of 174 pm and 181 pm, respectively. We can think of this as chloride ions forming a simple cubic unit cell, with a cesium ion in the center; or as cesium ions forming a unit cell with a chloride ion in the center; or as simple cubic unit cells formed by Cs^+ ions overlapping unit cells formed by Cl^- ions. Cesium ions and chloride ions touch along the body diagonals of the unit cells. One cesium ion and one chloride ion are present per unit cell, giving the l:l stoichiometry required by the formula for cesium chloride. Note that there is no lattice point in the center of the cell, and CsCl is not a BCC structure because a cesium ion is not identical to a chloride ion.



Figure **5.4.14**: Ionic compounds with similar-sized cations and anions, such as CsCl, usually form a simple cubic structure. They can be described by unit cells with either cations at the corners or anions at the corners.

Three images are shown. The first image shows a cube with black dots at each corner and a red dot in the center. This cube is stacked with seven others that are not colored to form a larger cube. The second image is composed of eight spheres that are grouped together to form a cube with one smaller sphere in the center. The name under this image reads “Body-centered simple cubic structure.” The third image shows five horizontal layers of purple spheres with layers of smaller green spheres in between.

We have said that the location of lattice points is arbitrary. This is illustrated by an alternate description of the CsCl structure in which the lattice points are located in the centers of the cesium ions. In this description, the cesium ions are located on the lattice points at the corners of the cell, and the chloride ion is located at the center of the cell. The two unit cells are different, but they describe identical structures.

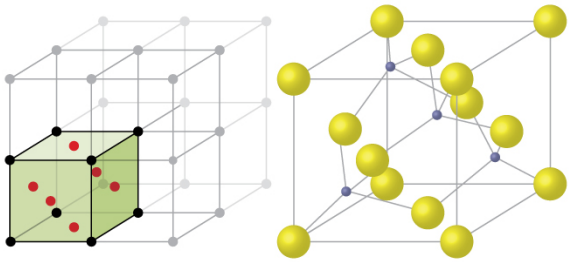
When an ionic compound is composed of a 1:1 ratio of cations and anions that differ significantly in size, it typically crystallizes with an FCC unit cell, like that shown in Figure **5.4.15**. Sodium chloride, NaCl, is an example of this, with Na^+ and Cl^- having radii of 102 pm and 181 pm, respectively. We can think of this as chloride ions forming an FCC cell, with sodium ions located in the octahedral holes in the middle of the cell edges and in the center of the cell. The sodium and chloride ions touch each other along the cell edges. The unit cell contains four sodium ions and four chloride ions, giving the 1:1 stoichiometry required by the formula, NaCl.



Figure **5.4.15**: Ionic compounds with anions that are much larger than cations, such as NaCl, usually form an FCC structure. They can be described by FCC unit cells with cations in the octahedral holes.

Three images are shown. The first image shows a cube with black dots at each corner and a red dot in the center. This cube is stacked with seven others that are not colored to form a larger cube. The second image is composed of eight spheres that are grouped together to form a cube with one much larger sphere in the center. The name under this image reads “Body-centered simple cubic structure.” The third image shows seven horizontal layers of alternating purple and green spheres that are slightly offset with one another and form a large cube.

The cubic form of zinc sulfide, zinc blende, also crystallizes in an FCC unit cell, as illustrated in Figure **5.4.16**. This structure contains sulfide ions on the lattice points of an FCC lattice. (The arrangement of sulfide ions is identical to the arrangement of chloride ions in sodium chloride.) The radius of a zinc ion is only about 40% of the radius of a sulfide ion, so these small Zn^{2+} ions are located in alternating tetrahedral holes, that is, in one half of the tetrahedral holes. There are four zinc ions and four sulfide ions in the unit cell, giving the empirical formula ZnS.

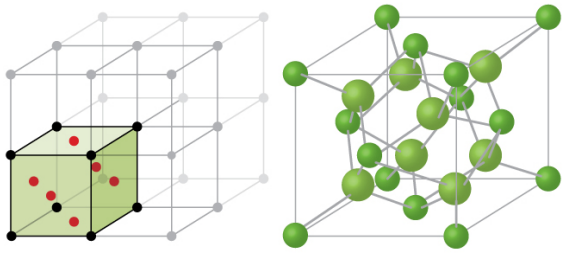


ZnS face-centered unit cell

Figure **5.4.16**: ZnS, zinc sulfide (or zinc blende) forms an FCC unit cell with sulfide ions at the lattice points and much smaller zinc ions occupying half of the tetrahedral holes in the structure.

Two images are shown. The first image shows a cube with black dots at each corner and a red dot in the center of each face of the cube. This cube is stacked with seven others that are not colored to form a larger cube. The second image is composed of eight spheres that form the corners of a cube with six other spheres located in the face of the cube. The spheres are connected to one another by lines. The name under this image reads “Z n S, face-centered unit cell.”

A calcium fluoride unit cell, like that shown in Figure **5.4.17**, is also an FCC unit cell, but in this case, the cations are located on the lattice points; equivalent calcium ions are located on the lattice points of an FCC lattice. All of the tetrahedral sites in the FCC array of calcium ions are occupied by fluoride ions. There are four calcium ions and eight fluoride ions in a unit cell, giving a calcium:fluorine ratio of 1:2, as required by the chemical formula, CaF_2. Close examination of Figure **5.4.17** will reveal a simple cubic array of fluoride ions with calcium ions in one half of the cubic holes. The structure cannot be described in terms of a space lattice of points on the fluoride ions because the fluoride ions do not all have identical environments. The orientation of the four calcium ions about the fluoride ions differs.



CaF_2 face-centered unit cell

Figure **5.4.17**: Calcium fluoride, CaF_2, forms an FCC unit cell with calcium ions (green) at the lattice points and fluoride ions (red) occupying all of the tetrahedral sites between them.

Two images are shown. The first image shows a cube with black dots at each corner and a red dot in the center of each face of the cube. This cube is stacked with seven others that are not colored to form a larger cube. The second image is composed of eight small green spheres that form the corners of a cube with six other small green spheres located in the faces of the cube. Eight larger green spheres are spaced inside the cube and all of the spheres are connect to one another by lines. The name under this image reads “C a F, subscript 2, face-centered unit cell.”

5.4.5: Calculation of Ionic Radii

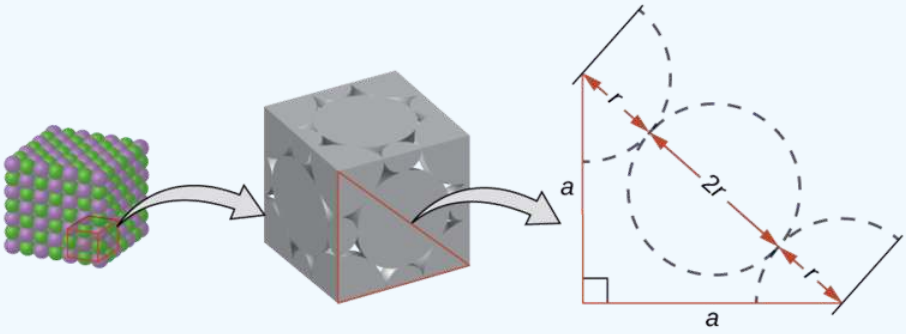
If we know the edge length of a unit cell of an ionic compound and the position of the ions in the cell, we can calculate ionic radii for the ions in the compound if we make assumptions about individual ionic shapes and contacts.

Example 5.4.5: Calculation of Ionic Radii

The edge length of the unit cell of LiCl (NaCl-like structure, FCC) is 0.514 nm or 5.14 Å. Assuming that the lithium ion is small enough so that the chloride ions are in contact, calculate the ionic radius for the chloride ion. Note: The length unit angstrom, Å, is often used to represent atomic-scale dimensions and is equivalent to 10^{-10} m.

Solution

On the face of a LiCl unit cell, chloride ions contact each other across the diagonal of the face:



Drawing a right triangle on the face of the unit cell, we see that the length of the diagonal is equal to four chloride radii (one radius from each corner chloride and one diameter—which equals two radii—from the chloride ion in the center of the face), so $d = 4r$. From the Pythagorean theorem, we have:

$$a^2 + a^2 = d^2$$

which yields:

$$(0.514\ \text{nm})^2 + (0.514\ \text{nm})^2 = (4r)^2 = 16r^2$$

Solving this gives:

$$r = \sqrt{\frac{(0.514\ \text{nm})^2 + (0.514\ \text{nm})^2}{16}} = 0.182\ \text{nm}\ (1.82\ \text{Å})\ \text{for a}\ Cl^-\ \text{radius.}$$

Exercise 5.4.6

The edge length of the unit cell of KCl (NaCl-like structure, FCC) is 6.28 Å. Assuming anion-cation contact along the cell edge, calculate the radius of the potassium ion. The radius of the chloride ion is 1.82 Å.

Answer

The radius of the potassium ion is 1.33 Å.

It is important to realize that values for ionic radii calculated from the edge lengths of unit cells depend on numerous assumptions, such as a perfect spherical shape for ions, which are approximations at best. Hence, such calculated values are themselves approximate and comparisons cannot be pushed too far. Nevertheless, this method has proved useful for calculating ionic radii from experimental measurements such as X-ray crystallographic determinations.

5.4.6: X-Ray Crystallography

The size of the unit cell and the arrangement of atoms in a crystal may be determined from measurements of the *diffraction* of X-rays by the crystal, termed X-ray crystallography. Diffraction is the change in the direction of travel experienced by an electromagnetic wave when it encounters a physical barrier whose dimensions are comparable to those of the wavelength of the light. X-rays are electromagnetic radiation with wavelengths about as long as the distance between neighboring atoms in crystals (on the order of a few Å).

When a beam of monochromatic X-rays strikes a crystal, its rays are scattered in all directions by the atoms within the crystal. When scattered waves traveling in the same direction encounter one another, they undergo *interference*, a process by which the waves combine to yield either an increase or a decrease in amplitude (intensity) depending upon the extent to which the combining waves' maxima are separated (Figure 5.4.18).

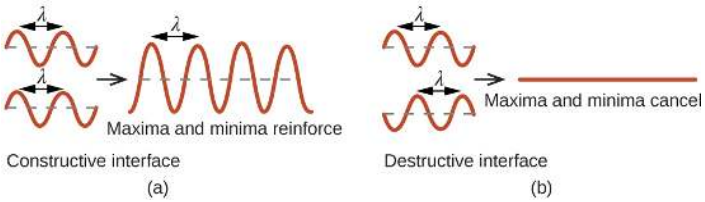


Figure 5.4.18: Light waves occupying the same space experience interference, combining to yield waves of greater (a) or lesser (b) intensity, depending upon the separation of their maxima and minima.

A pair of images is shown that has four sections. In the first section, two sinusoidal waves are shown, one drawn above the other, and a section from the top of one curve to the top of the next curve is labeled "lambda." The curves align with one another. The phrase below this reads "Constructive interference." A right facing arrow leads from the first section to the second, which shows one larger sinusoidal curve that has higher and lower peaks and troughs. A section from the top of one curve to the top of the next curve is labeled "lambda" and the phrase below this reads "Maxima and minima reinforce." In the second section, two sinusoidal waves are shown, one drawn above the other, and a section from the top of one curve to the top of the next curve is labeled "lambda." The curves do not align with one another. The phrase below this reads "Destructive interference." A right facing arrow leads from the first section to the second, which shows one flat line. The phrase below this reads "Maxima and minima cancel."

When X-rays of a certain wavelength, λ, are scattered by atoms in adjacent crystal planes separated by a distance, d, they may undergo constructive interference when the difference between the distances traveled by the two waves prior to their combination is an integer factor, n, of the wavelength. This condition is satisfied when the angle of the diffracted beam, θ, is related to the wavelength and interatomic distance by the equation:

$$n\lambda = 2d\sin\theta \tag{5.4.1}$$

This relation is known as the Bragg equation in honor of W. H. Bragg, the English physicist who first explained this phenomenon. Figure 5.4.18 illustrates two examples of diffracted waves from the same two crystal planes. The figure on the left depicts waves diffracted at the Bragg angle, resulting in constructive interference, while that on the right shows diffraction and a different angle that does not satisfy the Bragg condition, resulting in destructive interference.

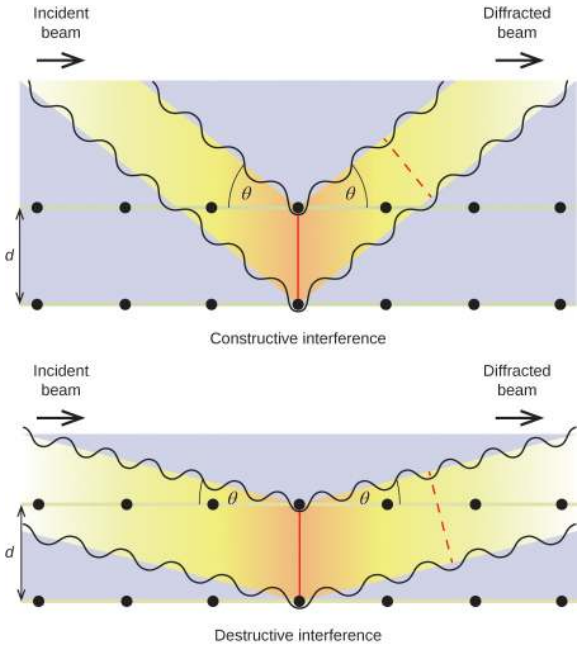


Figure 5.4.19: The diffraction of X-rays scattered by the atoms within a crystal permits the determination of the distance between the atoms. The top image depicts constructive interference between two scattered waves and a resultant diffracted wave of high intensity. The bottom image depicts destructive interference and a low intensity diffracted wave.

Two similar figures are shown. The first figure, labeled “Constructive Interference,” shows two horizontal rows of seven black dots with a line passing through them. The fourth dots of each row have a vertical line connecting them. The distance between these rows is labeled “d.” A beam labeled “Incident beam” descends at an angle labeled “theta” until it hits the line connecting the fourth dots, after which a diffracted beam ascends at the same angle “theta.” A dotted line is drawn across the diffracted beam. The second figure, labeled “Destructive interference,” is very similar, except that the angles “theta” are far more acute, making the slopes of the beams more shallow.

An X-ray diffractometer, such as the one illustrated in Figure 5.4.20, may be used to measure the angles at which X-rays are diffracted when interacting with a crystal as described earlier. From such measurements, the Bragg equation may be used to compute distances between atoms as demonstrated in the following example exercise.

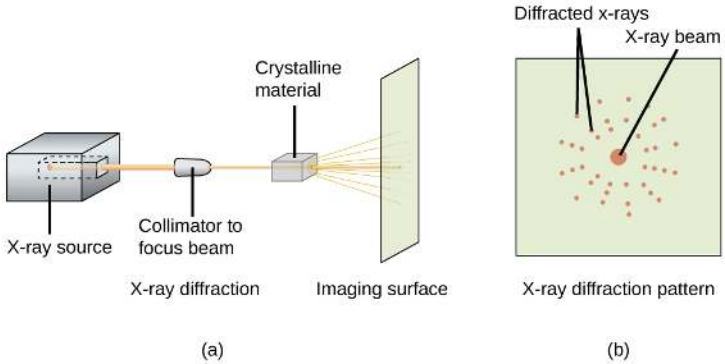


Figure 5.4.20: (a) In a diffractometer, a beam of X-rays strikes a crystalline material, producing (b) an X-ray diffraction pattern that can be analyzed to determine the crystal structure.

A diagram, labeled “a” shows a cube on the left with a channel bored into its right side labeled “X dash ray source.” A beam is leaving from this channel and traveling in a horizontal line toward an oval-shaped, short tube, labeled “Collimator to focus beam” and “X dash ray diffraction,” where it passes through a cube labeled “Crystalline material” and scatters onto a vertical sheet labeled “Imaging surface.” A second diagram, labeled “b,” shows a square sheet with a large dot in the center labeled “X dash ray beam,” that is surrounded by smaller dots arranged in rings and labeled “Diffracted X dash rays.”

Example 5.4.6: Using the Bragg Equation

In a diffractometer, X-rays with a wavelength of 0.1315 nm were used to produce a diffraction pattern for copper. The first order diffraction (n = 1) occurred at an angle θ = 25.25°. Determine the spacing between the diffracting planes in copper.

Solution

The distance between the planes is found by solving the Bragg equation (Equation 5.4.1) for d.

This gives

$$d = \frac{n\lambda}{2\sin\theta} = \frac{1(0.1315\ \text{nm})}{2\sin(25.25°)} = 0.154\ \text{nm}$$

? Exercise 5.4.6

A crystal with spacing between planes equal to 0.394 nm diffracts X-rays with a wavelength of 0.147 nm. What is the angle for the first order diffraction?

Answer

21.9°

X-ray Crystallographer Rosalind Franklin

The discovery of the structure of DNA in 1953 by Francis Crick and James Watson is one of the great achievements in the history of science. They were awarded the 1962 Nobel Prize in Physiology or Medicine, along with Maurice Wilkins, who provided experimental proof of DNA's structure. British chemist Rosalind Franklin made invaluable contributions to this monumental achievement through her work in measuring X-ray diffraction images of DNA. Early in her career, Franklin's research on the structure of coals proved helpful to the British war effort. After shifting her focus to biological systems in the early 1950s, Franklin and doctoral student Raymond Gosling discovered that DNA consists of two forms: a long, thin fiber formed when wet (type "B") and a short, wide fiber formed when dried (type "A"). Her X-ray diffraction images of DNA provided the crucial information that allowed Watson and Crick to confirm that DNA forms a double helix, and to determine details of its size and structure. Franklin also conducted pioneering research on viruses and the RNA that contains their genetic information, uncovering new information that radically changed the body of knowledge in the field. After developing ovarian cancer, Franklin continued to work until her death in 1958 at age 37. Among many posthumous recognitions of her work, the Chicago Medical School of Finch University of Health Sciences changed its name to the Rosalind Franklin University of Medicine and Science in 2004, and adopted an image of her famous X-ray diffraction image of DNA as its official university logo.

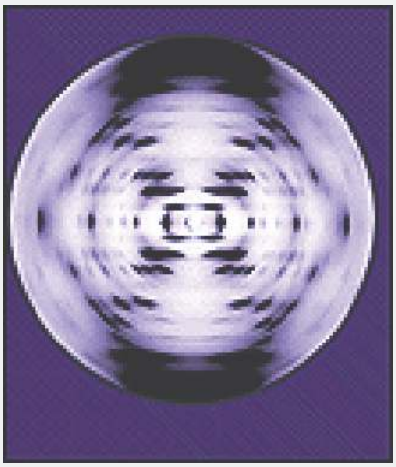


Figure 5.4.7.This illustration shows an X-ray diffraction image similar to the one Franklin found in her research. (credit: National Institutes of Health)

5.4.7: Key Concepts and Summary

The structures of crystalline metals and simple ionic compounds can be described in terms of packing of spheres. Metal atoms can pack in hexagonal closest-packed structures, cubic closest-packed structures, body-centered structures, and simple cubic structures.

The anions in simple ionic structures commonly adopt one of these structures, and the cations occupy the spaces remaining between the anions. Small cations usually occupy tetrahedral holes in a closest-packed array of anions. Larger cations usually occupy octahedral holes. Still larger cations can occupy cubic holes in a simple cubic array of anions. The structure of a solid can be described by indicating the size and shape of a unit cell and the contents of the cell. The type of structure and dimensions of the unit cell can be determined by X-ray diffraction measurements.

Glossary

body-centered cubic (BCC) solid
crystalline structure that has a cubic unit cell with lattice points at the corners and in the center of the cell

body-centered cubic unit cell
simplest repeating unit of a body-centered cubic crystal; it is a cube containing lattice points at each corner and in the center of the cube

Bragg equation
equation that relates the angles at which X-rays are diffracted by the atoms within a crystal

coordination number
number of atoms closest to any given atom in a crystal or to the central metal atom in a complex

cubic closest packing (CCP)
crystalline structure in which planes of closely packed atoms or ions are stacked as a series of three alternating layers of different relative orientations (ABC)

diffraction
redirection of electromagnetic radiation that occurs when it encounters a physical barrier of appropriate dimensions

face-centered cubic (FCC) solid
crystalline structure consisting of a cubic unit cell with lattice points on the corners and in the center of each face

face-centered cubic unit cell
simplest repeating unit of a face-centered cubic crystal; it is a cube containing lattice points at each corner and in the center of each face

hexagonal closest packing (HCP)
crystalline structure in which close packed layers of atoms or ions are stacked as a series of two alternating layers of different relative orientations (AB)

hole
(also, interstice) space between atoms within a crystal

isomorphous
possessing the same crystalline structure

octahedral hole
open space in a crystal at the center of six particles located at the corners of an octahedron

simple cubic unit cell
(also, primitive cubic unit cell) unit cell in the simple cubic structure

simple cubic structure
crystalline structure with a cubic unit cell with lattice points only at the corners

space lattice

all points within a crystal that have identical environments

tetrahedral hole

tetrahedral space formed by four atoms or ions in a crystal

unit cell

smallest portion of a space lattice that is repeated in three dimensions to form the entire lattice

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

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

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5.5: Bonding in Metals and Semiconductors

In the early 1900's, Paul Drüde came up with the "sea of electrons" metallic bonding theory by modeling metals as a mixture of atomic cores (atomic cores = positive nuclei + inner shell of electrons) and valence electrons. Metallic bonds occur among metal atoms. Whereas ionic bonds join metals to non-metals, *metallic bonding joins a bulk of metal atoms*. A sheet of aluminum foil and a copper wire are both places where you can see metallic bonding in action.

Metals tend to have high melting points and boiling points suggesting strong bonds between the atoms. Even a soft metal like sodium (melting point 97.8°C) melts at a considerably higher temperature than the element (neon) which precedes it in the Periodic Table. Sodium has the electronic structure $1s^2 2s^2 2p^6 3s^1$. When sodium atoms come together, the electron in the 3s atomic orbital of one sodium atom shares space with the corresponding electron on a neighboring atom to form a molecular orbital - in much the same sort of way that a covalent bond is formed.

The difference, however, is that each sodium atom is being touched by eight other sodium atoms - and the sharing occurs between the central atom and the 3s orbitals on all of the eight other atoms. Each of these eight is in turn being touched by eight sodium atoms, which in turn are touched by eight atoms - and so on and so on, until you have taken in all the atoms in that lump of sodium. *All* of the 3s orbitals on all of the atoms overlap to give a vast number of molecular orbitals that extend over the whole piece of metal. There have to be huge numbers of molecular orbitals, of course, because any orbital can only hold two electrons.

The electrons can move freely within these molecular orbitals, and so each electron becomes detached from its parent atom. The electrons are said to be delocalized. The metal is held together by the strong forces of attraction between the positive nuclei and the delocalized electrons (Figure **5.5.1**).

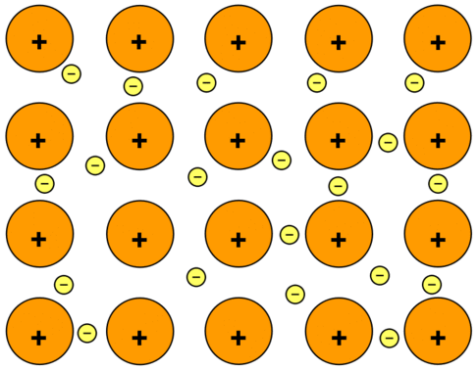


Figure **5.5.1**: Metallic Bonding: The Electron Sea Model: Positive atomic nuclei (orange circles) surrounded by a sea of delocalized electrons (yellow circles).

This is sometimes described as "an array of positive ions in a sea of electrons". If you are going to use this view, beware! Is a metal made up of atoms or ions? It is made of atoms**.** Each positive center in the diagram represents all the rest of the atom apart from the outer electron, but that electron has not been lost - it may no longer have an attachment to a particular atom, but it's still there in the structure. Sodium metal is therefore written as **Na**, not $\mathbf{Na^+}$.

✔ Example 5.5.1: Metallic bonding in magnesium

Use the sea of electrons model to explain why Magnesium has a higher melting point (650 °C) than sodium (97.79 °C).

Solution

If you work through the same argument above for sodium with magnesium, you end up with stronger bonds and hence a higher melting point.

Magnesium has the outer electronic structure $3s^2$. Both of these electrons become delocalized, so the "sea" has twice the electron density as it does in sodium. The remaining "ions" also have twice the charge (if you are going to use this particular view of the metal bond) and so there will be more attraction between "ions" and "sea".

More realistically, each magnesium atom has 12 protons in the nucleus compared with sodium's 11. In both cases, the nucleus is screened from the delocalized electrons by the same number of inner electrons - the 10 electrons in the $1s^2$ $2s^2$ $2p^6$ orbitals.

That means that there will be a net pull from the magnesium nucleus of 2+, but only 1+ from the sodium nucleus.

So not only will there be a greater number of delocalized electrons in magnesium, but there will also be a greater attraction for them from the magnesium nuclei. Magnesium atoms also have a slightly smaller radius than sodium atoms, and so the delocalized electrons are closer to the nuclei. Each magnesium atom also has twelve near neighbors rather than sodium's eight. Both of these factors increase the strength of the bond still further.

Note: Transition metals tend to have particularly high melting points and boiling points. The reason is that they can involve the 3d electrons in the delocalization as well as the 4s. The more electrons you can involve, the stronger the attractions tend to be.

Bulk properties of metals

Metals have several qualities that are unique, such as the ability to conduct electricity and heat, a low ionization energy, and a low electronegativity (so they will give up electrons easily to form cations). Their physical properties include a lustrous (shiny) appearance, and they are malleable and ductile. Metals have a crystal structure but can be easily deformed. In this model, the valence electrons are free, delocalized, mobile, and not associated with any particular atom. This model may account for:

- **Conductivity**: Since the electrons are free, if electrons from an outside source were pushed into a metal wire at one end (Figure 5.5.2), the electrons would move through the wire and come out at the other end at the same rate (conductivity is the movement of charge).

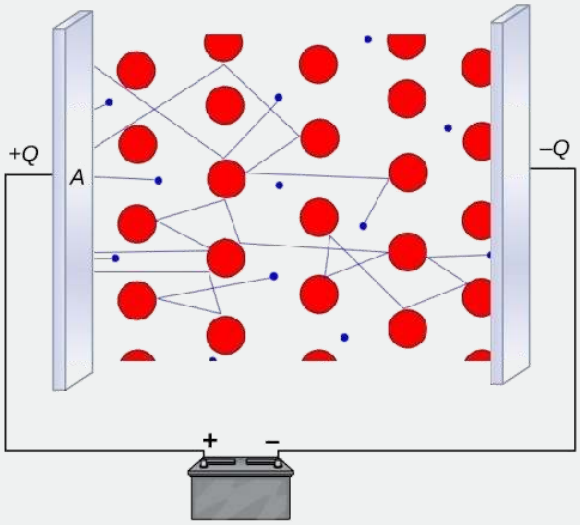


Figure 5.5.2: The "sea of electrons" is free to flow about the crystal of positive metal ions. These flowing electron can conduct electrical change when an electric field is applied (e.g., a battery). (CC-BY-SA; OpenStax and Rafaelgarcia).

- **Malleability** and **Ductility**: The electron-sea model of metals not only explains their electrical properties but their malleability and ductility as well. The sea of electrons surrounding the protons acts like a cushion, and so when the metal is hammered on, for instance, the overall composition of the structure of the metal is not harmed or changed. The protons may be rearranged but the sea of electrons with adjust to the new formation of protons and keep the metal intact. When one layer of ions in an electron sea moves along one space with respect to the layer below it, the crystal structure does not fracture but is only deformed (Figure 5.5.3).



Figure 5.5.3: Malleability of metals originate from each of moving layer of atoms with respect to each other. The final situation is much the same as the initial. Thus if we hit a metal with a hammer, the crystals do not shatter, but merely change their shape, This is very different from the behavior of ionic crystals.

- **Heat capacity**: This is explained by the ability of free electrons to move about the solid.
- **Luster**: The free electrons can absorb photons in the "sea," so metals are opaque-looking. Electrons on the surface can bounce back light at the same frequency that the light hits the surface, therefore the metal appears to be shiny.

> However, these observations are only qualitative, and not quantitative, so they cannot be tested. The "Sea of Electrons" theory stands today only as an oversimplified model of how metallic bonding works.

In a molten metal, the metallic bond is still present, although the ordered structure has been broken down. The metallic bond is not fully broken until the metal boils. That means that boiling point is actually a better guide to the strength of the metallic bond than melting point is. On melting, the bond is loosened, not broken. The strength of a metallic bond depends on three things:

1. The number of electrons that become delocalized from the metal
2. The charge of the cation (metal).
3. The size of the cation.

A **strong** metallic bond will be the result of more delocalized electrons, which causes the effective nuclear charge on electrons on the cation to increase, in effect making the size of the cation smaller. Metallic bonds are strong and require a great deal of energy to break, and therefore **metals have high melting and boiling points.** A metallic bonding theory must explain how so much bonding can occur with such few electrons (since metals are located on the left side of the periodic table and do not have many electrons in their valence shells). The theory must also account for all of a metal's unique chemical and physical properties.

Expanding the Range of Bonding Possible

Previously, we argued that bonding between atoms can classified as range of possible bonding between **ionic bonds** (fully charge transfer) and **covalent bonds** (fully shared electrons). When two atoms of slightly differing electronegativities come together to form a covalent bond, one atom attracts the electrons more than the other; this is called a polar covalent bond. However, simple “ionic” and “covalent” bonding are idealized concepts and most bonds exist on a two-dimensional continuum described by the van Arkel-Ketelaar Triangle (Figure **5.5.4**).

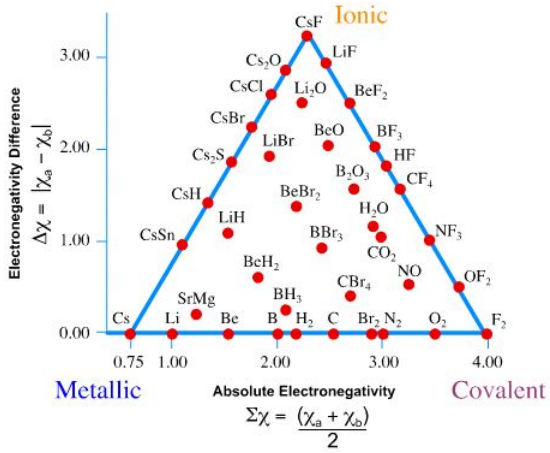


Figure **5.5.4**: van Arkel-Ketelaar Triangle plots the difference in electronegativity ($\Delta\chi$) and the average electronegativity in a bond ($\sum\chi$). the top region is where bonds are mostly ionic, the lower left region is where bonding is metallic, and the lower right region is where the bonding is covalent.

Bond triangles or **van Arkel–Ketelaar** triangles (named after Anton Eduard van Arkel and J. A. A. Ketelaar) are triangles used for showing different compounds in varying degrees of ionic, metallic and covalent bonding. In 1941 van Arkel recognized three extreme materials and associated bonding types. Using 36 main group elements, such as metals, metalloids and non-metals, he placed ionic, metallic and covalent bonds on the corners of an equilateral triangle, as well as suggested intermediate species. The bond triangle shows that chemical bonds are not just particular bonds of a specific type. Rather, bond types are interconnected and different compounds have varying degrees of different bonding character (for example, polar covalent bonds).



Video 5.5.1: What is the van Arkel-Ketelaar Triangle of Bonding?

Using electronegativity - two compound average electronegativity on x-axis of Figure 5.5.4.

$$\sum\chi = \frac{\chi_A + \chi_B}{2} \tag{5.5.1}$$

and electronegativity difference on y-axis,

$$\Delta\chi = |\chi_A - \chi_B| \tag{5.5.2}$$

we can rate the dominant bond between the compounds. On the right side of Figure 5.5.4 (from ionic to covalent) should be compounds with varying difference in electronegativity. The compounds with equal electronegativity, such as Cl_2 (chlorine) are placed in the covalent corner, while the ionic corner has compounds with large electronegativity difference, such as NaCl (table salt). The bottom side (from metallic to covalent) contains compounds with varying degree of directionality in the bond. At one extreme is metallic bonds with delocalized bonding and at the other are covalent bonds in which the orbitals overlap in a particular direction. The left side (from ionic to metallic) is meant for delocalized bonds with varying electronegativity difference.

The Three Extremes in bonding

In general:

- Metallic bonds have low $\Delta\chi$ **and** low average $\sum\chi$.
- Ionic bonds have moderate-to-high $\Delta\chi$ and moderate values of average $\sum\chi$.
- Covalent bonds have moderate to high average $\sum\chi$ and can exist with moderately low $\Delta\chi$.

Example 5.5.2

Use the tables of electronegativities (Table A2) and Figure 5.5.4 to estimate the following values

- difference in electronegativity ($\Delta\chi$)
- average electronegativity in a bond ($\sum\chi$)
- percent ionic character
- likely bond type

for the selected compounds:

a. AsH (e.g., in arsine AsH)
b. SrLi
c. KF.

Solution

a: AsH

- The electronegativity of As is 2.18

- The electronegativity of **H** is 2.22

Using Equations 5.5.1 and 5.5.2:

$$\begin{aligned}\sum\chi &= \frac{\chi_A + \chi_B}{2} \\ &= \frac{2.18 + 2.22}{2} \\ &= 2.2\end{aligned}$$

$$\begin{aligned}\Delta\chi &= \chi_A - \chi_B \\ &= 2.18 - 2.22 \\ &= 0.04\end{aligned}$$

- From Figure 5.5.4, the bond is fairly nonpolar and has a low ionic character (10% or less)
- The bonding is in the middle of a covalent bond and a metallic bond

b: **SrLi**

- The electronegativity of **Sr** is 0.95
- The electronegativity of **Li** is 0.98

Using Equations 5.5.1 and 5.5.2:

$$\begin{aligned}\sum\chi &= \frac{\chi_A + \chi_B}{2} \\ &= \frac{0.95 + 0.98}{2} \\ &= 0.965\end{aligned}$$

$$\begin{aligned}\Delta\chi &= \chi_A - \chi_B \\ &= 0.98 - 0.95 \\ &= 0.025\end{aligned}$$

- From Figure 5.5.4, the bond is fairly nonpolar and has a low ionic character (~3% or less)
- The bonding is likely metallic.

c: **KF**

- The electronegativity of **K** is 0.82
- The electronegativity of **F** is 3.98

Using Equations 5.5.1 and 5.5.2:

$$\begin{aligned}\sum\chi &= \frac{\chi_A + \chi_B}{2} \\ &= \frac{0.82 + 3.98}{2} \\ &= 2.4\end{aligned}$$

$$\begin{aligned}\Delta\chi &= \chi_A - \chi_B \\ &= |0.82 - 3.98| \\ &= 3.16\end{aligned}$$

- From Figure 5.5.4, the bond is fairly polar and has a high ionic character (~75%)
- The bonding is likely ionic.

? Exercise 5.5.2

Contrast the bonding of **NaCl** and silicon tetrafluoride.

Answer

NaCl is an ionic crystal structure, and an electrolyte when dissolved in water; $\Delta\chi = 1.58$, average $\sum\chi = 1.79$, while silicon tetrafluoride is covalent (molecular, non-polar gas; $\Delta\chi = 2.08$, average $\sum\chi = 2.94$.

Contributors and Attributions

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5.E: Liquids and Solids (Exercises)

5.E.1: 10.1: Intermolecular Forces

5.E.1.1: Q10.1.1

In terms of their bulk properties, how do liquids and solids differ? How are they similar?

5.E.1.2: S10.1.1

Liquids and solids are similar in that they are matter composed of atoms, ions, or molecules. They are incompressible and have similar densities that are both much larger than those of gases. They are different in that liquids have no fixed shape, and solids are rigid.

5.E.1.3: Q10.1.2

In terms of the kinetic molecular theory, in what ways are liquids similar to solids? In what ways are liquids different from solids?

5.E.1.4: Q10.1.3

In terms of the kinetic molecular theory, in what ways are liquids similar to gases? In what ways are liquids different from gases?

5.E.1.5: S10.1.3

They are similar in that the atoms or molecules are free to move from one position to another. They differ in that the particles of a liquid are confined to the shape of the vessel in which they are placed. In contrast, a gas will expand without limit to fill the space into which it is placed.

5.E.1.6: Q10.1.4

Explain why liquids assume the shape of any container into which they are poured, whereas solids are rigid and retain their shape.

5.E.1.7: Q10.1.5

What is the evidence that all neutral atoms and molecules exert attractive forces on each other?

5.E.1.8: S10.1.5

All atoms and molecules will condense into a liquid or solid in which the attractive forces exceed the kinetic energy of the molecules, at sufficiently low temperature.

5.E.1.9: Q10.1.6

Open the PhET States of Matter Simulation to answer the following questions:

a. Select the Solid, Liquid, Gas tab. Explore by selecting different substances, heating and cooling the systems, and changing the state. What similarities do you notice between the four substances for each phase (solid, liquid, gas)? What differences do you notice?
b. For each substance, select each of the states and record the given temperatures. How do the given temperatures for each state correlate with the strengths of their intermolecular attractions? Explain.
c. Select the Interaction Potential tab, and use the default neon atoms. Move the Ne atom on the right and observe how the potential energy changes. Select the Total Force button, and move the Ne atom as before. When is the total force on each atom attractive and large enough to matter? Then select the Component Forces button, and move the Ne atom. When do the attractive (van der Waals) and repulsive (electron overlap) forces balance? How does this relate to the potential energy versus the distance between atoms graph? Explain.

5.E.1.10: Q10.1.7

Define the following and give an example of each:

a. dispersion force
b. dipole-dipole attraction

c. hydrogen bond

5.E.1.11: S10.1.7

a. Dispersion forces occur as an atom develops a temporary dipole moment when its electrons are distributed asymmetrically about the nucleus. This structure is more prevalent in large atoms such as argon or radon. A second atom can then be distorted by the appearance of the dipole in the first atom. The electrons of the second atom are attracted toward the positive end of the first atom, which sets up a dipole in the second atom. The net result is rapidly fluctuating, temporary dipoles that attract one another (example: Ar).
b. A dipole-dipole attraction is a force that results from an electrostatic attraction of the positive end of one polar molecule for the negative end of another polar molecule (example: ICI molecules attract one another by dipole-dipole interaction).
c. Hydrogen bonds form whenever a hydrogen atom is bonded to one of the more electronegative atoms, such as a fluorine, oxygen, nitrogen, or chlorine atom. The electrostatic attraction between the partially positive hydrogen atom in one molecule and the partially negative atom in another molecule gives rise to a strong dipole-dipole interaction called a hydrogen bond (example: $\mathbf{HF\cdots HF}$).

5.E.1.12: Q10.1.8

The types of intermolecular forces in a substance are identical whether it is a solid, a liquid, or a gas. Why then does a substance change phase from a gas to a liquid or to a solid?

5.E.1.13: Q10.1.9

Why do the boiling points of the noble gases increase in the order He < Ne < Ar < Kr < Xe?

5.E.1.14: S10.1.9

The London forces typically increase as the number of electrons increase.

5.E.1.15: Q10.1.10

Neon and HF have approximately the same molecular masses.

a. Explain why the boiling points of Neon and HF differ.
b. Compare the change in the boiling points of Ne, Ar, Kr, and Xe with the change of the boiling points of HF, HCl, HBr, and HI, and explain the difference between the changes with increasing atomic or molecular mass.

5.E.1.16: Q10.1.11

Arrange each of the following sets of compounds in order of increasing boiling point temperature:

a. HCl, H_2O, SiH_4
b. F_2, Cl_2, Br_2
c. CH_4, C_2H_6, C_3H_8
d. O_2, NO, N_2

5.E.1.17: S10.1.11

(a) SiH_4 < HCl < H_2O; (b) F_2 < Cl_2 < Br_2; (c) CH_4 < C_2H_6 < C_3H_8; (d) N_2 < O_2 < NO

5.E.1.18: Q10.1.12

The molecular mass of butanol, C_4H_9OH, is 74.14; that of ethylene glycol, $CH_2(OH)CH_2OH$, is 62.08, yet their boiling points are 117.2 °C and 174 °C, respectively. Explain the reason for the difference.

5.E.1.19: Q10.1.13

On the basis of intermolecular attractions, explain the differences in the boiling points of *n*–butane (−1 °C) and chloroethane (12 °C), which have similar molar masses.

5.E.1.20: S10.1.13

Only rather small dipole-dipole interactions from C-H bonds are available to hold *n*-butane in the liquid state. Chloroethane, however, has rather large dipole interactions because of the Cl-C bond; the interaction is therefore stronger, leading to a higher boiling point.

5.E.1.21: Q10.1.14

On the basis of dipole moments and/or hydrogen bonding, explain in a qualitative way the differences in the boiling points of acetone (56.2 °C) and 1-propanol (97.4 °C), which have similar molar masses.

5.E.1.22: Q10.1.15

The melting point of $H_2O(s)$ is 0 °C. Would you expect the melting point of $H_2S(s)$ to be −85 °C, 0 °C, or 185 °C? Explain your answer.

5.E.1.23: S10.1.15

−85 °C. Water has stronger hydrogen bonds so it melts at a higher temperature.

5.E.1.24: Q10.1.16

Silane (SiH_4), phosphine (PH_3), and hydrogen sulfide (H_2S) melt at −185 °C, −133 °C, and −85 °C, respectively. What does this suggest about the polar character and intermolecular attractions of the three compounds?

5.E.1.25: Q10.1.17

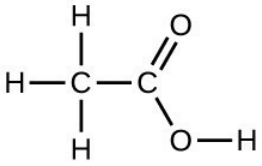
Explain why a hydrogen bond between two water molecules is weaker than a hydrogen bond between two hydrogen fluoride molecules.

5.E.1.26: S10.1.17

The hydrogen bond between two hydrogen fluoride molecules is stronger than that between two water molecules because the electronegativity of F is greater than that of O. Consequently, the partial negative charge on F is greater than that on O. The hydrogen bond between the partially positive H and the larger partially negative F will be stronger than that formed between H and O.

5.E.1.27: Q10.1.18

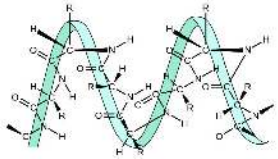
Under certain conditions, molecules of acetic acid, CH_3COOH, form “dimers,” pairs of acetic acid molecules held together by strong intermolecular attractions:



Draw a dimer of acetic acid, showing how two CH_3COOH molecules are held together, and stating the type of IMF that is responsible.

5.E.1.28: Q10.1.19

Proteins are chains of amino acids that can form in a variety of arrangements, one of which is a helix. What kind of IMF is responsible for holding the protein strand in this shape? On the protein image, show the locations of the IMFs that hold the protein together:



5.E.1.29: S10.1.19

H-bonding is the principle IMF holding the DNA strands together. The H-bonding is between the $\mathbf{N-H}$ and $\mathbf{C=O}$.

5.E.1.30: Q10.1.20

The density of liquid NH_3 is 0.64 g/mL; the density of gaseous NH_3 at STP is 0.0007 g/mL. Explain the difference between the densities of these two phases.

5.E.1.31: Q10.1.21

Identify the intermolecular forces present in the following solids:

a. CH_3CH_2OH
b. $CH_3CH_2CH_3$
c. CH_3CH_2Cl

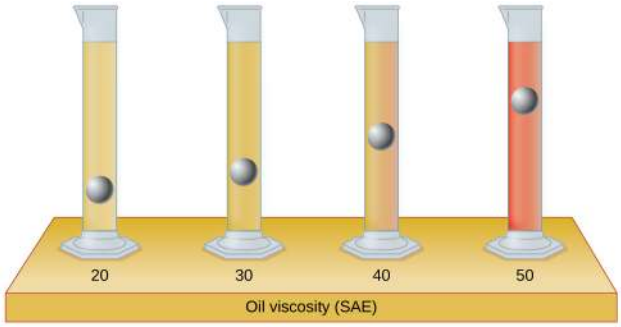
5.E.1.32: S10.1.21

(a) hydrogen bonding and dispersion forces; (b) dispersion forces; (c) dipole-dipole attraction and dispersion forces

5.E.2: 10.2: Properties of Liquids

5.E.2.1: Q10.2.1

The test tubes shown here contain equal amounts of the specified motor oils. Identical metal spheres were dropped at the same time into each of the tubes, and a brief moment later, the spheres had fallen to the heights indicated in the illustration. Rank the motor oils in order of increasing viscosity, and explain your reasoning:



5.E.2.2: Q10.2.2

Although steel is denser than water, a steel needle or paper clip placed carefully lengthwise on the surface of still water can be made to float. Explain at a molecular level how this is possible:



(credit: Cory Zanker)

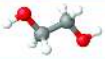
5.E.2.3: S10.2.2

The water molecules have strong intermolecular forces of hydrogen bonding. The water molecules are thus attracted strongly to one another and exhibit a relatively large surface tension, forming a type of “skin” at its surface. This skin can support a bug or

paper clip if gently placed on the water.

5.E.2.4: Q10.2.3

The surface tension and viscosity values for diethyl ether, acetone, ethanol, and ethylene glycol are shown here.

Compound	Molecule	Surface Tension (mN/m)	Viscosity (mPa s)
diethyl ether $C_2H_5OC_2H_5$		17	0.22
acetone $C_2H_5OC_2H_5$		23	0.31
ethanol C_2H_5OH		22	1.07
ethylene glycol $CH_2(OH)CH_2(OH)$		48	16.1

a. Explain their differences in viscosity in terms of the size and shape of their molecules and their IMFs.
b. Explain their differences in surface tension in terms of the size and shape of their molecules and their IMFs:

5.E.2.5: Q10.2.4

You may have heard someone use the figure of speech “slower than molasses in winter” to describe a process that occurs slowly. Explain why this is an apt idiom, using concepts of molecular size and shape, molecular interactions, and the effect of changing temperature.

5.E.2.6: S10.2.4

Temperature has an effect on intermolecular forces: the higher the temperature, the greater the kinetic energies of the molecules and the greater the extent to which their intermolecular forces are overcome, and so the more fluid (less viscous) the liquid; the lower the temperature, the lesser the intermolecular forces are overcome, and so the less viscous the liquid.

5.E.2.7: Q10.2.5

It is often recommended that you let your car engine run idle to warm up before driving, especially on cold winter days. While the benefit of prolonged idling is dubious, it is certainly true that a warm engine is more fuel efficient than a cold one. Explain the reason for this.

5.E.2.8: Q10.2.6

The surface tension and viscosity of water at several different temperatures are given in this table.

Water	Surface Tension (mN/m)	Viscosity (mPa s)
0 °C	75.6	1.79
20 °C	72.8	1.00
60 °C	66.2	0.47
100 °C	58.9	0.28

a. As temperature increases, what happens to the surface tension of water? Explain why this occurs, in terms of molecular interactions and the effect of changing temperature.
b. As temperature increases, what happens to the viscosity of water? Explain why this occurs, in terms of molecular interactions and the effect of changing temperature.

5.E.2.9: S10.2.6

(a) As the water reaches higher temperatures, the increased kinetic energies of its molecules are more effective in overcoming hydrogen bonding, and so its surface tension decreases. Surface tension and intermolecular forces are directly related. (b) The same

trend in viscosity is seen as in surface tension, and for the same reason.

5.E.2.10: Q10.2.7

At 25 °C, how high will water rise in a glass capillary tube with an inner diameter of 0.63 mm? Refer to Example for the required information.

5.E.2.11: Q10.2.8

Water rises in a glass capillary tube to a height of 17 cm. What is the diameter of the capillary tube?

5.E.2.12: S10.2.8

9.5×10^{-5} m

5.E.3: 10.3: Phase Transitions

5.E.3.1: Q10.3.1

Heat is added to boiling water. Explain why the temperature of the boiling water does not change. What does change?

5.E.3.2: Q10.3.2

Heat is added to ice at 0 °C. Explain why the temperature of the ice does not change. What does change?

5.E.3.3: S10.3.2

The heat is absorbed by the ice, providing the energy required to partially overcome intermolecular attractive forces in the solid and causing a phase transition to liquid water. The solution remains at 0 °C until all the ice is melted. Only the amount of water existing as ice changes until the ice disappears. Then the temperature of the water can rise.

5.E.3.4: Q10.3.3

What feature characterizes the dynamic equilibrium between a liquid and its vapor in a closed container?

5.E.3.5: Q10.3.4

Identify two common observations indicating some liquids have sufficient vapor pressures to noticeably evaporate?

5.E.3.6: S10.3.4

We can see the amount of liquid in an open container decrease and we can smell the vapor of some liquids.

5.E.3.7: Q10.3.5

Identify two common observations indicating some solids, such as dry ice and mothballs, have vapor pressures sufficient to sublime?

5.E.3.8: Q10.3.6

What is the relationship between the intermolecular forces in a liquid and its vapor pressure?

5.E.3.9: S10.3.7

The vapor pressure of a liquid decreases as the strength of its intermolecular forces increases.

5.E.3.10: Q10.3.7

What is the relationship between the intermolecular forces in a solid and its melting temperature?

5.E.3.11: Q10.3.8

Why does spilled gasoline evaporate more rapidly on a hot day than on a cold day?

5.E.3.12: S10.3.8

As the temperature increases, the average kinetic energy of the molecules of gasoline increases and so a greater fraction of molecules have sufficient energy to escape from the liquid than at lower temperatures.

5.E.3.13: Q10.3.9

Carbon tetrachloride, CCl_4, was once used as a dry cleaning solvent, but is no longer used because it is carcinogenic. At 57.8 °C, the vapor pressure of CCl_4 is 54.0 kPa, and its enthalpy of vaporization is 33.05 kJ/mol. Use this information to estimate the normal boiling point for CCl_4.

5.E.3.14: Q10.3.10

When is the boiling point of a liquid equal to its normal boiling point?

5.E.3.15: S10.3.10

When the pressure of gas above the liquid is exactly 1 atm

5.E.3.16: Q10.3.11

How does the boiling of a liquid differ from its evaporation?

5.E.3.17: Q10.3.12

Use the information in Figure to estimate the boiling point of water in Denver when the atmospheric pressure is 83.3 kPa.

5.E.3.18: S10.3.12

approximately 95 °C

5.E.3.19: Q10.3.13

A syringe at a temperature of 20 °C is filled with liquid ether in such a way that there is no space for any vapor. If the temperature is kept constant and the plunger is withdrawn to create a volume that can be occupied by vapor, what would be the approximate pressure of the vapor produced?

5.E.3.20: Q10.3.14

Explain the following observations:

a. It takes longer to cook an egg in Ft. Davis, Texas (altitude, 5000 feet above sea level) than it does in Boston (at sea level).
b. Perspiring is a mechanism for cooling the body.

5.E.3.21: S10.3.14

(a) At 5000 feet, the atmospheric pressure is lower than at sea level, and water will therefore boil at a lower temperature. This lower temperature will cause the physical and chemical changes involved in cooking the egg to proceed more slowly, and a longer time is required to fully cook the egg. (b) As long as the air surrounding the body contains less water vapor than the maximum that air can hold at that temperature, perspiration will evaporate, thereby cooling the body by removing the heat of vaporization required to vaporize the water.

5.E.3.22: Q10.3.15

The enthalpy of vaporization of water is larger than its enthalpy of fusion. Explain why.

5.E.3.23: Q10.3.16

Explain why the molar enthalpies of vaporization of the following substances increase in the order $CH_4 < C_2H_6 < C_3H_8$, even though all three substances experience the same dispersion forces when in the liquid state.

5.E.3.24: S10.3.16

Dispersion forces increase with molecular mass or size. As the number of atoms composing the molecules in this homologous series increases, so does the extent of intermolecular attraction via dispersion forces and, consequently, the energy required to overcome these forces and vaporize the liquids.

5.E.3.25: Q10.3.17

Explain why the enthalpies of vaporization of the following substances increase in the order $CH_4 < NH_3 < H_2O$, even though all three substances have approximately the same molar mass.

5.E.3.26: Q10.3.18

The enthalpy of vaporization of $CO_2(l)$ is 9.8 kJ/mol. Would you expect the enthalpy of vaporization of $CS_2(l)$ to be 28 kJ/mol, 9.8 kJ/mol, or −8.4 kJ/mol? Discuss the plausibility of each of these answers.

5.E.3.27: S10.3.18

The boiling point of CS_2 is higher than that of CO_2 partially because of the higher molecular weight of CS_2; consequently, the attractive forces are stronger in CS_2. It would be expected, therefore, that the heat of vaporization would be greater than that of 9.8 kJ/mol for CO_2. A value of 28 kJ/mol would seem reasonable. A value of −8.4 kJ/mol would indicate a release of energy upon vaporization, which is clearly implausible.

5.E.3.28: Q10.3.19

The hydrogen fluoride molecule, HF, is more polar than a water molecule, H_2O (for example, has a greater dipole moment), yet the molar enthalpy of vaporization for liquid hydrogen fluoride is lesser than that for water. Explain.

5.E.3.29: Q10.3.20

Ethyl chloride (boiling point, 13 °C) is used as a local anesthetic. When the liquid is sprayed on the skin, it cools the skin enough to freeze and numb it. Explain the cooling effect of liquid ethyl chloride.

5.E.3.30: S10.3.20

The thermal energy (heat) needed to evaporate the liquid is removed from the skin.

5.E.3.31: Q10.3.21

Which contains the compounds listed correctly in order of increasing boiling points?

a. $N_2 < CS_2 < H_2O < KCl$
b. $H_2O < N_2 < CS_2 < KCl$
c. $N_2 < KCl < CS_2 < H_2O$
d. $CS_2 < N_2 < KCl < H_2O$
e. $KCl < H_2O < CS_2 < N_2$

5.E.3.32: Q10.3.22

How much heat is required to convert 422 g of liquid H_2O at 23.5 °C into steam at 150 °C?

5.E.3.33: S10.3.22

1130 kJ

5.E.3.34: Q10.3.22

Evaporation of sweat requires energy and thus take excess heat away from the body. Some of the water that you drink may eventually be converted into sweat and evaporate. If you drink a 20-ounce bottle of water that had been in the refrigerator at 3.8 °C, how much heat is needed to convert all of that water into sweat and then to vapor?? (Note: Your body temperature is 36.6 °C. For the purpose of solving this problem, assume that the thermal properties of sweat are the same as for water.)

5.E.3.35: Q10.3.24

Titanium tetrachloride, $TiCl_4$, has a melting point of −23.2 °C and has a $\Delta H_{\text{fusion}} = 9.37$ kJ/mol.

a. How much energy is required to melt 263.1 g $TiCl_4$?
b. For $TiCl_4$, which will likely have the larger magnitude: ΔH_{fusion} or $\Delta H_{\text{vaporization}}$? Explain your reasoning.

5.E.3.36: S10.3.24

(a) 13.0 kJ; (b) It is likely that the heat of vaporization will have a larger magnitude since in the case of vaporization the intermolecular interactions have to be completely overcome, while melting weakens or destroys only some of them.

5.E.4: 10.4: Phase Diagrams

5.E.4.1: Q10.4.1

From the phase diagram for water, determine the state of water at:

a. 35 °C and 85 kPa
b. −15 °C and 40 kPa
c. −15 °C and 0.1 kPa
d. 75 °C and 3 kPa
e. 40 °C and 0.1 kPa
f. 60 °C and 50 kPa

5.E.4.2: Q10.4.2

What phase changes will take place when water is subjected to varying pressure at a constant temperature of 0.005 °C? At 40 °C? At −40 °C?

5.E.4.3: S10.4.2

At low pressures and 0.005 °C, the water is a gas. As the pressure increases to 4.6 torr, the water becomes a solid; as the pressure increases still more, it becomes a liquid. At 40 °C, water at low pressure is a vapor; at pressures higher than about 75 torr, it converts into a liquid. At −40 °C, water goes from a gas to a solid as the pressure increases above very low values.

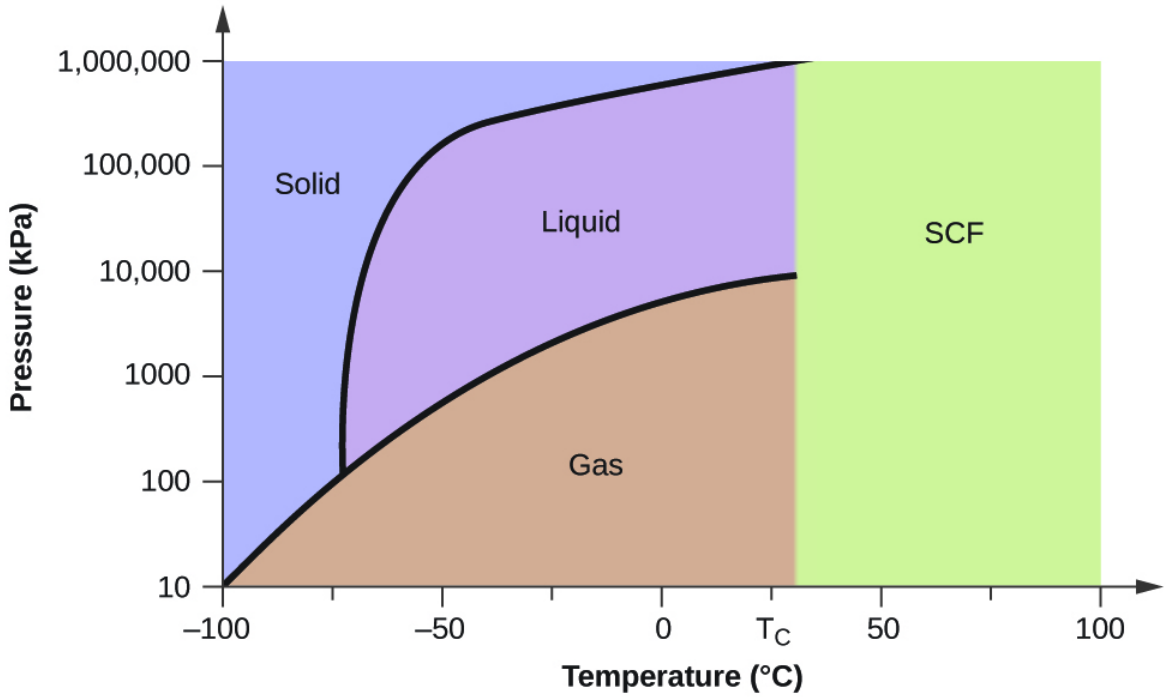
5.E.4.4: Q10.4.3

Pressure cookers allow food to cook faster because the higher pressure inside the pressure cooker increases the boiling temperature of water. A particular pressure cooker has a safety valve that is set to vent steam if the pressure exceeds 3.4 atm. What is the approximate maximum temperature that can be reached inside this pressure cooker? Explain your reasoning.

5.E.4.5: Q10.4.4

From the phase diagram for carbon dioxide, determine the state of CO_2 at:

a. 20 °C and 1000 kPa
b. 10 °C and 2000 kPa
c. 10 °C and 100 kPa
d. −40 °C and 500 kPa
e. −80 °C and 1500 kPa
f. −80 °C and 10 kPa



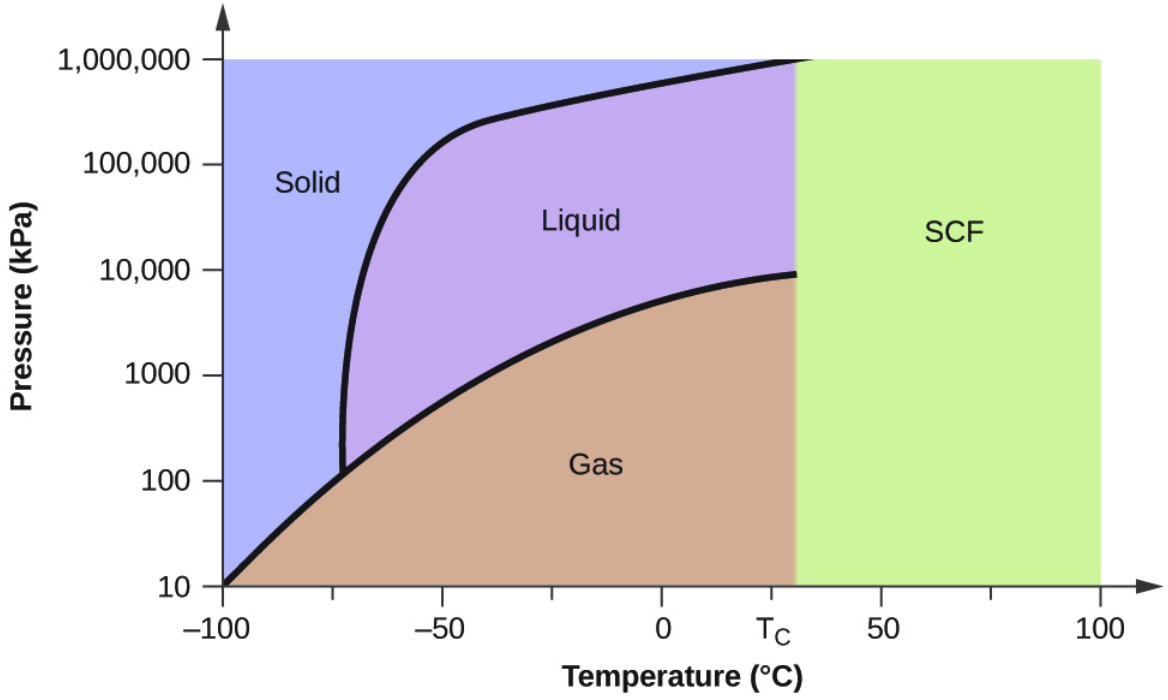
The pressure and temperature axes on this phase diagram of carbon dioxide are not drawn to constant scale in order to illustrate several important properties.

5.E.4.6: S10.4.4

(a) liquid; (b) solid; (c) gas; (d) gas; (e) gas; (f) gas

5.E.4.7: Q10.4.5

Determine the phase changes that carbon dioxide undergoes as the pressure changes if the temperature is held at −50 °C? If the temperature is held at −40 °C? At 20 °C?



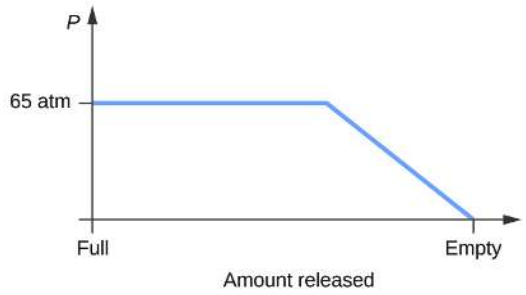
https://chem.libretexts.org/@go/page/436282

The pressure and temperature axes on this phase diagram of carbon dioxide are not drawn to constant scale in order to illustrate several important properties.

5.E.4.8: Q10.4.6

Consider a cylinder containing a mixture of liquid carbon dioxide in equilibrium with gaseous carbon dioxide at an initial pressure of 65 atm and a temperature of 20 °C. Sketch a plot depicting the change in the cylinder pressure with time as gaseous carbon dioxide is released at constant temperature.

5.E.4.9: S10.4.6



5.E.4.10: Q10.4.7

Dry ice, $CO_2(s)$, does not melt at atmospheric pressure. It sublimes at a temperature of −78 °C. What is the lowest pressure at which $CO_2(s)$ will melt to give $CO_2(l)$? At approximately what temperature will this occur? (See Figure for the phase diagram.)

5.E.4.11: S10.4.7

Dry ice, $CO_2(s)$, will melt to give $CO_2(l)$ at 5.11 atm at −56.6 °C, the triple point of carbon dioxide.

5.E.4.12: Q10.4.8

If a severe storm results in the loss of electricity, it may be necessary to use a clothesline to dry laundry. In many parts of the country in the dead of winter, the clothes will quickly freeze when they are hung on the line. If it does not snow, will they dry anyway? Explain your answer.

5.E.4.13: S10.4.8

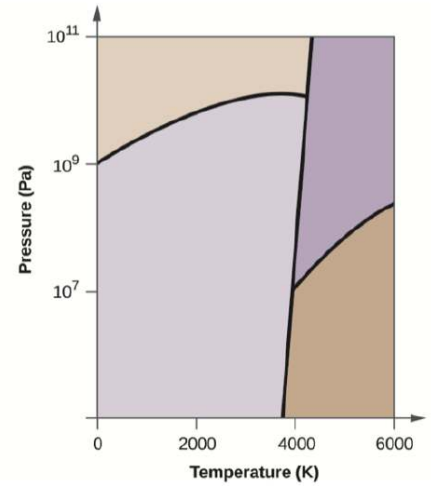
Yes, ice will sublime, although it may take it several days. Ice has a small vapor pressure, and some ice molecules form gas and escape from the ice crystals. As time passes, more and more solid converts to gas until eventually the clothes are dry.

5.E.4.14: Q10.4.9

Is it possible to liquefy nitrogen at room temperature (about 25 °C)? Is it possible to liquefy sulfur dioxide at room temperature? Explain your answers.

5.E.4.15: Q10.4.10

Elemental carbon has one gas phase, one liquid phase, and three different solid phases, as shown in the phase diagram:



a. On the phase diagram, label the gas and liquid regions.
b. Graphite is the most stable phase of carbon at normal conditions. On the phase diagram, label the graphite phase.
c. If graphite at normal conditions is heated to 2500 K while the pressure is increased to 10^{10} Pa, it is converted into diamond. Label the diamond phase.
d. Circle each triple point on the phase diagram.
e. In what phase does carbon exist at 5000 K and 10^{8} Pa?
f. If the temperature of a sample of carbon increases from 3000 K to 5000 K at a constant pressure of 10^{6} Pa, which phase transition occurs, if any?

5.E.5: 10.5: The Solid State of Matter

5.E.5.1: Q10.5.1

What types of liquids typically form amorphous solids?

5.E.5.2: S10.5.1

Amorphous solids lack an ordered internal structure. Liquid materials that contain large, cumbersome molecules that cannot move readily into ordered positions generally form such solids.

5.E.5.3: Q10.5.2

At very low temperatures oxygen, O_2, freezes and forms a crystalline solid. Which best describes these crystals?

a. ionic
b. covalent network
c. metallic
d. amorphous
e. molecular crystals

5.E.5.4: S10.5.3

(e) molecular crystals

5.E.5.5: Q10.5.4

As it cools, olive oil slowly solidifies and forms a solid over a range of temperatures. Which best describes the solid?

a. ionic
b. covalent network
c. metallic
d. amorphous

e. molecular crystals

5.E.5.6: S10.5.4

(d) amorphous

5.E.5.7: Q10.5.5

Explain why ice, which is a crystalline solid, has a melting temperature of 0 °C, whereas butter, which is an amorphous solid, softens over a range of temperatures.

5.E.5.8: S10.5.6

Ice has a crystalline structure stabilized by hydrogen bonding. These intermolecular forces are of comparable strength and thus require the same amount of energy to overcome. As a result, ice melts at a single temperature and not over a range of temperatures. The various, very large molecules that compose butter experience varied van der Waals attractions of various strengths that are overcome at various temperatures, and so the melting process occurs over a wide temperature range.

5.E.5.9: Q10.5.7

Identify the type of crystalline solid (metallic, network covalent, ionic, or molecular) formed by each of the following substances:

a. SiO_2
b. KCl
c. Cu
d. CO_2
e. C (diamond)
f. $BaSO_4$
g. NH_3
h. NH_4F
i. C_2H_5OH

5.E.5.10: S10.5.7

(a) SiO_2, covalent network; (b) KCl, ionic; (c) Cu, metallic; (d) CO, molecular; (e) C (diamond), covalent network; (f) $BaSO_4$, ionic; (g) NH_3, molecular; (h) NH_4F, ionic; (i) C_2H_5OH, molecular

5.E.5.11: Q10.5.8

Identify the type of crystalline solid (metallic, network covalent, ionic, or molecular) formed by each of the following substances:

a. $CaCl_2$
b. SiC
c. N_2
d. Fe
e. C (graphite)
f. $CH_3CH_2CH_2CH_3$
g. HCl
h. NH_4NO_3
i. K_3PO_4

5.E.5.12: S10.5.8

(a) $CaCl_2$, ionic; (b) SiC, covalent network; (c) N_2, molecular; (d) Fe, metallic; (e) C (graphite), covalent network; (f) $CH_3CH_2CH_2CH_3$, molecular; (g) HCl, molecular; (h) NH_4NO_3, ionic; (i) K_3PO_4, ionic

5.E.5.13: Q10.5.9

Classify each substance in the table as either a metallic, ionic, molecular, or covalent network solid:

Substance	Appearance	Melting Point	Electrical Conductivity	Solubility in Water
X	lustrous, malleable	1500 °C	high	insoluble
Y	soft, yellow	113 °C	none	insoluble
Z	hard, white	800 °C	only if melted/dissolved	soluble

5.E.5.14: S10.5.9

X = metallic; Y = covalent network; Z = ionic

5.E.5.15: Q10.5.10

Classify each substance in the table as either a metallic, ionic, molecular, or covalent network solid:

Substance	Appearance	Melting Point	Electrical Conductivity	Solubility in Water
X	brittle, white	800 °C	only if melted/dissolved	soluble
Y	shiny, malleable	1100 °C	high	insoluble
Z	hard, colorless	3550 °C	none	insoluble

5.E.5.16: S10.5.10

X = ionic; Y = metallic; Z = covalent network

5.E.5.17: Q10.5.11

Identify the following substances as ionic, metallic, covalent network, or molecular solids:

Substance A is malleable, ductile, conducts electricity well, and has a melting point of 1135 °C. Substance B is brittle, does not conduct electricity as a solid but does when molten, and has a melting point of 2072 °C. Substance C is very hard, does not conduct electricity, and has a melting point of 3440 °C. Substance D is soft, does not conduct electricity, and has a melting point of 185 °C.

5.E.5.18: S10.5.11

A = metallic; B = ionic; C = covalent network; D = molecular

5.E.5.19: Q10.5.12

Substance A is shiny, conducts electricity well, and melts at 975 °C. Substance A is likely a(n):

a. ionic solid
b. metallic solid
c. molecular solid
d. covalent network solid

5.E.5.20: S10.5.12

(b) metallic solid

5.E.5.21: Q10.5.13

Substance B is hard, does not conduct electricity, and melts at 1200 °C. Substance B is likely a(n):

a. ionic solid
b. metallic solid
c. molecular solid
d. covalent network solid

5.E.5.22: S10.5.13

(d) covalent network solid

5.E.6: 10.6: Lattice Structures

5.E.6.1: Q10.6.1

Describe the crystal structure of iron, which crystallizes with two equivalent metal atoms in a cubic unit cell.

5.E.6.2: S10.6.1

The structure of this low-temperature form of iron (below 910 °C) is body-centered cubic. There is one-eighth atom at each of the eight corners of the cube and one atom in the center of the cube.

5.E.6.3: Q10.6.2

Describe the crystal structure of Pt, which crystallizes with four equivalent metal atoms in a cubic unit cell.

5.E.6.4: Q10.6.3

What is the coordination number of a chromium atom in the body-centered cubic structure of chromium?

5.E.6.5: S10.6.3

eight

5.E.6.6: Q10.6.4

What is the coordination number of an aluminum atom in the face-centered cubic structure of aluminum?

5.E.6.7: Q10.6.5

Cobalt metal crystallizes in a hexagonal closest packed structure. What is the coordination number of a cobalt atom?

5.E.6.8: S10.6.5

12

5.E.6.9: Q10.6.6

Nickel metal crystallizes in a cubic closest packed structure. What is the coordination number of a nickel atom?

5.E.6.10: Q10.6.7

Tungsten crystallizes in a body-centered cubic unit cell with an edge length of 3.165 Å.

a. What is the atomic radius of tungsten in this structure?
b. Calculate the density of tungsten.

5.E.6.11: S10.6.7

(a) 1.370 Å; (b) 19.26 g/cm

5.E.6.12: Q10.6.8

Platinum (atomic radius = 1.38 Å) crystallizes in a cubic closely packed structure. Calculate the edge length of the face-centered cubic unit cell and the density of platinum.

5.E.6.13: Q10.6.9

Barium crystallizes in a body-centered cubic unit cell with an edge length of 5.025 Å

a. What is the atomic radius of barium in this structure?
b. Calculate the density of barium.

5.E.6.14: S10.6.9

(a) 2.176 Å; (b) 3.595 g/cm^3

5.E.6.15: Q10.6.10

Aluminum (atomic radius = 1.43 Å) crystallizes in a cubic closely packed structure. Calculate the edge length of the face-centered cubic unit cell and the density of aluminum.

5.E.6.16: Q10.6.11

The density of aluminum is 2.7 g/cm^3; that of silicon is 2.3 g/cm^3. Explain why Si has the lower density even though it has heavier atoms.

5.E.6.17: S10.6.11

The crystal structure of Si shows that it is less tightly packed (coordination number 4) in the solid than Al (coordination number 12).

5.E.6.18: Q10.6.12

The free space in a metal may be found by subtracting the volume of the atoms in a unit cell from the volume of the cell. Calculate the percentage of free space in each of the three cubic lattices if all atoms in each are of equal size and touch their nearest neighbors. Which of these structures represents the most efficient packing? That is, which packs with the least amount of unused space?

5.E.6.19: Q10.6.13

Cadmium sulfide, sometimes used as a yellow pigment by artists, crystallizes with cadmium, occupying one-half of the tetrahedral holes in a closest packed array of sulfide ions. What is the formula of cadmium sulfide? Explain your answer.

5.E.6.20: S10.6.13

In a closest-packed array, two tetrahedral holes exist for each anion. If only half the tetrahedral holes are occupied, the numbers of anions and cations are equal. The formula for cadmium sulfide is CdS.

5.E.6.21: Q10.6.14

A compound of cadmium, tin, and phosphorus is used in the fabrication of some semiconductors. It crystallizes with cadmium occupying one-fourth of the tetrahedral holes and tin occupying one-fourth of the tetrahedral holes in a closest packed array of phosphide ions. What is the formula of the compound? Explain your answer.

5.E.6.22: Q10.6.15

What is the formula of the magnetic oxide of cobalt, used in recording tapes, that crystallizes with cobalt atoms occupying one-eighth of the tetrahedral holes and one-half of the octahedral holes in a closely packed array of oxide ions?

5.E.6.23: S10.6.15

Co_3O_4

5.E.6.24: Q10.6.16

A compound containing zinc, aluminum, and sulfur crystallizes with a closest-packed array of sulfide ions. Zinc ions are found in one-eighth of the tetrahedral holes and aluminum ions in one-half of the octahedral holes. What is the empirical formula of the compound?

5.E.6.25: Q10.6.17

A compound of thallium and iodine crystallizes in a simple cubic array of iodide ions with thallium ions in all of the cubic holes. What is the formula of this iodide? Explain your answer.

5.E.6.26: S10.6.17

In a simple cubic array, only one cubic hole can be occupied be a cation for each anion in the array. The ratio of thallium to iodide must be 1:1; therefore, the formula for thallium is TlI.

5.E.6.27: Q10.6.18

Which of the following elements reacts with sulfur to form a solid in which the sulfur atoms form a closest-packed array with all of the octahedral holes occupied: Li, Na, Be, Ca, or Al?

5.E.6.28: Q10.6.19

What is the percent by mass of titanium in rutile, a mineral that contains titanium and oxygen, if structure can be described as a closest packed array of oxide ions with titanium ions in one-half of the octahedral holes? What is the oxidation number of titanium?

5.E.6.29: S10.6.19

59.95%; The oxidation number of titanium is +4.

5.E.6.30: Q10.6.20

Explain why the chemically similar alkali metal chlorides NaCl and CsCl have different structures, whereas the chemically different NaCl and MnS have the same structure.

5.E.6.31: Q10.6.21

As minerals were formed from the molten magma, different ions occupied the same cites in the crystals. Lithium often occurs along with magnesium in minerals despite the difference in the charge on their ions. Suggest an explanation.

5.E.6.32: S10.6.21

Both ions are close in size: Mg, 0.65; Li, 0.60. This similarity allows the two to interchange rather easily. The difference in charge is generally compensated by the switch of Si^{4+} for Al^{3+}.

5.E.6.33: Q10.6.22

Rubidium iodide crystallizes with a cubic unit cell that contains iodide ions at the corners and a rubidium ion in the center. What is the formula of the compound?

5.E.6.34: Q10.6.23

One of the various manganese oxides crystallizes with a cubic unit cell that contains manganese ions at the corners and in the center. Oxide ions are located at the center of each edge of the unit cell. What is the formula of the compound?

5.E.6.35: S10.6.23

Mn_2O_3

5.E.6.36: Q10.6.24

NaH crystallizes with the same crystal structure as NaCl. The edge length of the cubic unit cell of NaH is 4.880 Å.

a. Calculate the ionic radius of H^-. (The ionic radius of Li^+ is 0.0.95 Å.)
b. Calculate the density of NaH.

5.E.6.37: Q10.6.25

Thallium(I) iodide crystallizes with the same structure as CsCl. The edge length of the unit cell of TlI is 4.20 Å. Calculate the ionic radius of TI^+. (The ionic radius of I^- is 2.16 Å.)

5.E.6.38: S10.6.25

1.48 Å

5.E.6.39: Q10.6.26

A cubic unit cell contains manganese ions at the corners and fluoride ions at the center of each edge.

a. What is the empirical formula of this compound? Explain your answer.
b. What is the coordination number of the Mn^{3+} ion?
c. Calculate the edge length of the unit cell if the radius of a Mn^{3+} ion is 0.65 A.
d. Calculate the density of the compound.

5.E.6.40: Q10.6.27

What is the spacing between crystal planes that diffract X-rays with a wavelength of 1.541 nm at an angle θ of 15.55° (first order reflection)?

5.E.6.41: S10.6.27

2.874 Å

5.E.6.42: Q10.6.28

A diffractometer using X-rays with a wavelength of 0.2287 nm produced first-order diffraction peak for a crystal angle θ = 16.21°. Determine the spacing between the diffracting planes in this crystal.

5.E.6.43: Q10.6.29

A metal with spacing between planes equal to 0.4164 nm diffracts X-rays with a wavelength of 0.2879 nm. What is the diffraction angle for the first order diffraction peak?

5.E.6.44: S10.6.29

20.2°

5.E.6.45: Q10.6.30

Gold crystallizes in a face-centered cubic unit cell. The second-order reflection (n = 2) of X-rays for the planes that make up the tops and bottoms of the unit cells is at θ = 22.20°. The wavelength of the X-rays is 1.54 Å. What is the density of metallic gold?

5.E.6.46: Q10.6.31

When an electron in an excited molybdenum atom falls from the L to the K shell, an X-ray is emitted. These X-rays are diffracted at an angle of 7.75° by planes with a separation of 2.64 Å. What is the difference in energy between the K shell and the L shell in molybdenum assuming a first-order diffraction?

5.E.6.47: S10.6.31

1.74×10^4 eV

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CHAPTER OVERVIEW

6: Solutions and their Physical Properties

Topic hierarchy

6.1: Types of Solutions- Some Terminology
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6.3: Intermolecular Forces and the Solution Process
6.4: Solution Formation and Equilibrium
6.5: Solubilities of Gases
6.6: Vapor Pressures of Solutions
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6.11.9: Qualitative Cation Analysis

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6.1: Types of Solutions- Some Terminology

Learning Objectives

- To understand how enthalpy and entropy changes affect solution formation.
- To use the magnitude of the changes in both enthalpy and entropy to predict whether a given solute–solvent combination will spontaneously form a solution.

In all solutions, whether gaseous, liquid, or solid, the substance present in the greatest amount is the solvent, and the substance or substances present in lesser amounts are the solute(s). The solute does not have to be in the same physical state as the solvent, but the physical state of the solvent usually determines the state of the solution. As long as the solute and solvent combine to give a homogeneous solution, the solute is said to be soluble in the solvent. Table **6.1.1** lists some common examples of gaseous, liquid, and solid solutions and identifies the physical states of the solute and solvent in each.

Table **6.1.1**: Types of Solutions

Solution	Solute	Solvent	Examples
gas	gas	gas	air, natural gas
liquid	gas	liquid	seltzer water (CO_2 gas in water)
liquid	liquid	liquid	alcoholic beverage (ethanol in water), gasoline
liquid	solid	liquid	tea, salt water
solid	gas	solid	H_2 in Pd (used for H_2 storage)
solid	solid	liquid	mercury in silver or gold (amalgam often used in dentistry)

The formation of a solution from a solute and a solvent is a physical process, not a chemical one. That is, both solute and solvent can be recovered in chemically unchanged forms using appropriate separation methods. For example, solid zinc nitrate dissolves in water to form an aqueous solution of zinc nitrate:

$$Zn(NO_3)_2\,(s) + H_2O\,(l) \rightarrow Zn^{2+}\,(aq) + 2\,NO_3^-\,(aq)$$

Because $Zn(NO_3)_2$ can be recovered easily by evaporating the water, this is a physical process. In contrast, metallic zinc appears to dissolve in aqueous hydrochloric acid. In fact, the two substances undergo a chemical reaction to form an aqueous solution of zinc chloride with evolution of hydrogen gas:

$$Zn\,(s) + 2\,H^+\,(aq) + 2\,Cl^-\,(aq) \rightarrow Zn^{2+}\,(aq) + 2\,Cl^-\,(aq) + H_2\,(g)$$

> *Dissolution of a solute in a solvent to form a solution typically does not involve a chemical transformation and largely consist of breaking intermolecular forces rather than covalent bonds.*

When the solution evaporates, we do not recover metallic zinc, so we cannot say that metallic zinc is soluble in aqueous hydrochloric acid because it is chemically transformed when it dissolves. The dissolution of a solute in a solvent to form a solution does not involve a chemical transformation.

Mercury Amalgams: Examples of solid Solutions

An amalgam is an alloy of mercury with another metal. It may be a liquid, a soft paste or a solid, depending upon the proportion of mercury. These alloys are formed through metallic bonding, with the electrostatic attractive force of the

conduction electrons working to bind all the positively charged metal ions together into a crystal lattice structure. Almost all metals can form amalgams with mercury including aluminum (Video **6.1.1**), the notable exceptions being iron, platinum, tungsten, and tantalum. Silver-mercury amalgams are important in dentistry, and gold-mercury amalgam is used in the extraction of gold from ore.



Video **6.1.1**: Aluminum dissolving into Mercury.

Substances that form a single homogeneous phase in all proportions are said to be completely **miscible** in one another. Ethanol and water are miscible, just as mixtures of gases are miscible. If two substances are essentially insoluble in each other, such as oil and water, they are immiscible. Examples of gaseous solutions that we have already discussed include Earth's atmosphere.

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6.2: Solution Concentration

Learning Objectives

- To describe the concentration of a solution in the way that is most appropriate for a particular problem or application.
- To be familiar with the different units used to express the concentrations of a solution.

There are several different ways to quantitatively describe the concentration of a solution. For example, molarity is a useful way to describe solution concentrations for reactions that are carried out in solution. Mole fractions are used not only to describe gas concentrations but also to determine the vapor pressures of mixtures of similar liquids. Example **6.2.1** reviews the methods for calculating the molarity and mole fraction of a solution when the masses of its components are known.

Example 6.2.1: Molarity and Mole Fraction

Commercial vinegar is essentially a solution of acetic acid in water. A bottle of vinegar has 3.78 g of acetic acid per 100.0 g of solution. Assume that the density of the solution is 1.00 g/mL.

a. What is its molarity?
b. What is its mole fraction?

Given: mass of substance and mass and density of solution

Asked for: molarity and mole fraction

Strategy:

A. Calculate the number of moles of acetic acid in the sample. Then calculate the number of liters of solution from its mass and density. Use these results to determine the molarity of the solution.
B. Determine the mass of the water in the sample and calculate the number of moles of water. Then determine the mole fraction of acetic acid by dividing the number of moles of acetic acid by the total number of moles of substances in the sample.

Solution:

A: The molarity is the number of moles of acetic acid per liter of solution. We can calculate the number of moles of acetic acid as its mass divided by its molar mass.

$$\text{moles } CH_3CO_2H = \frac{3.78 \cancel{\text{ g}}\ CH_3CO_2H}{60.05 \cancel{\text{ g}}/\text{mol}}$$
$$= 0.0629 \text{ mol}$$

The volume of the solution equals its mass divided by its density.

$$\text{volume} = \frac{\text{mass}}{\text{density}}$$
$$= \frac{100.0 \cancel{\text{ g}}\ \text{solution}}{1.00 \cancel{\text{ g}}/\text{mL}} = 100\ mL$$

Then calculate the molarity directly.

$$\text{molarity of } CH_3CO_2H = \frac{\text{moles } CH_3CO_2H}{\text{liter solution}}$$
$$= \frac{0.0629\ mol\ CH_3CO_2H}{(100 \cancel{\text{ mL}})(1\ L/1000 \cancel{\text{ mL}})} = 0.629\ M\ CH_3CO_2H$$

This result makes intuitive sense. If 100.0 g of aqueous solution (equal to 100 mL) contains 3.78 g of acetic acid, then 1 L of solution will contain 37.8 g of acetic acid, which is a little more than $\frac{1}{2}$ mole. Keep in mind, though, that the mass and volume of a solution are related by its density; concentrated aqueous solutions often have densities greater than 1.00 g/mL.

B: To calculate the mole fraction of acetic acid in the solution, we need to know the number of moles of both acetic acid and water. The number of moles of acetic acid is 0.0629 mol, as calculated in part (a). We know that 100.0 g of vinegar contains 3.78 g of acetic acid; hence the solution also contains (100.0 g − 3.78 g) = 96.2 g of water. We have

$$moles\ H_2O = \frac{96.2\ \cancel{g}\ H_2O}{18.02\ \cancel{g}/mol} = 5.34\ mol\ H_2O$$

The mole fraction χ of acetic acid is the ratio of the number of moles of acetic acid to the total number of moles of substances present:

$$\begin{aligned}\chi_{CH_3CO_2H} &= \frac{moles\ CH_3CO_2H}{moles\ CH_3CO_2H + moles\ H_2O} \\ &= \frac{0.0629\ mol}{0.0629\ mol + 5.34\ mol} \\ &= 0.0116 = 1.16 \times 10^{-2}\end{aligned}$$

This answer makes sense, too. There are approximately 100 times as many moles of water as moles of acetic acid, so the ratio should be approximately 0.01.

? Exercise 6.2.1: Molarity and Mole Fraction

A solution of **HCl** gas dissolved in water (sold commercially as “muriatic acid,” a solution used to clean masonry surfaces) has 20.22 g of **HCl** per 100.0 g of solution, and its density is 1.10 g/mL.

a. What is its molarity?
b. What is its mole fraction?

Answer a

6.10 M HCl

Answer b

$\chi_{HCl} = 0.111$

The concentration of a solution can also be described by its molality (m), the number of moles of solute per kilogram of solvent:

$$\text{molality (m)} = \frac{\text{moles solute}}{\text{kilogram solvent}} \tag{6.2.1}$$

Molality, therefore, has the same numerator as molarity (the number of moles of solute) but a different denominator (kilogram of solvent rather than liter of solution). For dilute aqueous solutions, the molality and molarity are nearly the same because dilute solutions are mostly solvent. Thus because the density of water under standard conditions is very close to 1.0 g/mL, the volume of 1.0 kg of H_2O under these conditions is very close to 1.0 L, and a 0.50 M solution of KBr in water, for example, has approximately the same concentration as a 0.50 m solution.

Another common way of describing concentration is as the ratio of the mass of the solute to the total mass of the solution. The result can be expressed as mass percentage, parts per million (ppm), or parts per billion (ppb):

$$\text{mass percentage} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100 \tag{6.2.2}$$

$$\text{parts per million (ppm)} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6 \tag{6.2.3}$$

$$\text{parts per billion (ppb)} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^9 \tag{6.2.4}$$

In the health sciences, the concentration of a solution is often expressed as parts per thousand (ppt), indicated as a proportion. For example, adrenalin, the hormone produced in high-stress situations, is available in a 1:1000 solution, or one gram of adrenalin per 1000 g of solution.

The labels on bottles of commercial reagents often describe the contents in terms of mass percentage. Sulfuric acid, for example, is sold as a 95% aqueous solution, or 95 g of H_2SO_4 per 100 g of solution. Parts per million and parts per billion are used to describe concentrations of highly dilute solutions. These measurements correspond to milligrams and micrograms of solute per kilogram of solution, respectively. For dilute aqueous solutions, this is equal to milligrams and micrograms of solute per liter of solution (assuming a density of 1.0 g/mL).

Example 6.2.2: Molarity and Mass

Several years ago, millions of bottles of mineral water were contaminated with benzene at ppm levels. This incident received a great deal of attention because the lethal concentration of benzene in rats is 3.8 ppm. A 250 mL sample of mineral water has 12.7 ppm of benzene. Because the contaminated mineral water is a very dilute aqueous solution, we can assume that its density is approximately 1.00 g/mL.

a. What is the molarity of the solution?
b. What is the mass of benzene in the sample?

Given: volume of sample, solute concentration, and density of solution

Asked for: molarity of solute and mass of solute in 250 mL

Strategy:

A. Use the concentration of the solute in parts per million to calculate the molarity.
B. Use the concentration of the solute in parts per million to calculate the mass of the solute in the specified volume of solution.

Solution:

a. A To calculate the molarity of benzene, we need to determine the number of moles of benzene in 1 L of solution. We know that the solution contains 12.7 ppm of benzene. Because 12.7 ppm is equivalent to 12.7 mg/1000 g of solution and the density of the solution is 1.00 g/mL, the solution contains 12.7 mg of benzene per liter (1000 mL). The molarity is therefore

$$\begin{aligned}\text{molarity} &= \frac{\text{moles}}{\text{liter solution}} \\ &= \frac{(12.7\ \cancel{mg})\left(\frac{1\ \cancel{g}}{1000\ \cancel{mg}}\right)\left(\frac{1\ mol}{78.114\ \cancel{g}}\right)}{1.00\ L} \\ &= 1.63 \times 10^{-4} M\end{aligned}$$

b. B We are given that there are 12.7 mg of benzene per 1000 g of solution, which is equal to 12.7 mg/L of solution. Hence the mass of benzene in 250 mL (250 g) of solution is

$$\begin{aligned}\text{mass of benzene} &= \frac{(12.7\ mg\ \text{benzene})(250\ \cancel{mL})}{1000\ \cancel{mL}} \\ &= 3.18\ mg \\ &= 3.18 \times 10^{-3}\ g\ \text{benzene}\end{aligned}$$

Exercise 6.2.2: Molarity of Lead Solution

The maximum allowable concentration of lead in drinking water is 9.0 ppb.

a. What is the molarity of Pb^{2+} in a 9.0 ppb aqueous solution?
b. Use your calculated concentration to determine how many grams of Pb^{2+} are in an 8 oz glass of water.

Answer a

4.3×10^{-8} M

Answer b

2×10^{-6} g

How do chemists decide which units of concentration to use for a particular application? Although molarity is commonly used to express concentrations for reactions in solution or for titrations, it does have one drawback—molarity is the number of moles of solute divided by the volume of the solution, and the volume of a solution depends on its density, which is a function of temperature. Because volumetric glassware is calibrated at a particular temperature, typically 20°C, the molarity may differ from the original value by several percent if a solution is prepared or used at a significantly different temperature, such as 40°C or 0°C. For many applications this may not be a problem, but for precise work these errors can become important. In contrast, mole fraction, molality, and mass percentage depend on only the masses of the solute and solvent, which are independent of temperature.

Mole fraction is not very useful for experiments that involve quantitative reactions, but it is convenient for calculating the partial pressure of gases in mixtures, as discussed previously. Mole fractions are also useful for calculating the vapor pressures of certain types of solutions. Molality is particularly useful for determining how properties such as the freezing or boiling point of a solution vary with solute concentration. Because mass percentage and parts per million or billion are simply different ways of expressing the ratio of the mass of a solute to the mass of the solution, they enable us to express the concentration of a substance even when the molecular mass of the substance is unknown. Units of ppb or ppm are also used to express very low concentrations, such as those of residual impurities in foods or of pollutants in environmental studies.

Table **6.2.1** summarizes the different units of concentration and typical applications for each. When the molar mass of the solute and the density of the solution are known, it becomes relatively easy with practice to convert among the units of concentration we have discussed, as illustrated in Example **6.2.3**.

Table **6.2.1**: Different Units for Expressing the Concentrations of Solutions*

Unit	Definition	Application
molarity (M)	moles of solute/liter of solution (mol/L)	Used for quantitative reactions in solution and titrations; mass and molecular mass of solute and volume of solution are known.
mole fraction (χ)	moles of solute/total moles present (mol/mol)	Used for partial pressures of gases and vapor pressures of some solutions; mass and molecular mass of each component are known.
molality (m)	moles of solute/kg of solvent (mol/kg)	Used in determining how colligative properties vary with solute concentration; masses and molecular mass of solute are known.
mass percentage (%)	[mass of solute (g)/mass of solution (g)] × 100	Useful when masses are known but molecular masses are unknown.
parts per thousand (ppt)	[mass of solute/mass of solution] × 10^3 (g solute/kg solution)	Used in the health sciences, ratio solutions are typically expressed as a proportion, such as 1:1000.
parts per million (ppm)	[mass of solute/mass of solution] × 10^6 (mg solute/kg solution)	Used for trace quantities; masses are known but molecular masses may be unknown.
parts per billion (ppb)	[mass of solute/mass of solution] × 10^9 (µg solute/kg solution)	Used for trace quantities; masses are known but molecular masses may be unknown.

*The molarity of a solution is temperature dependent, but the other units shown in this table are independent of temperature.

Example 6.2.3: Vodka

Vodka is essentially a solution of ethanol in water. Typical vodka is sold as "80 proof," which means that it contains 40.0% ethanol by volume. The density of pure ethanol is 0.789 g/mL at 20°C. If we assume that the volume of the solution is the sum of the volumes of the components (which is not strictly correct), calculate the following for the ethanol in 80-proof vodka.

a. the mass percentage
b. the mole fraction
c. the molarity
d. the molality

Given: volume percent and density

Asked for: mass percentage, mole fraction, molarity, and molality

Strategy:

A. Use the density of the solute to calculate the mass of the solute in 100.0 mL of solution. Calculate the mass of water in 100.0 mL of solution.
B. Determine the mass percentage of solute by dividing the mass of ethanol by the mass of the solution and multiplying by 100.
C. Convert grams of solute and solvent to moles of solute and solvent. Calculate the mole fraction of solute by dividing the moles of solute by the total number of moles of substances present in solution.
D. Calculate the molarity of the solution: moles of solute per liter of solution. Determine the molality of the solution by dividing the number of moles of solute by the kilograms of solvent.

Solution:

The key to this problem is to use the density of pure ethanol to determine the mass of ethanol (CH_3CH_2OH), abbreviated as EtOH, in a given volume of solution. We can then calculate the number of moles of ethanol and the concentration of ethanol in any of the required units. A Because we are given a percentage by volume, we assume that we have 100.0 mL of solution. The volume of ethanol will thus be 40.0% of 100.0 mL, or 40.0 mL of ethanol, and the volume of water will be 60.0% of 100.0 mL, or 60.0 mL of water. The mass of ethanol is obtained from its density:

$$mass\ of\ EtOH = (40.0\ \cancel{mL}) \left(\frac{0.789\ g}{\cancel{mL}} \right) = 31.6\ g\ EtOH$$

If we assume the density of water is 1.00 g/mL, the mass of water is 60.0 g. We now have all the information we need to calculate the concentration of ethanol in the solution.

B The mass percentage of ethanol is the ratio of the mass of ethanol to the total mass of the solution, expressed as a percentage:

$$\begin{aligned} \%EtOH &= \left(\frac{mass\ of\ EtOH}{mass\ of\ solution} \right) (100) \\ &= \left(\frac{31.6\ \cancel{g}\ EtOH}{31.6\ \cancel{g}\ EtOH + 60.0\ \cancel{g}\ H_2O} \right) (100) \\ &= 34.5\% \end{aligned}$$

C The mole fraction of ethanol is the ratio of the number of moles of ethanol to the total number of moles of substances in the solution. Because 40.0 mL of ethanol has a mass of 31.6 g, we can use the molar mass of ethanol (46.07 g/mol) to determine the number of moles of ethanol in 40.0 mL:

$$\begin{aligned} moles\ CH_3CH_2OH &= (31.6\ \cancel{g\ CH_3CH_2OH}) \left(\frac{1\ mol}{46.07\ \cancel{g\ CH_3CH_2OH}} \right) \\ &= 0.686\ mol\ CH_3CH_2OH \end{aligned}$$

Similarly, the number of moles of water is

$$moles\ H_2O = (60.0\ \cancel{g\ H_2O})\left(\frac{1\ mol\ H_2O}{18.02\ \cancel{g\ H_2O}}\right) = 3.33\ mol\ H_2O$$

The mole fraction of ethanol is thus

$$\chi_{CH_3CH_2OH} = \frac{0.686\ \cancel{mol}}{0.686\ \cancel{mol} + 3.33\ \cancel{mol}} = 0.171$$

D The molarity of the solution is the number of moles of ethanol per liter of solution. We already know the number of moles of ethanol per 100.0 mL of solution, so the molarity is

$$M_{CH_3CH_2OH} = \left(\frac{0.686\ mol}{100\ \cancel{mL}}\right)\left(\frac{1000\ \cancel{mL}}{L}\right) = 6.86\ M$$

The molality of the solution is the number of moles of ethanol per kilogram of solvent. Because we know the number of moles of ethanol in 60.0 g of water, the calculation is again straightforward:

$$m_{CH_3CH_2OH} = \left(\frac{0.686\ mol\ EtOH}{60.0\ \cancel{g}\ H_2O}\right)\left(\frac{1000\ \cancel{g}}{kg}\right) = \frac{11.4\ mol\ EtOH}{kg\ H_2O} = 11.4\ m$$

? Exercise 6.2.3: Toluene/Benzene Solution

A solution is prepared by mixing 100.0 mL of toluene with 300.0 mL of benzene. The densities of toluene and benzene are 0.867 g/mL and 0.874 g/mL, respectively. Assume that the volume of the solution is the sum of the volumes of the components. Calculate the following for toluene.

a. mass percentage
b. mole fraction
c. molarity
d. molality

Answer a

mass percentage toluene = 24.8%

Answer b

$\chi_{toluene} = 0.219$

Answer c

2.35 M toluene

Answer d

3.59 m toluene



A Video Discussing Different Measures of Concentration. Video Link: Measures of Concentration, YouTube (opens in new window) [youtu.be]



A Video Discussing how to Convert Measures of Concentration. Video Link: Converting Units of Concentration, YouTube(opens in new window) [youtu.be]

Summary

Different units are used to express the concentrations of a solution depending on the application. The concentration of a solution is the quantity of solute in a given quantity of solution. It can be expressed in several ways: molarity (moles of solute per liter of solution); mole fraction, the ratio of the number of moles of solute to the total number of moles of substances present; mass percentage, the ratio of the mass of the solute to the mass of the solution times 100; parts per thousand (ppt), grams of solute per kilogram of solution; parts per million (ppm), milligrams of solute per kilogram of solution; parts per billion (ppb), micrograms of solute per kilogram of solution; and molality (m), the number of moles of solute per kilogram of solvent.

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6.3: Intermolecular Forces and the Solution Process

Learning Objectives

- To understand the relationship between solubility and molecular structure.
- To demonstrate how the strength of intramolecular bonding determines the solubility of a solute in a given solvent.

The interactions that determine the solubility of a substance in a liquid depend largely on the chemical nature of the solute (such as whether it is ionic or molecular) rather than on its physical state (solid, liquid, or gas). We will first describe the general case of forming a solution of a molecular species in a liquid solvent and then describe the formation of a solution of an ionic compound.

The Role of Enthalpy in Solution Formation

Energy is required to overcome the intermolecular interactions in a solute, which can be supplied only by the new interactions that occur in the solution, when each solute particle is surrounded by particles of the solvent in a process called **solvation**, or hydration when the solvent is water. Thus all of the solute–solute interactions and many of the solvent–solvent interactions must be disrupted for a solution to form. In this section, we describe the role of enthalpy in this process.

Because enthalpy is a state function, we can use a thermochemical cycle to analyze the energetics of solution formation. The process occurs in three discrete steps, indicated by ΔH1, ΔH_2 , and ΔH_3. in Figure 1 The overall enthalpy change in the formation of the solution $\Delta H_{solution}$ is the sum of the enthalpy changes in the three steps:

$\Delta H_{solution} = \Delta H1 + \Delta H_2 + \Delta H_3$. (Figure 1)

When a solvent is added to a solution, steps 1 and 2 are both endothermic because energy is required to overcome the intermolecular interactions in the solvent ΔH1 and the solute ΔH_2. Because ΔH is positive for both steps 1 and 2, the solute–solvent interactions ΔH_3. must be stronger than the solute–solute and solvent–solvent interactions they replace in order for the dissolution process to be exothermic $\Delta H_{solution} < 0$, When the solute is an ionic solid, ΔH_2 corresponds to the lattice energy that must be overcome to form a solution. The higher the charge of the ions in an ionic solid, the higher the lattice energy. Consequently, solids that have very high lattice energies, such as Lattice Energy for MgO (3791 kJ/mol), are generally insoluble in all solvents.

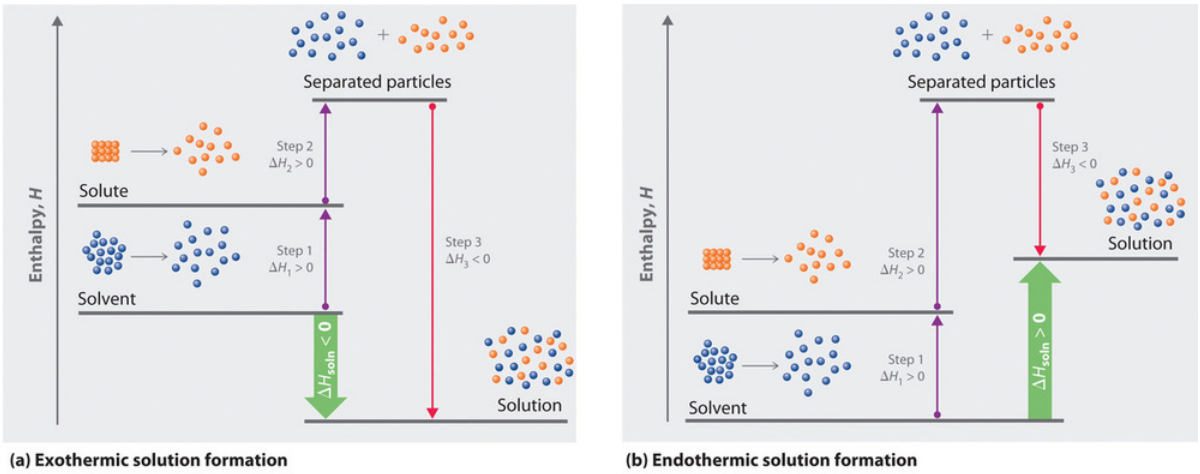


Figure 1. Enthalpy Changes That Accompany the Formation of a Solution. Solvation can be an exothermic or endothermic process depending on the nature of the solute and solvent. In both cases, step 1, separation of the solvent particles, is energetically uphill ($\Delta H_1 > 0$), as is step 2, separation of the solute particles ($\Delta H_2 > 0$). In contrast, energy is released in step 3 ΔH_3. < 0 because of interactions between the solute and solvent. (a) When ΔH_3. is larger in magnitude than the sum of ΔH1 and ΔH_2, the overall process is exothermic $\Delta H_{solution} < 0$, as shown in the thermochemical cycle. (b) When ΔH_3. is smaller in magnitude than the sum of ΔH1 and ΔH_2,, the overall process is endothermic $\Delta H_{solution} > 0$).

A positive value for $\Delta H_{solution}$ does not mean that a solution will not form. Whether a given process, including formation of a solution, occurs spontaneously depends on whether the total energy of the system is lowered as a result. Enthalpy is only one of the contributing factors. A high $\Delta H_{solution}$ is usually an indication that the substance is not very soluble. Instant cold packs used to treat

athletic injuries, for example, take advantage of the large positive $\Delta H_{solution}$ of ammonium nitrate during dissolution (+25.7 kJ/mol), which produces temperatures less than 0°C (Figure 2.)



Figure 2Commercial Cold Packs for Treating Injuries. These packs contain solid ammonium nitrate and water in separate compartments. When the seal between the compartments is broken, the ammonium nitrate dissolves in the water. Because $\Delta H_{solution}$ for ammonium nitrateis much greater than zero, heat is absorbed by the cold pack during the dissolution process, producing local temperatures less than 0°C.

Solutions of Molecular Substances in Liquids

The London dispersion forces, dipole–dipole interactions, and hydrogen bonds that hold molecules to other molecules are generally weak. Even so, energy is required to disrupt these interactions. Unless some of that energy is recovered in the formation of new, favorable solute–solvent interactions, the increase in entropy on solution formation is not enough for a solution to form.

For solutions of gases in liquids, we can safely ignore the energy required to separate the solute molecules ($\Delta H_2 = 0$) because the molecules are already separated. Thus we need to consider only the energy required to separate the solvent molecules (ΔH_1) and the energy released by new solute–solvent interactions (ΔH_3). Nonpolar gases such as N_2, O_2, and Ar have no dipole moment and cannot engage in dipole–dipole interactions or hydrogen bonding. Consequently, the only way they can interact with a solvent is by means of London dispersion forces, which may be weaker than the solvent–solvent interactions in a polar solvent. It is not surprising, then, that nonpolar gases are most soluble in nonpolar solvents. In this case, ΔH_1 and ΔH_3 are both small and of similar magnitude. In contrast, for a solution of a nonpolar gas in a polar solvent, ΔH_1 is far greater than ΔH_3. As a result, nonpolar gases are less soluble in polar solvents than in nonpolar solvents. For example, the concentration of N_2 in a saturated solution of N_2 in water, a polar solvent, is only $7.07 \times 10^{-4}\ M$ compared with $4.5 \times 10^{-3}\ M$ for a saturated solution of N_2 in benzene, a nonpolar solvent.

The solubilities of nonpolar gases in water generally increase as the molecular mass of the gas increases, as shown in Table **6.3.1**. This is precisely the trend expected: as the gas molecules become larger, the strength of the solvent–solute interactions due to London dispersion forces increases, approaching the strength of the solvent–solvent interactions.

Table **6.3.1**: Solubilities of Selected Gases in Water at 20°C and 1 atm Pressure

Gas	Solubility (M) × 10^{-4}
He	3.90
Ne	4.65
Ar	15.2
Kr	27.9
Xe	50.2
H_2	8.06
N_2	7.07
CO	10.6
O_2	13.9
N_2O	281
CH_4	15.5

Virtually all common organic liquids, whether polar or not, are miscible. The strengths of the intermolecular attractions are comparable; thus the enthalpy of solution is expected to be small ($\Delta H_{soln} \approx 0$), and the increase in entropy drives the formation of a solution. If the predominant intermolecular interactions in two liquids are very different from one another, however, they may be immiscible. For example, organic liquids such as benzene, hexane, CCl_4, and CS_2 (S=C=S) are nonpolar and have no ability to act as hydrogen bond donors or acceptors with hydrogen-bonding solvents such as H_2O, HF, and NH_3; hence they are immiscible in these solvents. When shaken with water, they form separate phases or layers separated by an interface (Figure **6.3.3**), the region between the two layers. Just because two liquids are immiscible, however, does not mean that they are completely insoluble in each other. For example, 188 mg of benzene dissolves in 100 mL of water at 23.5°C. Adding more benzene results in the separation of an upper layer consisting of benzene with a small amount of dissolved water (the solubility of water in benzene is only 178 mg/100 mL of benzene).



Figure **6.3.3**: Immiscible Liquids. Separatory funnel demonstrating the separation of oil and colored water. from Wikipedia

The solubilities of simple alcohols in water are given in Table **6.3.2**.

Table **6.3.2**: Solubilities of Straight-Chain Organic Alcohols in Water at 20°C

Alcohol	Solubility (mol/100 g of H_2O)
methanol	completely miscible
ethanol	completely miscible
n-propanol	completely miscible
n-butanol	0.11
n-pentanol	0.030
n-hexanol	0.0058
n-heptanol	0.0008

Only the three lightest alcohols (methanol, ethanol, and n-propanol) are completely miscible with water. As the molecular mass of the alcohol increases, so does the proportion of hydrocarbon in the molecule. Correspondingly, the importance of hydrogen bonding and dipole–dipole interactions in the pure alcohol decreases, while the importance of London dispersion forces increases, which leads to progressively fewer favorable electrostatic interactions with water. Organic liquids such as acetone, ethanol, and tetrahydrofuran are sufficiently polar to be completely miscible with water yet sufficiently nonpolar to be completely miscible with all organic solvents.



Tetrahydrofuran (THF)

The same principles govern the solubilities of molecular solids in liquids. For example, elemental sulfur is a solid consisting of cyclic S_8 molecules that have no dipole moment. Because the S_8 rings in solid sulfur are held to other rings by London dispersion forces, elemental sulfur is insoluble in water. It is, however, soluble in nonpolar solvents that have comparable London dispersion forces, such as CS_2 (23 g/100 mL). In contrast, glucose contains five –OH groups that can form hydrogen bonds. Consequently, glucose is very soluble in water (91 g/120 mL of water) but essentially insoluble in nonpolar solvents such as benzene. The structure of one isomer of glucose is shown here.



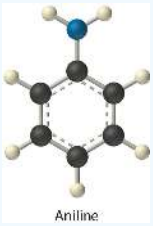
D-Glucose

Low-molecular-mass hydrocarbons with highly electronegative and polarizable halogen atoms, such as chloroform ($CHCl_3$) and methylene chloride (CH_2Cl_2), have both significant dipole moments and relatively strong London dispersion forces. These hydrocarbons are therefore powerful solvents for a wide range of polar and nonpolar compounds. Naphthalene, which is nonpolar, and phenol (C_6H_5OH), which is polar, are very soluble in chloroform. In contrast, the solubility of ionic compounds is largely determined not by the polarity of the solvent but rather by its dielectric constant, a measure of its ability to separate ions in solution, as you will soon see.

Example 6.3.1

Identify the most important solute–solvent interactions in each solution.

a. iodine in benzene
b. aniline ($C_6H_5NH_2$) in dichloromethane (CH_2Cl_2)



c. iodine in water

Given: components of solutions

Asked for: predominant solute–solvent interactions

Strategy:

Identify all possible intermolecular interactions for both the solute and the solvent: London dispersion forces, dipole–dipole interactions, or hydrogen bonding. Determine which is likely to be the most important factor in solution formation.

Solution

a. Benzene and $I2$ are both nonpolar molecules. The only possible attractive forces are London dispersion forces.
b. Aniline is a polar molecule with an $-NH_2$ group, which can act as a hydrogen bond donor. Dichloromethane is also polar, but it has no obvious hydrogen bond acceptor. Therefore, the most important interactions between aniline and CH_2Cl_2 are likely to be London interactions.
c. Water is a highly polar molecule that engages in extensive hydrogen bonding, whereas I_2 is a nonpolar molecule that cannot act as a hydrogen bond donor or acceptor. The slight solubility of I_2 in water ($1.3 \times 10^{-3}\ mol/L$ at 25°C) is due to London dispersion forces.

Exercise 6.3.1

Identify the most important interactions in each solution:

a. ethylene glycol ($HOCH_2CH_2OH$) in acetone
b. acetonitrile ($CH_3C{\equiv}N$) in acetone
c. n-hexane in benzene

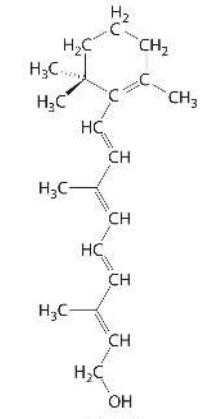
Answer:

a. hydrogen bonding
b. London interactions
c. London dispersion forces

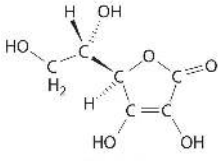
Hydrophilic and Hydrophobic Solutes

A solute can be classified as hydrophilic (literally, “water loving”), meaning that it has an electrostatic attraction to water, or hydrophobic (“water fearing”), meaning that it repels water. A hydrophilic substance is polar and often contains O–H or N–H groups that can form hydrogen bonds to water. For example, glucose with its five O–H groups is hydrophilic. In contrast, a hydrophobic substance may be polar but usually contains C–H bonds that do not interact favorably with water, as is the case with naphthalene and n-octane. Hydrophilic substances tend to be very soluble in water and other strongly polar solvents, whereas hydrophobic substances are essentially insoluble in water and soluble in nonpolar solvents such as benzene and cyclohexane.

The difference between hydrophilic and hydrophobic substances has substantial consequences in biological systems. For example, vitamins can be classified as either fat soluble or water soluble. Fat-soluble vitamins, such as vitamin A, are mostly nonpolar, hydrophobic molecules. As a result, they tend to be absorbed into fatty tissues and stored there. In contrast, water-soluble vitamins, such as vitamin C, are polar, hydrophilic molecules that circulate in the blood and intracellular fluids, which are primarily aqueous. Water-soluble vitamins are therefore excreted much more rapidly from the body and must be replenished in our daily diet. A comparison of the chemical structures of vitamin A and vitamin C quickly reveals why one is hydrophobic and the other hydrophilic.



Vitamin A
(*trans*-Retinol)

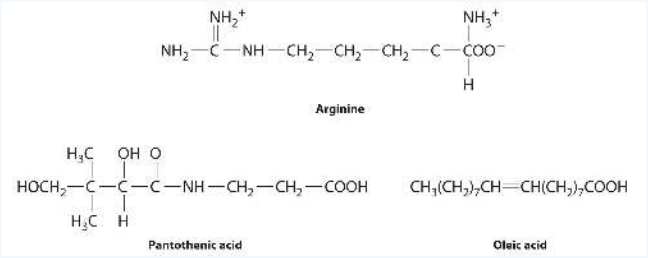


Vitamin C
(L-Ascorbic acid)

Because water-soluble vitamins are rapidly excreted, the risk of consuming them in excess is relatively small. Eating a dozen oranges a day is likely to make you tired of oranges long before you suffer any ill effects due to their high vitamin C content. In contrast, fat-soluble vitamins constitute a significant health hazard when consumed in large amounts. For example, the livers of polar bears and other large animals that live in cold climates contain large amounts of vitamin A, which have occasionally proven fatal to humans who have eaten them.

Example 6.3.2

The following substances are essential components of the human diet:



Arginine

Pantothenic acid

Oleic acid

Using what you know of hydrophilic and hydrophobic solutes, classify each as water soluble or fat soluble and predict which are likely to be required in the diet on a daily basis.

a. arginine
b. pantothenic acid
c. oleic acid

Given: chemical structures

Asked for: classification as water soluble or fat soluble; dietary requirement

Strategy:

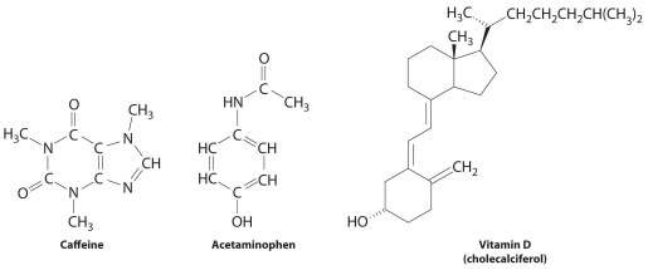
Based on the structure of each compound, decide whether it is hydrophilic or hydrophobic. If it is hydrophilic, it is likely to be required on a daily basis.

Solution:

a. Arginine is a highly polar molecule with two positively charged groups and one negatively charged group, all of which can form hydrogen bonds with water. As a result, it is hydrophilic and required in our daily diet.
b. Although pantothenic acid contains a hydrophobic hydrocarbon portion, it also contains several polar functional groups ($-OH$ and $-CO_2H$) that should interact strongly with water. It is therefore likely to be water soluble and required in the diet. (In fact, pantothenic acid is almost always a component of multiple-vitamin tablets.)
c. Oleic acid is a hydrophobic molecule with a single polar group at one end. It should be fat soluble and not required daily.

Exercise 6.3.2

These compounds are consumed by humans: caffeine, acetaminophen, and vitamin D. Identify each as primarily hydrophilic (water soluble) or hydrophobic (fat soluble), and predict whether each is likely to be excreted from the body rapidly or slowly.



Answer: Caffeine and acetaminophen are water soluble and rapidly excreted, whereas vitamin D is fat soluble and slowly excreted

Solid Solutions

Solutions are not limited to gases and liquids; solid solutions also exist. For example, amalgams, which are usually solids, are solutions of metals in liquid mercury. Because most metals are soluble in mercury, amalgams are used in gold mining, dentistry, and many other applications. A major difficulty when mining gold is separating very small particles of pure gold from tons of crushed rock. One way to accomplish this is to agitate a suspension of the crushed rock with liquid mercury, which dissolves the gold (as well as any metallic silver that might be present). The very dense liquid gold–mercury amalgam is then isolated and the mercury distilled away.

An alloy is a solid or liquid solution that consists of one or more elements in a metallic matrix. A solid alloy has a single homogeneous phase in which the crystal structure of the solvent remains unchanged by the presence of the solute. Thus the microstructure of the alloy is uniform throughout the sample. Examples are substitutional and interstitial alloys such as brass or solder. Liquid alloys include sodium/potassium and gold/mercury. In contrast, a partial alloy solution has two or more phases that can be homogeneous in the distribution of the components, but the microstructures of the two phases are not the same. As a liquid solution of lead and tin is cooled, for example, different crystalline phases form at different cooling temperatures. Alloys usually have properties that differ from those of the component elements.

Network solids such as diamond, graphite, and $ceSiO_2$ are insoluble in all solvents with which they do not react chemically. The covalent bonds that hold the network or lattice together are simply too strong to be broken under normal conditions. They are certainly much stronger than any conceivable combination of intermolecular interactions that might occur in solution. Most metals are insoluble in virtually all solvents for the same reason: the delocalized metallic bonding is much stronger than any favorable metal atom–solvent interactions. Many metals react with solutions such as aqueous acids or bases to produce a solution. However, in these instances the metal undergoes a chemical transformation that cannot be reversed by simply removing the solvent.

Solids with very strong intermolecular bonding tend to be insoluble.

Solubilities of Ionic Substances in Liquids

Ionic substances are generally most soluble in polar solvents; the higher the lattice energy, the more polar the solvent must be to overcome the lattice energy and dissolve the substance. Because of its high polarity, water is the most common solvent for ionic compounds. Many ionic compounds are soluble in other polar solvents, however, such as liquid ammonia, liquid hydrogen fluoride, and methanol. Because all these solvents consist of molecules that have relatively large dipole moments, they can interact favorably with the dissolved ions.

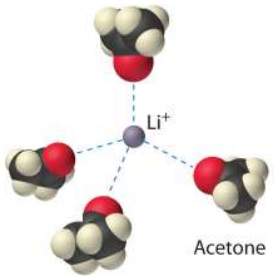


Figure **6.3.4**: Ion–Dipole Interactions in the Solvation of Li+ Ions by Acetone, a Polar Solvent

The interaction of water with Na+ and Cl− ions in an aqueous solution of **NaCl** was illustrated in Figure 4.3. The ion–dipole interactions between Li+ ions and acetone molecules in a solution of LiCl in acetone are shown in Figure **6.3.4**. The energetically favorable Li+–acetone interactions make ΔH_3 in Figure 13.1 sufficiently negative to overcome the positive ΔH_1 and ΔH_2. Because the dipole moment of acetone (2.88 D), and thus its polarity, is actually larger than that of water (1.85 D), one might even expect that LiCl would be more soluble in acetone than in water. In fact, the opposite is true: 83 g of LiCl dissolve in 100 mL of water at 20°C, but only about 4.1 g of LiCl dissolve in 100 mL of acetone. This apparent contradiction arises from the fact that the dipole moment is a property of a single molecule in the gas phase. A more useful measure of the ability of a solvent to dissolve ionic compounds is its dielectric constant (ε), which is the ability of a bulk substance to decrease the electrostatic forces between two charged particles. By definition, the dielectric constant of a vacuum is 1. In essence, a solvent with a high dielectric constant causes the charged particles to behave as if they have been moved farther apart. At 25°C, the dielectric constant of water is 80.1, one of the highest known, and that of acetone is only 21.0. Hence water is better able to decrease the electrostatic attraction between Li+ and Cl− ions, so LiCl is more soluble in water than in acetone. This behavior is in contrast to that of molecular substances, for which polarity is the dominant factor governing solubility.

A solvent's dielectric constant is the most useful measure of its ability to dissolve ionic compounds. A solvent's polarity is the dominant factor in dissolving molecular substances.

Summary

The solubility of a substance is the maximum amount of a solute that can dissolve in a given quantity of solvent; it depends on the chemical nature of both the solute and the solvent and on the temperature and pressure. The solubility of a substance in a liquid is determined by intermolecular interactions, which also determine whether two liquids are miscible. Solutes can be classified as hydrophilic (water loving) or hydrophobic (water fearing). Vitamins with hydrophilic structures are water soluble, whereas those with hydrophobic structures are fat soluble. Many metals dissolve in liquid mercury to form amalgams. Covalent network solids and most metals are insoluble in nearly all solvents. The solubility of ionic compounds is largely determined by the dielectric constant (ε) of the solvent, a measure of its ability to decrease the electrostatic forces between charged particles. Solutions of many ionic compounds in organic solvents can be dissolved using crown ethers, cyclic polyethers large enough to accommodate a metal ion in the center, or cryptands, compounds that completely surround a cation.

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6.4: Solution Formation and Equilibrium

Learning Objectives

- To understand the relationship among temperature, pressure, and solubility.
- The understand that the solubility of a solid may increase or decrease with increasing temperature,

When a solute dissolves, its individual atoms, molecules, or ions interact with the solvent, become solvated, and are able to diffuse independently throughout the solution (part (a) in Figure **6.4.1**). This is not, however, a unidirectional process. If the molecule or ion happens to collide with the surface of a particle of the undissolved solute, it may adhere to the particle in a process called crystallization. Dissolution and crystallization continue as long as excess solid is present, resulting in a dynamic equilibrium analogous to the equilibrium that maintains the vapor pressure of a liquid. We can represent these opposing processes as follows:

$$\text{solute} + \text{solvent} \underset{\text{dissolution}}{\overset{\text{crystallization}}{\rightleftharpoons}} \text{solution} \tag{6.4.1}$$

Although the terms precipitation and crystallization are both used to describe the separation of solid solute from a solution, crystallization refers to the formation of a solid with a well-defined crystalline structure, whereas precipitation refers to the formation of any solid phase, often one with very small particles.

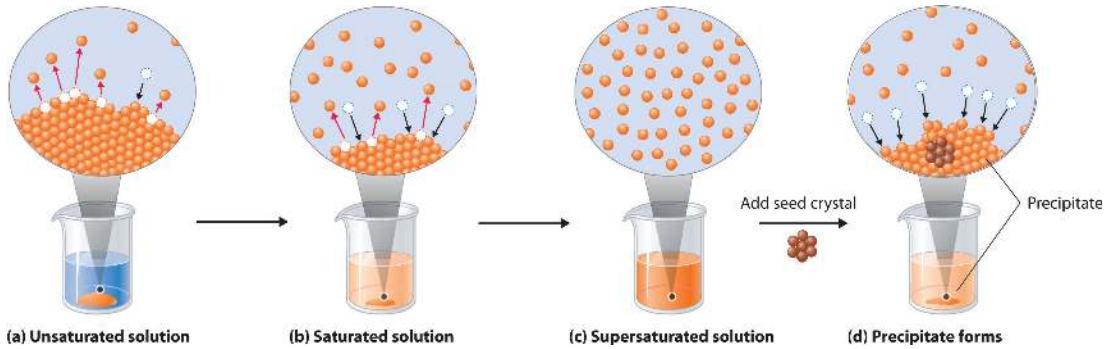


Figure **6.4.1** Dissolution and Precipitation. (a) When a solid is added to a solvent in which it is soluble, solute particles leave the surface of the solid and become solvated by the solvent, initially forming an unsaturated solution. (b) When the maximum possible amount of solute has dissolved, the solution becomes saturated. If excess solute is present, the rate at which solute particles leave the surface of the solid equals the rate at which they return to the surface of the solid. (c) A supersaturated solution can usually be formed from a saturated solution by filtering off the excess solute and lowering the temperature. (d) When a seed crystal of the solute is added to a supersaturated solution, solute particles leave the solution and form a crystalline precipitate. (CC BY-SA-NC 3.0; anonymous)

Solubility as a Function of Temperature

Figure **6.4.2** shows plots of the solubilities of several organic and inorganic compounds in water as a function of temperature. Although the solubility of a solid generally increases with increasing temperature, there is no simple relationship between the structure of a substance and the temperature dependence of its solubility. Many compounds (such as glucose and CH_3CO_2Na) exhibit a dramatic increase in solubility with increasing temperature. Others (such as $NaCl$ and K_2SO_4) exhibit little variation, and still others (such as Li_2SO_4) become less soluble with increasing temperature.

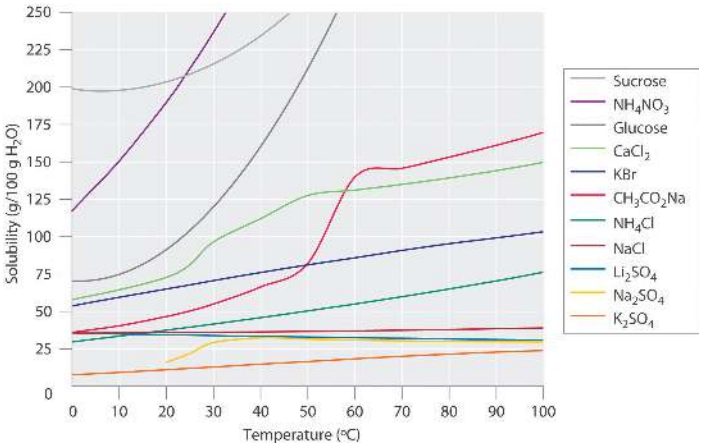


Figure **6.4.2**: Solubilities of Several Inorganic and Organic Solids in Water as a Function of Temperature. Solubility may increase or decrease with temperature; the magnitude of this temperature dependence varies widely among compounds. (CC BY-SA-NC 3.0; anonymous)

Notice in particular the curves for NH_4NO_3 and $CaCl_2$. The dissolution of ammonium nitrate in water is endothermic ($\Delta H_{soln} = +25.7\ kJ/mol$), whereas the dissolution of calcium chloride is exothermic ($\Delta H_{soln} = -68.2\ kJ/mol$), yet Figure **6.4.2** shows that the solubility of both compounds increases sharply with increasing temperature. In fact, the magnitudes of the changes in both enthalpy and entropy for dissolution are temperature dependent. Because the solubility of a compound is ultimately determined by relatively small differences between large numbers, there is generally no good way to predict how the solubility will vary with temperature.

Fractional Crystallization

The variation of solubility with temperature has been measured for a wide range of compounds, and the results are published in many standard reference books. Chemists are often able to use this information to separate the components of a mixture by fractional crystallization, the separation of compounds on the basis of their solubilities in a given solvent (Figure **6.4.3**). For example, if we have a mixture of 150 g of sodium acetate (CH_3CO_2Na) and 50 g of KBr, we can separate the two compounds by dissolving the mixture in 100 g of water at 80°C and then cooling the solution slowly to 0°C. According to the temperature curves in Figure **6.4.2**, both compounds dissolve in water at 80°C, and all 50 g of KBr remains in solution at 0°C. Only about 36 g of CH_3CO_2Na are soluble in 100 g of water at 0°C, however, so approximately 114 g (150 g − 36 g) of CH_3CO_2Na crystallizes out on cooling. The crystals can then be separated by filtration. Thus fractional crystallization allows us to recover about 75% of the original CH_3CO_2Na in essentially pure form in only one step.

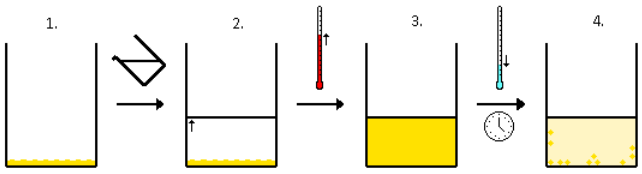


Figure **6.4.3**: Steps in a Fractional crystallization technique: (1 to 2) Solvent added (clear) to compound (orange) (2 to 3) Solvent heated to give saturated compound solution (orange) (3 to 4) Saturated compound solution (orange) allowed to cool over time to give crystals (orange) and a saturated solution (pale-orange). (Public Domain; Quantockgoblin via Wikipedia)

Fractional crystallization is a common technique for purifying compounds as diverse as those shown in Figure **6.4.2** and from antibiotics to enzymes to drugs (Figure **6.4.4**). For the technique to work properly, the compound of interest must be more soluble at high temperature than at low temperature, so that lowering the temperature causes it to crystallize out of solution. In addition, the impurities must be more soluble than the compound of interest (as was KBr in this example) and preferably present in relatively small amounts.



Figure **6.4.4**: Image of a single solvent, slowly cooling ibuprofen salt crystallizing. (CC BY-SA 2.5 Generic; Jacopo Werther via Wikipedia).

Summary

When a solution contains the maximum amount of solute that can dissolve under a given set of conditions, it is a saturated solution. Otherwise, it is unsaturated. Supersaturated solutions, which contain more dissolved solute than allowed under particular conditions, are not stable; the addition of a seed crystal, a small particle of solute, will usually cause the excess solute to crystallize. A system in which crystallization and dissolution occur at the same rate is in dynamic equilibrium. The solubility of most substances depends strongly on the temperature. The solubility of most solid or liquid solutes increases with increasing temperature. The components of a mixture can often be separated using fractional crystallization, which separates compounds according to their solubilities. The solubility of a gas decreases with increasing temperature.

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6.5: Solubilities of Gases

The chemical structures of the solute and solvent dictate the types of forces possible and, consequently, are important factors in determining solubility. For example, under similar conditions, the water solubility of oxygen is approximately three times greater than that of helium, but 100 times less than the solubility of chloromethane, $CHCl_3$. Considering the role of the solvent's chemical structure, note that the solubility of oxygen in the liquid hydrocarbon hexane, C_6H_{14}, is approximately 20 times greater than it is in water.

Other factors also affect the solubility of a given substance in a given solvent. Temperature is one such factor, with gas solubility typically decreasing as temperature increases (Figure **6.5.1**). This is one of the major impacts resulting from the thermal pollution of natural bodies of water.

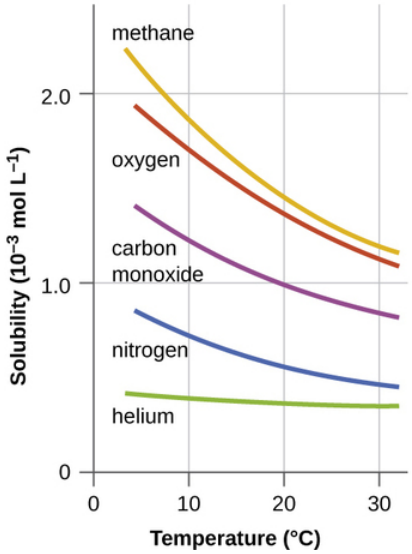


Figure **6.5.1**: The solubilities of these gases in water decrease as the temperature increases. All solubilities were measured with a constant pressure of 101.3 kPa (1 atm) of gas above the solutions.

When the temperature of a river, lake, or stream is raised abnormally high, usually due to the discharge of hot water from some industrial process, the solubility of oxygen in the water is decreased. Decreased levels of dissolved oxygen may have serious consequences for the health of the water's ecosystems and, in severe cases, can result in large-scale fish kills (Figure **6.5.2**).



(a) (b)

Figure **6.5.2**: (a) The small bubbles of air in this glass of chilled water formed when the water warmed to room temperature and the solubility of its dissolved air decreased. (b) The decreased solubility of oxygen in natural waters subjected to thermal pollution can result in large-scale fish kills. (credit a: modification of work by Liz West; credit b: modification of work by U.S. Fish and Wildlife Service)

The solubility of a gaseous solute is also affected by the partial pressure of solute in the gas to which the solution is exposed. Gas solubility increases as the pressure of the gas increases. Carbonated beverages provide a nice illustration of this relationship. The carbonation process involves exposing the beverage to a relatively high pressure of carbon dioxide gas and then sealing the beverage container, thus saturating the beverage with CO_2 at this pressure. When the beverage container is opened, a familiar hiss

is heard as the carbon dioxide gas pressure is released, and some of the dissolved carbon dioxide is typically seen leaving solution in the form of small bubbles (Figure **6.5.3**). At this point, the beverage is *supersaturated* with carbon dioxide and, with time, the dissolved carbon dioxide concentration will decrease to its equilibrium value and the beverage will become "flat."

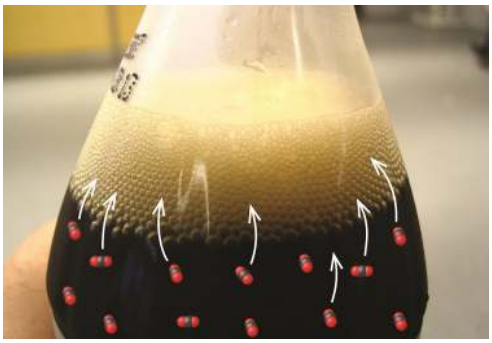


Figure **6.5.3**: Opening the bottle of carbonated beverage reduces the pressure of the gaseous carbon dioxide above the beverage. The solubility of CO_2 is thus lowered, and some dissolved carbon dioxide may be seen leaving the solution as small gas bubbles. (credit: modification of work by Derrick Coetzee)

For many gaseous solutes, the relation between solubility, C_g, and partial pressure, P_g, is a proportional one:

$$C_g = kP_g \tag{6.5.1}$$

where k is a proportionality constant that depends on the identities of the gaseous solute and solvent, and on the solution temperature. This is a mathematical statement of Henry's law: *The quantity of an ideal gas that dissolves in a definite volume of liquid is directly proportional to the pressure of the gas.*

Example 6.5.1: Application of Henry's Law

At 20 °C, the concentration of dissolved oxygen in water exposed to gaseous oxygen at a partial pressure of 101.3 kPa (760 torr) is 1.38×10^{-3} mol L^{-1}. Use Henry's law to determine the solubility of oxygen when its partial pressure is 20.7 kPa (155 torr), the approximate pressure of oxygen in earth's atmosphere.

Solution

According to Henry's law, for an ideal solution the solubility, C_g, of a gas (1.38×10^{-3} mol L^{-1}, in this case) is directly proportional to the pressure, P_g, of the undissolved gas above the solution (101.3 kPa, or 760 torr, in this case). Because we know both C_g and P_g, we can rearrange this expression to solve for k.

$$\begin{aligned} C_g &= kP_g \\ k &= \frac{C_g}{P_g} \\ &= \frac{1.38 \times 10^{-3}\ \text{mol L}^{-1}}{101.3\ \text{kPa}} \\ &= 1.36 \times 10^{-5}\ \text{mol L}^{-1}\ \text{kPa}^{-1} \\ &\quad (1.82 \times 10^{-6}\ \text{mol L}^{-1}\ \text{torr}^{-1}) \end{aligned}$$

Now we can use k to find the solubility at the lower pressure.

$$C_g = kP_g \tag{6.5.2}$$

$$\begin{aligned} &1.36 \times 10^{-5}\ \text{mol L}^{-1}\ \text{kPa}^{-1} \times 20.7\ \text{kPa} \\ &(\text{or } 1.82 \times 10^{-6}\ \text{mol L}^{-1}\ \text{torr}^{-1} \times 155\ \text{torr}) \\ &= 2.82 \times 10^{-4}\ \text{mol L}^{-1} \end{aligned} \tag{6.5.3}$$

Note that various units may be used to express the quantities involved in these sorts of computations. Any combination of units that yield to the constraints of dimensional analysis are acceptable.

Exercise 6.5.1

Exposing a 100.0 mL sample of water at 0 °C to an atmosphere containing a gaseous solute at 20.26 kPa (152 torr) resulted in the dissolution of 1.45×10^{-3} g of the solute. Use Henry's law to determine the solubility of this gaseous solute when its pressure is 101.3 kPa (760 torr).

Answer

7.25×10^{-3} g in 100.0 mL or 0.0725 g/L

Case Study: Decompression Sickness ("The Bends")

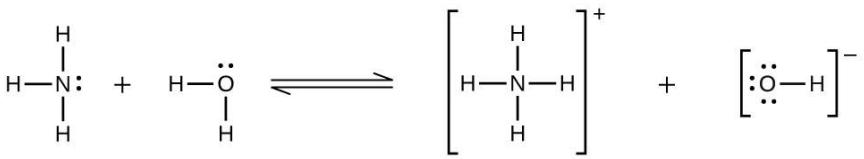
Decompression sickness (DCS), or "the bends," is an effect of the increased pressure of the air inhaled by scuba divers when swimming underwater at considerable depths. In addition to the pressure exerted by the atmosphere, divers are subjected to additional pressure due to the water above them, experiencing an increase of approximately 1 atm for each 10 m of depth. Therefore, the air inhaled by a diver while submerged contains gases at the corresponding higher ambient pressure, and the concentrations of the gases dissolved in the diver's blood are proportionally higher per Henry's law.



Figure 6.5.4: (a) US Navy divers undergo training in a recompression chamber. (b) Divers receive hyperbaric oxygen therapy.

As the diver ascends to the surface of the water, the ambient pressure decreases and the dissolved gases becomes less soluble. If the ascent is too rapid, the gases escaping from the diver's blood may form bubbles that can cause a variety of symptoms ranging from rashes and joint pain to paralysis and death. To avoid DCS, divers must ascend from depths at relatively slow speeds (10 or 20 m/min) or otherwise make several decompression stops, pausing for several minutes at given depths during the ascent. When these preventive measures are unsuccessful, divers with DCS are often provided hyperbaric oxygen therapy in pressurized vessels called decompression (or recompression) chambers (Figure 6.5.4).

Deviations from Henry's law are observed when a chemical reaction takes place between the gaseous solute and the solvent. Thus, for example, the solubility of ammonia in water does not increase as rapidly with increasing pressure as predicted by the law because ammonia, being a base, reacts to some extent with water to form ammonium ions and hydroxide ions.



Gases can form supersaturated solutions. If a solution of a gas in a liquid is prepared either at low temperature or under pressure (or both), then as the solution warms or as the gas pressure is reduced, the solution may become supersaturated. In 1986, more than 1700 people in Cameroon were killed when a cloud of gas, almost certainly carbon dioxide, bubbled from Lake Nyos (Figure 6.5.5), a deep lake in a volcanic crater. The water at the bottom of Lake Nyos is saturated with carbon dioxide by volcanic activity beneath the lake. It is believed that the lake underwent a turnover due to gradual heating from below the lake, and the warmer, less-dense water saturated with carbon dioxide reached the surface. Consequently, tremendous quantities of dissolved CO_2 were released, and the colorless gas, which is denser than air, flowed down the valley below the lake and suffocated humans and animals living in the valley.



(a) (b)

Figure **6.5.5**: (a) It is believed that the 1986 disaster that killed more than 1700 people near Lake Nyos in Cameroon resulted when a large volume of carbon dioxide gas was released from the lake. (b) A CO_2 vent has since been installed to help outgas the lake in a slow, controlled fashion and prevent a similar catastrophe from happening in the future. (credit a: modification of work by Jack Lockwood; credit b: modification of work by Bill Evans)



Henry's Law (The Solubility of Gases in Solvents): https://youtu.be/fiJZCGpArJI

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6.6: Vapor Pressures of Solutions

Learning Objectives

- To describe the relationship between solute concentration and the physical properties of a solution.
- To understand that the total number of nonvolatile solute particles determines the decrease in vapor pressure, increase in boiling point, and decrease in freezing point of a solution versus the pure solvent.

Raoult's Law

Adding a nonvolatile solute, one whose vapor pressure is too low to measure readily, to a volatile solvent decreases the vapor pressure of the solvent. We can understand this phenomenon qualitatively by examining Figure **6.6.1**, which is a schematic diagram of the surface of a solution of glucose in water. In an aqueous solution of glucose, a portion of the surface area is occupied by nonvolatile glucose molecules rather than by volatile water molecules. As a result, fewer water molecules can enter the vapor phase per unit time, even though the surface water molecules have the same kinetic energy distribution as they would in pure water. At the same time, the rate at which water molecules in the vapor phase collide with the surface and reenter the solution is unaffected. The net effect is to shift the dynamic equilibrium between water in the vapor and the liquid phases, decreasing the vapor pressure of the solution compared with the vapor pressure of the pure solvent.

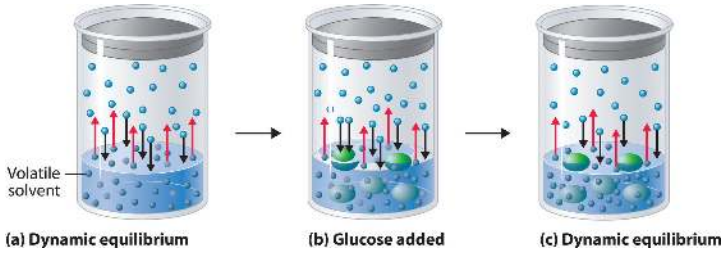


Figure **6.6.1**: A Model Depicting Why the Vapor Pressure of a Solution of Glucose Is Less Than the Vapor Pressure of Pure Water. (a) When water or any volatile solvent is in a closed container, water molecules move into and out of the liquid phase at the same rate in a dynamic equilibrium. (b) If a nonvolatile solute such as glucose is added, some fraction of the surface area is occupied by solvated solute molecules. As a result, the rate at which water molecules evaporate is decreased, although initially their rate of condensation is unchanged. (c) When the glucose solution reaches equilibrium, the concentration of water molecules in the vapor phase, and hence the vapor pressure, is less than that of pure water.

Figure **6.6.2** shows two beakers, one containing pure water and one containing an aqueous glucose solution, in a sealed chamber. We can view the system as having two competing equilibria: water vapor will condense in both beakers at the same rate, but water molecules will evaporate more slowly from the glucose solution because fewer water molecules are at the surface. Eventually all of the water will evaporate from the beaker containing the liquid with the higher vapor pressure (pure water) and condense in the beaker containing the liquid with the lower vapor pressure (the glucose solution). If the system consisted of only a beaker of water inside a sealed container, equilibrium between the liquid and vapor would be achieved rather rapidly, and the amount of liquid water in the beaker would remain constant.

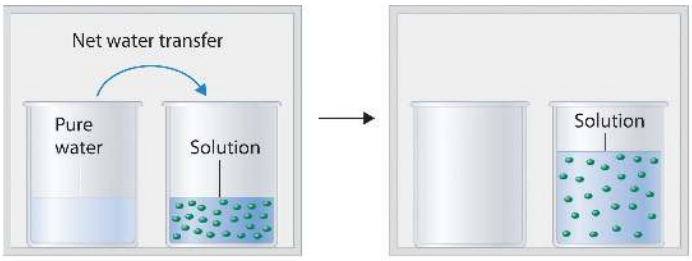


Figure **6.6.2**: Transfer of Water to a Beaker Containing a Glucose Solution. (top) One beaker contains an aqueous solution of glucose, and the other contains pure water. If they are placed in a sealed chamber, the lower vapor pressure of water in the glucose solution results in a net transfer of water from the beaker containing pure water to the beaker containing the glucose solution. (bottom) Eventually, all of the water is transferred to the beaker that has the glucose solution.

If the particles of a solute are essentially the same size as those of the solvent and both solute and solvent have roughly equal probabilities of being at the surface of the solution, then the effect of a solute on the vapor pressure of the solvent is proportional to

the number of sites occupied by solute particles at the surface of the solution. Doubling the concentration of a given solute causes twice as many surface sites to be occupied by solute molecules, resulting in twice the decrease in vapor pressure. The relationship between solution composition and vapor pressure is therefore

$$P_A = X_A P_A^0 \tag{6.6.1}$$

where P_A is the vapor pressure of component A of the solution (in this case the solvent), XA is the mole fraction of A in solution, and P_A^0 is the vapor pressure of pure A. Equation 6.6.1 is known as **Raoult's law**, after the French chemist who developed it. If the solution contains only a single nonvolatile solute (B), then $X_A + X_B = 1$, and we can substitute $X_A = 1 - X_B$ to obtain

$$P_A = (1 - X_B)P_A^0 \tag{6.6.2}$$

$$= P_A^0 - X_B P_A^0 \tag{6.6.3}$$

Rearranging and defining $\Delta P_A = P_A^0 - P_A$, we obtain a relationship between the decrease in vapor pressure and the mole fraction of nonvolatile solute:

$$P_A^0 - P_A = \Delta P_A = X_B P_A^0 \tag{6.6.4}$$

We can solve vapor pressure problems in either of two ways: by using Equation 6.6.1 to calculate the actual vapor pressure above a solution of a nonvolatile solute, or by using Equation 6.6.4 to calculate the decrease in vapor pressure caused by a specified amount of a nonvolatile solute.

Example 6.6.1

Ethylene glycol ($\mathbf{HOCH_2CH_2OH}$), the major ingredient in commercial automotive antifreeze, increases the boiling point of radiator fluid by lowering its vapor pressure. At 100°C, the vapor pressure of pure water is 760 mmHg. Calculate the vapor pressure of an aqueous solution containing 30.2% ethylene glycol by mass, a concentration commonly used in climates that do not get extremely cold in winter.

Given: identity of solute, percentage by mass, and vapor pressure of pure solvent

Asked for: vapor pressure of solution

Strategy:

A. Calculate the number of moles of ethylene glycol in an arbitrary quantity of water, and then calculate the mole fraction of water.
B. Use Raoult's law to calculate the vapor pressure of the solution.

Solution:

A A 30.2% solution of ethylene glycol contains 302 g of ethylene glycol per kilogram of solution; the remainder (698 g) is water. To use Raoult's law to calculate the vapor pressure of the solution, we must know the mole fraction of water. Thus we must first calculate the number of moles of both ethylene glycol (EG) and water present:

$$moles\ EG = (302\ \cancel{g}) \left(\frac{1\ mol}{62.07\ \cancel{g}} \right) = 4.87\ mol\ EG$$

$$moles\ \mathrm{H_2O} = (698\ \cancel{g}) \left(\frac{1\ mol}{18.02\ \cancel{g}} \right) = 38.7\ mol\ H_2O$$

The mole fraction of water is thus

$$X_{\mathrm{H_2O}} = \frac{38.7\ \cancel{mol}\ H_2O}{38.7\ \cancel{mol}\ H_2O + 4.87\ \cancel{mol}\ EG} = 0.888$$

B From Raoult's law (Equation 6.6.1), the vapor pressure of the solution is

$$P_{\mathrm{H_2O}} = (X_{H_2O})(P_{H_2O}^0) = (0.888)(760\ mmHg) = 675\ mmHg$$

Alternatively, we could solve this problem by calculating the mole fraction of ethylene glycol and then using Equation 6.6.4 to calculate the resulting decrease in vapor pressure:

$$X_{EG} = \frac{4.87\ mol\ EG}{4.87\ mol\ EG + 38.7\ mol\ H_2O} = 0.112$$

$$\Delta P_{H_2O} = (X_{EG})(P^0_{H_2O}) = (0.112)(760\ mmHg) = 85.1\ mmHg$$

$$P_{H_2O} = P^0 H_2O - \Delta P_{H_2O} = 760\ mmHg - 85.1\ mmHg = 675\ mmHg$$

The same result is obtained using either method.

? Exercise 6.6.1

Seawater is an approximately 3.0% aqueous solution of $NaCl$ by mass with about 0.5% of other salts by mass. Calculate the decrease in the vapor pressure of water at 25°C caused by this concentration of $NaCl$, remembering that 1 mol of $NaCl$ produces 2 mol of solute particles. The vapor pressure of pure water at 25°C is 23.8 mmHg.

Answer

0.45 mmHg. This may seem like a small amount, but it constitutes about a 2% decrease in the vapor pressure of water and accounts in part for the higher humidity in the north-central United States near the Great Lakes, which are freshwater lakes. The decrease therefore has important implications for climate modeling.



Finding the Vapor Pressure of a Solution (Ionic-Nonvolatile Solute):

https://youtu.be/sRBaRXsql9s

Volatile Solutes

Even when a solute is volatile, meaning that it has a measurable vapor pressure, we can still use Raoult's law. In this case, we calculate the vapor pressure of each component separately. The total vapor pressure of the solution (P_T) is the sum of the vapor pressures of the components:

$$P_T = P_A + P_B \tag{6.6.5}$$

$$= X_A P^0_A + X_B P^0_B \tag{6.6.6}$$

Because $X_B = 1 - X_A$ for a two-component system,

$$P_T = X_A P^0_A + (1 - X_A) P^0_B \tag{6.6.7}$$

Thus we need to specify the mole fraction of only one of the components in a two-component system. Consider, for example, the vapor pressure of solutions of benzene and toluene of various compositions. At 20°C, the vapor pressures of pure benzene and

toluene are 74.7 and 22.3 mmHg, respectively. The vapor pressure of benzene in a benzene–toluene solution is

$$P_{C_6H_6} = X_{C_6H_6}P^0_{C_6H_6} \tag{6.6.8}$$

and the vapor pressure of toluene in the solution is

$$P_{C_6H_5CH_3} = X_{C_6H_5CH_3}P^0_{C_6H_5CH3} \tag{6.6.9}$$

Equations 6.6.8 and 6.6.9 are both in the form of the equation for a straight line: $y = mx + b$, where $b = 0$. Plots of the vapor pressures of both components versus the mole fractions are therefore straight lines that pass through the origin, as shown in Figure Figure **6.6.3**. Furthermore, a plot of the total vapor pressure of the solution versus the mole fraction is a straight line that represents the sum of the vapor pressures of the pure components. Thus the vapor pressure of the solution is always greater than the vapor pressure of either component.

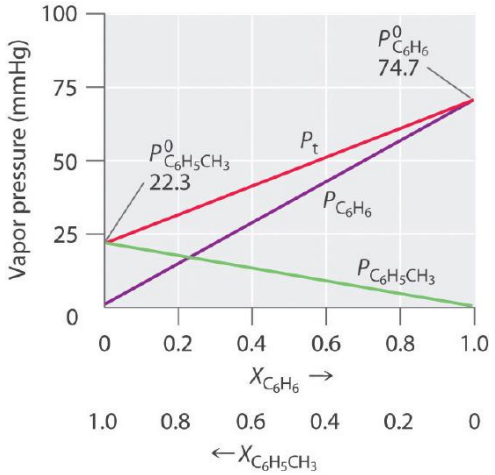


Figure **6.6.3**: Vapor Pressures of Benzene–Toluene Solutions. Plots of the vapor pressures of benzene (C_6H_6) and toluene ($C_6H_5CH_3$) versus the mole fractions at 20°C are straight lines. For a solution like this, which approximates an ideal solution, the total vapor pressure of the solution (Pt) is the sum of the vapor pressures of the components.

A solution of two volatile components that behaves like the solution in Figure **6.6.3**, which is defined as a solution that obeys Raoult's law. Like an ideal gas, an ideal solution is a hypothetical system whose properties can be described in terms of a simple model. Mixtures of benzene and toluene approximate an ideal solution because the intermolecular forces in the two pure liquids are almost identical in both kind and magnitude. Consequently, the change in enthalpy on solution formation is essentially zero ($\Delta H_{soln} \approx 0$), which is one of the defining characteristics of an ideal solution.

> Ideal solutions and ideal gases are both simple models that ignore intermolecular interactions.

Most real solutions, however, do not obey Raoult's law precisely, just as most real gases do not obey the ideal gas law exactly. Real solutions generally deviate from Raoult's law because the intermolecular interactions between the two components A and B differ. We can distinguish between two general kinds of behavior, depending on whether the intermolecular interactions between molecules A and B are stronger or weaker than the A–A and B–B interactions in the pure components. If the A–B interactions are stronger than the A–A and B–B interactions, each component of the solution exhibits a lower vapor pressure than expected for an ideal solution, as does the solution as a whole. The favorable A–B interactions effectively stabilize the solution compared with the vapor. This kind of behavior is called a negative deviation from Raoult's law. Systems stabilized by hydrogen bonding between two molecules, such as acetone and ethanol, exhibit negative deviations from Raoult's law. Conversely, if the A–B interactions are weaker than the A–A and B–B interactions yet the entropy increase is enough to allow the solution to form, both A and B have an increased tendency to escape from the solution into the vapor phase. The result is a higher vapor pressure than expected for an ideal solution, producing a positive deviation from Raoult's law. In a solution of CCl_4 and methanol, for example, the nonpolar CCl_4 molecules interrupt the extensive hydrogen bonding network in methanol, and the lighter methanol molecules have weaker London dispersion forces than the heavier CCl_4 molecules. Consequently, solutions of CCl_4 and methanol exhibit positive deviations from Raoult's law.

Example 6.6.2

For each system, compare the intermolecular interactions in the pure liquids and in the solution to decide whether the vapor pressure will be greater than that predicted by Raoult's law (positive deviation), approximately equal to that predicted by Raoult's law (an ideal solution), or less than the pressure predicted by Raoult's law (negative deviation).

a. cyclohexane and ethanol
b. methanol and acetone
c. n-hexane and isooctane (2,2,4-trimethylpentane)

Given: identity of pure liquids

Asked for: predicted deviation from Raoult's law

Strategy:

Identify whether each liquid is polar or nonpolar, and then predict the type of intermolecular interactions that occur in solution.

Solution:

a. Liquid ethanol contains an extensive hydrogen bonding network, and cyclohexane is nonpolar. Because the cyclohexane molecules cannot interact favorably with the polar ethanol molecules, they will disrupt the hydrogen bonding. Hence the A–B interactions will be weaker than the A–A and B–B interactions, leading to a higher vapor pressure than predicted by Raoult's law (a positive deviation).
b. Methanol contains an extensive hydrogen bonding network, but in this case the polar acetone molecules create A–B interactions that are stronger than the A–A or B–B interactions, leading to a negative enthalpy of solution and a lower vapor pressure than predicted by Raoult's law (a negative deviation).
c. Hexane and isooctane are both nonpolar molecules (isooctane actually has a very small dipole moment, but it is so small that it can be ignored). Hence the predominant intermolecular forces in both liquids are London dispersion forces. We expect the A–B interactions to be comparable in strength to the A–A and B–B interactions, leading to a vapor pressure in good agreement with that predicted by Raoult's law (an ideal solution).

Exercise 6.6.2

For each system, compare the intermolecular interactions in the pure liquids with those in the solution to decide whether the vapor pressure will be greater than that predicted by Raoult's law (positive deviation), approximately equal to that predicted by Raoult's law (an ideal solution), or less than the pressure predicted by Raoult's law (negative deviation):

a. benzene and n-hexane
b. ethylene glycol and CCl_4
c. acetic acid and n-propanol

Answer a

approximately equal

Answer b

positive deviation (vapor pressure greater than predicted)

Answer c

negative deviation (vapor pressure less than predicted)



Finding Vapor Pressure of a Solution (Nonionic-Volatile Solute):

https://youtu.be/s06fzZZtLl0

Summary

- **Henry's law:**

$$C = kP$$

- **Raoult's law**:

$$P_A = X_A P_A^0$$

- **vapor pressure lowering**:

$$P_A^0 - P_A = \Delta P_A = X_B P_A^0$$

- **vapor pressure of a system containing two volatile components**:

$$P_T = X_A P_A^0 + (1 - X_A) P_B^0$$

The vapor pressure of the solution is proportional to the mole fraction of solvent in the solution, a relationship known as **Raoult's law**. Solutions that obey Raoult's law are called ideal solutions. Most real solutions exhibit positive or negative deviations from Raoult's law.

Contributors and Attributions

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6.7: Osmotic Pressure

Learning Objectives

- To describe the relationship between solute concentration and the physical properties of a solution.
- To understand that the total number of nonvolatile solute particles determines the decrease in vapor pressure, increase in boiling point, and decrease in freezing point of a solution versus the pure solvent.

Osmotic pressure is a colligative property of solutions that is observed using a semipermeable membrane, a barrier with pores small enough to allow solvent molecules to pass through but not solute molecules or ions. The net flow of solvent through a semipermeable membrane is called osmosis (from the Greek osmós, meaning “push”). The direction of net solvent flow is always from the side with the lower concentration of solute to the side with the higher concentration.

Osmosis can be demonstrated using a U-tube like the one shown in Figure **6.7.1**, which contains pure water in the left arm and a dilute aqueous solution of glucose in the right arm. A net flow of water through the membrane occurs until the levels in the arms eventually stop changing, which indicates that equilibrium has been reached. The osmotic pressure (**Π**) of the glucose solution is the difference in the pressure between the two sides, in this case the heights of the two columns. Although the semipermeable membrane allows water molecules to flow through in either direction, the rate of flow is not the same in both directions because the concentration of water is not the same in the two arms. The net flow of water through the membrane can be prevented by applying a pressure to the right arm that is equal to the osmotic pressure of the glucose solution.

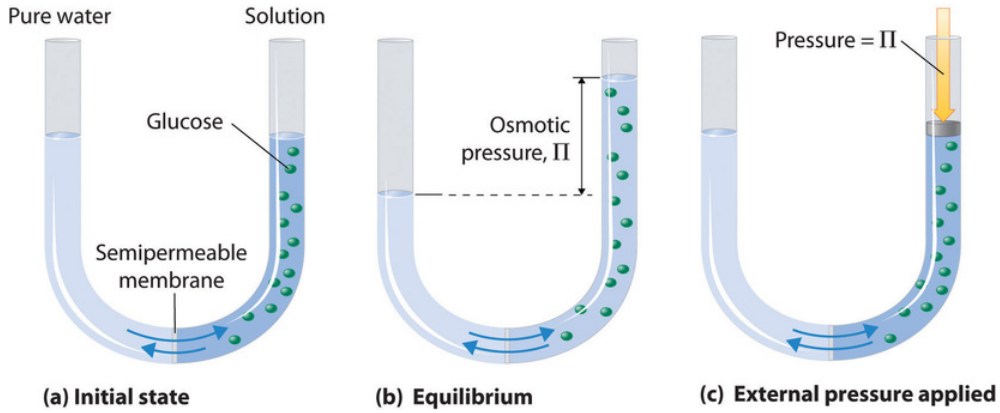


Figure **6.7.1**: Osmotic Pressure. (a) A dilute solution of glucose in water is placed in the right arm of a U-tube, and the left arm is filled to the same height with pure water; a semipermeable membrane separates the two arms. Because the flow of pure solvent through the membrane from left to right (from pure water to the solution) is greater than the flow of solvent in the reverse direction, the level of liquid in the right tube rises. (b) At equilibrium, the pressure differential, equal to the osmotic pressure of the solution (Π_{soln}), *equalizes the flow rate of solvent in both directions. (c) Applying an external pressure equal to the osmotic pressure of the original glucose solution to the liquid in the right arm reverses the flow of solvent and restores the original situation.*

The osmotic pressure of a solution depends on the concentration of dissolved solute particles. Osmotic pressure obeys a law that resembles the ideal gas equation:

$$\Pi = \frac{nRT}{V} = MRT \tag{6.7.1}$$

where

- M is the number of moles of solute per unit volume of solution (i.e., the molarity of the solution),
- R is the ideal gas constant, and
- T is the absolute temperature.

As shown in Example **6.7.1**, osmotic pressures tend to be quite high, even for rather dilute solutions.

Example 6.7.1: Yeast Cells

When placed in a concentrated salt solution, certain yeasts are able to produce high internal concentrations of glycerol to counteract the osmotic pressure of the surrounding medium. Suppose that the yeast cells are placed in an aqueous solution containing 4.0% $NaCl$ by mass; the solution density is 1.02 g/mL at 25°C.

Calculate the osmotic pressure of a 4.0% aqueous $NaCl$ solution at 25°C.

If the normal osmotic pressure inside a yeast cell is 7.3 atm, corresponding to a total concentration of dissolved particles of 0.30 M, what concentration of glycerol must the cells synthesize to exactly balance the external osmotic pressure at 25°C?

Given: concentration, density, and temperature of $NaCl$ solution; internal osmotic pressure of cell

Asked for: osmotic pressure of $NaCl$ solution and concentration of glycerol needed

Strategy:

A. Calculate the molarity of the $NaCl$ solution using the formula mass of the solute and the density of the solution. Then calculate the total concentration of dissolved particles.
B. Use Equation 6.7.1 to calculate the osmotic pressure of the solution.
C. Subtract the normal osmotic pressure of the cells from the osmotic pressure of the salt solution to obtain the additional pressure needed to balance the two. Use Equation 6.7.1 to calculate the molarity of glycerol needed to create this osmotic pressure.

Solution:

A The solution contains 4.0 g of $NaCl$ per 100 g of solution. Using the formula mass of $NaCl$ (58.44 g/mol) and the density of the solution (1.02 g/mL), we can calculate the molarity:

$$\begin{aligned} M_{NaCl} &= \frac{moles\ NaCl}{\text{liter solution}} \\ &= \left(\frac{4.0\ \cancel{g}\ NaCl}{58.44\ \cancel{g}/mol\ NaCl}\right)\left(\frac{1}{100\ \cancel{g\ solution}}\right)\left(\frac{1.02\ \cancel{g\ solution}}{1.00\ \cancel{mL}\ solution}\right)\left(\frac{1000\ \cancel{mL}}{1\ L}\right) \\ &= 0.70\ M\ NaCl \end{aligned}$$

Because 1 mol of $NaCl$ produces 2 mol of particles in solution, the total concentration of dissolved particles in the solution is (2)(0.70 M) = 1.4 M.

B Now we can use Equation 6.7.1 to calculate the osmotic pressure of the solution:

$$\begin{aligned} \Pi &= MRT \\ &= (1.4\ mol/L)\,[0.0821\ (L \cdot atm)/(K \cdot mol)]\,(298\ K) \\ &= 34\ atm \end{aligned}$$

C If the yeast cells are to exactly balance the external osmotic pressure, they must produce enough glycerol to give an additional internal pressure of (34 atm − 7.3 atm) = 27 atm. Glycerol is a nonelectrolyte, so we can solve Equation 6.7.1 for the molarity corresponding to this osmotic pressure:

$$\begin{aligned} M &= \frac{\Pi}{RT} \\ &= \frac{27\ \cancel{atm}}{[0.0821(L \cdot \cancel{atm})/(\cancel{K} \cdot mol)](298\ \cancel{K})} \\ &= 1.1\ M\ glycerol \end{aligned}$$

In solving this problem, we could also have recognized that the only way the osmotic pressures can be the same inside the cells and in the solution is if the concentrations of dissolved particles are the same. We are given that the normal concentration of dissolved particles in the cells is 0.3 M, and we have calculated that the $NaCl$ solution is effectively 1.4 M in dissolved particles. The yeast cells must therefore synthesize enough glycerol to increase the internal concentration of dissolved particles from 0.3 M to 1.4 M—that is, an additional 1.1 M concentration of glycerol.

? Exercise 6.7.1

Assume that the fluids inside a sausage are approximately 0.80 M in dissolved particles due to the salt and sodium nitrite used to prepare them. Calculate the osmotic pressure inside the sausage at 100°C to learn why experienced cooks pierce the semipermeable skin of sausages before boiling them.

Answer: 24 atm

Because of the large magnitude of osmotic pressures, osmosis is extraordinarily important in biochemistry, biology, and medicine. Virtually every barrier that separates an organism or cell from its environment acts like a semipermeable membrane, permitting the flow of water but not solutes. The same is true of the compartments inside an organism or cell. Some specialized barriers, such as those in your kidneys, are slightly more permeable and use a related process called dialysis, which permits both water and small molecules to pass through but not large molecules such as proteins.

The same principle has long been used to preserve fruits and their essential vitamins over the long winter. High concentrations of sugar are used in jams and jellies not for sweetness alone but because they greatly increase the osmotic pressure. Thus any bacteria not killed in the cooking process are dehydrated, which keeps them from multiplying in an otherwise rich medium for bacterial growth. A similar process using salt prevents bacteria from growing in ham, bacon, salt pork, salt cod, and other preserved meats. The effect of osmotic pressure is dramatically illustrated in Figure **6.7.2**, which shows what happens when red blood cells are placed in a solution whose osmotic pressure is much lower or much higher than the internal pressure of the cells.

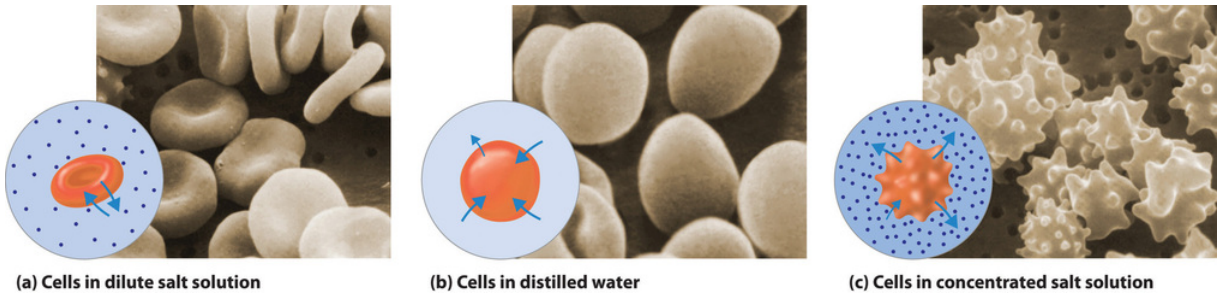


Figure **6.7.2**: Effect on Red Blood Cells of the Surrounding Solution's Osmotic Pressure. (a) When red blood cells are placed in a dilute salt solution having the same osmotic pressure as the intracellular fluid, the rate of flow of water into and out of the cells is the same and their shape does not change. (b) When cells are placed in distilled water whose osmotic pressure is less than that of the intracellular fluid, the rate of flow of water into the cells is greater than the rate of flow out of the cells. The cells swell and eventually burst. (c) When cells are placed in a concentrated salt solution with an osmotic pressure greater than that of the intracellular fluid, the rate of flow of water out of the cells is greater than the rate of flow into the cells. The cells shrivel and become so deformed that they cannot function.

In addition to capillary action, trees use osmotic pressure to transport water and other nutrients from the roots to the upper branches. Evaporation of water from the leaves results in a local increase in the salt concentration, which generates an osmotic pressure that pulls water up the trunk of the tree to the leaves.

Finally, a process called reverse osmosis can be used to produce pure water from seawater. As shown schematically in Figure **6.7.3**, applying high pressure to seawater forces water molecules to flow through a semipermeable membrane that separates pure water from the solution, leaving the dissolved salt behind. Large-scale desalinization plants that can produce hundreds of thousands of gallons of freshwater per day are common in the desert lands of the Middle East, where they supply a large proportion of the freshwater needed by the population. Similar facilities are now being used to supply freshwater in southern California. Small, hand-operated reverse osmosis units can produce approximately 5 L of freshwater per hour, enough to keep 25 people alive, and are now standard equipment on US Navy lifeboats.

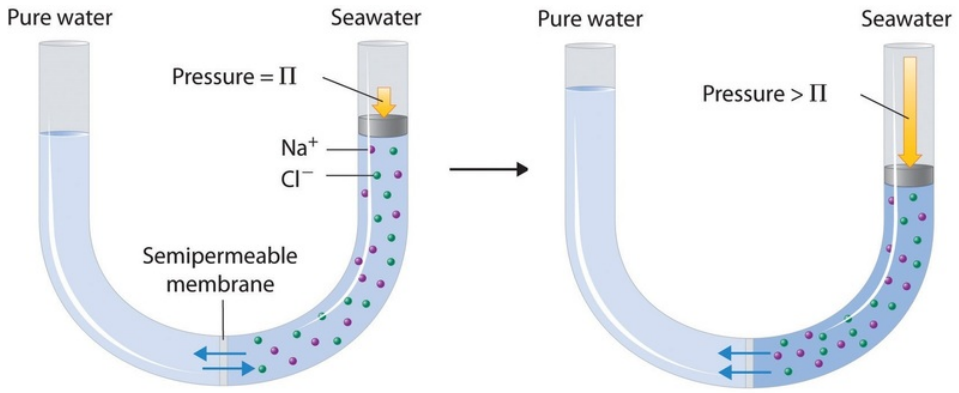


Figure **6.7.3**: Desalinization of Seawater by Reverse Osmosis. (top) When the pressure applied to seawater equals its osmotic pressure (Π_{soln}), *there is no net flow of water across the semipermeable membrane. (bottom) The application of pressure greater than the osmotic pressure of seawater forces water molecules to flow through the membrane, leaving behind a concentrated salt solution. In desalinization plants, seawater is continuously introduced under pressure and pure water is collected, so the process continues indefinitely.*



Osmotic Pressure: https://youtu.be/uYQxI4mi3DA

Summary

When a solution and a pure solvent are separated by a semipermeable membrane, a barrier that allows solvent molecules but not solute molecules to pass through, the flow of solvent in opposing directions is unequal and produces an osmotic pressure, which is the difference in pressure between the two sides of the membrane. Osmosis is the net flow of solvent through such a membrane due to different solute concentrations. Dialysis uses a semipermeable membrane with pores that allow only small solute molecules and solvent molecules to pass through.

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6.8: Freezing-Point Depression and Boiling-Point Elevation of Nonelectrolyte Solutions

Learning Objectives

- To describe the relationship between solute concentration and the physical properties of a solution.
- To understand that the total number of nonvolatile solute particles determines the decrease in vapor pressure, increase in boiling point, and decrease in freezing point of a solution versus the pure solvent.

Many of the physical properties of solutions differ significantly from those of the pure substances discussed in earlier chapters, and these differences have important consequences. For example, the limited temperature range of liquid water (0°C–100°C) severely limits its use. Aqueous solutions have both a lower freezing point and a higher boiling point than pure water. Probably one of the most familiar applications of this phenomenon is the addition of ethylene glycol (“antifreeze”) to the water in an automobile radiator. This solute lowers the freezing point of the water, preventing the engine from cracking in very cold weather from the expansion of pure water on freezing. Antifreeze also enables the cooling system to operate at temperatures greater than 100°C without generating enough pressure to explode.

Changes in the freezing point and boiling point of a solution depend primarily on the number of solute particles present rather than the kind of particles. Such properties of solutions are called colligative properties (from the Latin colligatus, meaning “bound together” as in a quantity). As we will see, the vapor pressure and osmotic pressure of solutions are also colligative properties.

When we determine the number of particles in a solution, it is important to remember that not all solutions with the same molarity contain the same concentration of solute particles. Consider, for example, 0.01 M aqueous solutions of sucrose, $NaCl$, and $CaCl_2$. Because sucrose dissolves to give a solution of neutral molecules, the concentration of solute particles in a 0.01 M sucrose solution is 0.01 M. In contrast, both $NaCl$ and $CaCl_2$ are ionic compounds that dissociate in water to yield solvated ions. As a result, a 0.01 M aqueous solution of $NaCl$ contains 0.01 M Na+ ions and 0.01 M Cl^- ions, for a total particle concentration of 0.02 M. Similarly, the $CaCl_2$ solution contains 0.01 M Ca^{2+} ions and 0.02 M Cl^- ions, for a total particle concentration of 0.03 M.These values are correct for dilute solutions, where the dissociation of the compounds to form separately solvated ions is complete. At higher concentrations (typically >1 M), especially with salts of small, highly charged ions (such as Mg^{2+} or Al^{3+}), or in solutions with less polar solvents, dissociation to give separate ions is often incomplete. The sum of the concentrations of the dissolved solute particles dictates the physical properties of a solution. In the following discussion, we must therefore keep the chemical nature of the solute firmly in mind.

Boiling Point Elevation

Recall that the normal boiling point of a substance is the temperature at which the vapor pressure equals 1 atm. If a nonvolatile solute lowers the vapor pressure of a solvent, it must also affect the boiling point. Because the vapor pressure of the solution at a given temperature is less than the vapor pressure of the pure solvent, achieving a vapor pressure of 1 atm for the solution requires a higher temperature than the normal boiling point of the solvent. Thus the boiling point of a solution is always greater than that of the pure solvent. We can see why this must be true by comparing the phase diagram for an aqueous solution with the phase diagram for pure water (Figure **6.8.1**). The vapor pressure of the solution is less than that of pure water at all temperatures. Consequently, the liquid–vapor curve for the solution crosses the horizontal line corresponding to P = 1 atm at a higher temperature than does the curve for pure water.

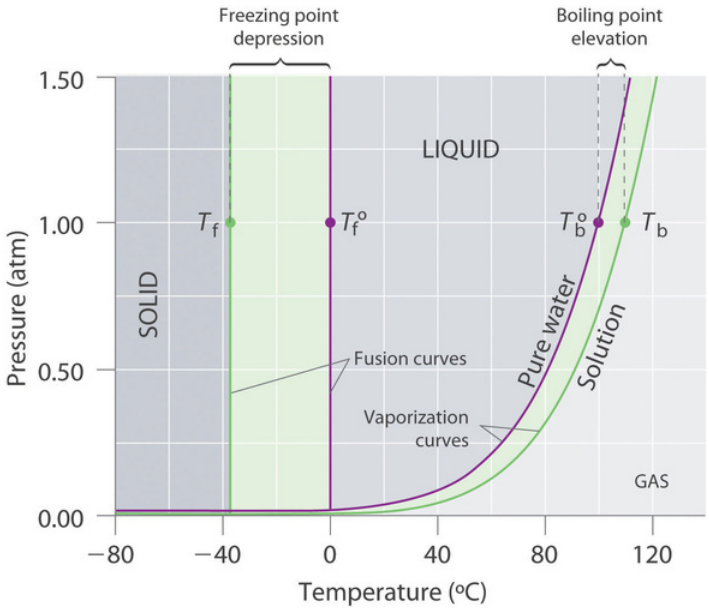


Figure **6.8.1**: Phase Diagrams of Pure Water and an Aqueous Solution of a Nonvolatile Solute. The vaporization curve for the solution lies below the curve for pure water at all temperatures, which results in an increase in the boiling point and a decrease in the freezing point of the solution.

> The boiling point of a solution with a nonvolatile solute is always greater than the boiling point of the pure solvent.

The magnitude of the increase in the boiling point is related to the magnitude of the decrease in the vapor pressure. As we have just discussed, the decrease in the vapor pressure is proportional to the concentration of the solute in the solution. Hence the magnitude of the increase in the boiling point must also be proportional to the concentration of the solute (Figure **6.8.2**). We can define the boiling point elevation (ΔT_b) as the difference between the boiling points of the solution and the pure solvent:

$$\Delta T_b = T_b - T_b^0 \tag{6.8.1}$$

where T_b is the boiling point of the solution and T_b^0 is the boiling point of the pure solvent. We can express the relationship between ΔT_b and concentration as follows

$$\Delta T_b = mK_b \tag{6.8.2}$$

where m is the concentration of the solute expressed in molality, and K_b is the molal boiling point elevation constant of the solvent, which has units of °C/m. Table **6.8.1** lists characteristic Kb values for several commonly used solvents.

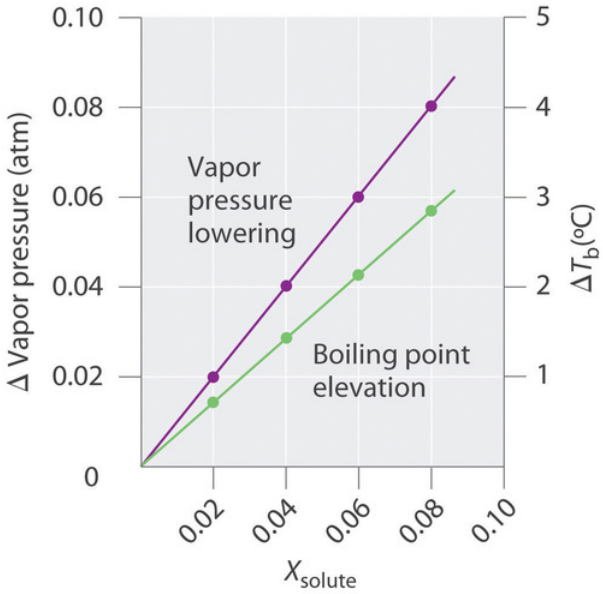


Figure 6.8.2: Vapor Pressure Decrease and Boiling Point Increase as Functions of the Mole Fraction of a Nonvolatile Solute

For relatively dilute solutions, the magnitude of both properties is proportional to the solute concentration.

Table 6.8.1: Boiling Point Elevation Constants (K_b) and Freezing Point Depression Constants (K_f) for Some Solvents

Solvent	Boiling Point (°C)	K_b (°C/m)	Freezing Point (°C)	K_f (°C/m)
acetic acid	117.90	3.22	16.64	3.63
benzene	80.09	2.64	5.49	5.07
d-(+)-camphor	207.4	4.91	178.8	37.8
carbon disulfide	46.2	2.42	−112.1	3.74
carbon tetrachloride	76.8	5.26	−22.62	31.4
chloroform	61.17	3.80	−63.41	4.60
nitrobenzene	210.8	5.24	5.70	6.87
water	100.00	0.51	0.00	1.86

The concentration of the solute is typically expressed as molality rather than mole fraction or molarity for two reasons. First, because the density of a solution changes with temperature, the value of molarity also varies with temperature. If the boiling point depends on the solute concentration, then by definition the system is not maintained at a constant temperature. Second, molality and mole fraction are proportional for relatively dilute solutions, but molality has a larger numerical value (a mole fraction can be only between zero and one). Using molality allows us to eliminate nonsignificant zeros.

According to Table 6.8.1, the molal boiling point elevation constant for water is 0.51°C/m. Thus a 1.00 m aqueous solution of a nonvolatile molecular solute such as glucose or sucrose will have an increase in boiling point of 0.51°C, to give a boiling point of 100.51°C at 1.00 atm. The increase in the boiling point of a 1.00 m aqueous NaCl solution will be approximately twice as large as that of the glucose or sucrose solution because 1 mol of NaCl produces 2 mol of dissolved ions. Hence a 1.00 m NaCl solution will have a boiling point of about 101.02°C.

Example 6.8.3

In Example 6.8.1, we calculated that the vapor pressure of a 30.2% aqueous solution of ethylene glycol at 100°C is 85.1 mmHg less than the vapor pressure of pure water. We stated (without offering proof) that this should result in a higher boiling point for

the solution compared with pure water. Now that we have seen why this assertion is correct, calculate the boiling point of the aqueous ethylene glycol solution.

Given: composition of solution

Asked for: boiling point

Strategy:

Calculate the molality of ethylene glycol in the 30.2% solution. Then use Equation 6.8.2 to calculate the increase in boiling point.

Solution:

From Example 6.8.1, we know that a 30.2% solution of ethylene glycol in water contains 302 g of ethylene glycol (4.87 mol) per 698 g of water. The molality of the solution is thus

$$\text{molality of ethylene glycol} = \left(\frac{4.87\ mol}{698\ \cancel{g}\ H_2O}\right)\left(\frac{1000\ \cancel{g}}{1\ kg}\right) = 6.98m \tag{6.8.3}$$

From Equation 6.8.2, the increase in boiling point is therefore

$$\Delta T_b = mK_b = (6.98\ \cancel{m})(0.51°C/\cancel{m}) = 3.6°C \tag{6.8.4}$$

The boiling point of the solution is thus predicted to be 104°C. With a solute concentration of almost 7 m, however, the assumption of a dilute solution used to obtain Equation 6.8.2 may not be valid.

? Exercise 6.8.3

Assume that a tablespoon (5.00 g) of NaCl is added to 2.00 L of water at 20.0°C, which is then brought to a boil to cook spaghetti. At what temperature will the water boil?

Answer

100.04°C, or 100°C to three significant figures. (Recall that 1 mol of NaCl produces 2 mol of dissolved particles. The small increase in temperature means that adding salt to the water used to cook pasta has essentially no effect on the cooking time.)

Freezing Point Depression

The phase diagram in Figure 6.8.1 shows that dissolving a nonvolatile solute in water not only raises the boiling point of the water but also lowers its freezing point. The solid–liquid curve for the solution crosses the line corresponding to P = 1 atm at a lower temperature than the curve for pure water.

This phenomenon is exploited in “de-icing” schemes that use salt (Figure 6.8.3), calcium chloride, or urea to melt ice on roads and sidewalks, and in the use of ethylene glycol as an “antifreeze” in automobile radiators. Seawater freezes at a lower temperature than fresh water, and so the Arctic and Antarctic oceans remain unfrozen even at temperatures below 0 °C (as do the body fluids of fish and other cold-blooded sea animals that live in these oceans).



Figure 6.8.3: Rock salt (NaCl), calcium chloride ($CaCl_2$), or a mixture of the two are used to melt ice. (credit: modification of work by Eddie Welker)

We can understand this result by imagining that we have a sample of water at the normal freezing point temperature, where there is a dynamic equilibrium between solid and liquid. Water molecules are continuously colliding with the ice surface and entering the solid phase at the same rate that water molecules are leaving the surface of the ice and entering the liquid phase. If we dissolve a nonvolatile solute such as glucose in the liquid, the dissolved glucose molecules will reduce the number of collisions per unit time between water molecules and the ice surface because some of the molecules colliding with the ice will be glucose. Glucose, though, has a very different structure than water, and it cannot fit into the ice lattice. Consequently, the presence of glucose molecules in the solution can only decrease the rate at which water molecules in the liquid collide with the ice surface and solidify. Meanwhile, the rate at which the water molecules leave the surface of the ice and enter the liquid phase is unchanged. The net effect is to cause the ice to melt. The only way to reestablish a dynamic equilibrium between solid and liquid water is to lower the temperature of the system, which decreases the rate at which water molecules leave the surface of the ice crystals until it equals the rate at which water molecules in the solution collide with the ice.

By analogy to our treatment of boiling point elevation,the freezing point depression (ΔT_f) is defined as the difference between the freezing point of the pure solvent and the freezing point of the solution:

$$\Delta T_f = T_f^0 - T_f \tag{6.8.5}$$

where

- T_f^0 is the freezing point of the pure solvent and
- T_f is the freezing point of the solution.

The order of the terms is reversed compared with Equation 6.8.1 to express the freezing point depression as a positive number. The relationship between ΔT_f and the solute concentration is given by an equation analogous to Equation 6.8.2:

$$\Delta T_f = mK_f \tag{6.8.6}$$

where

- m is the molality of the solution and
- K_f is the molal freezing point depression constant for the solvent (in units of °C/m).

Like K_b, each solvent has a characteristic value of K_f (Table 6.8.1). Freezing point depression depends on the total number of dissolved nonvolatile solute particles, just as with boiling point elevation. Thus an aqueous NaCl solution has twice as large a freezing point depression as a glucose solution of the same molality.

People who live in cold climates use freezing point depression to their advantage in many ways. For example, ethylene glycol is added to engine coolant water to prevent an automobile engine from being destroyed, and methanol is added to windshield washer fluid to prevent the fluid from freezing. Heated glycols are often sprayed onto the surface of airplanes prior to takeoff in inclement weather in the winter to remove ice that has already formed and prevent the formation of more ice, which would be particularly dangerous if formed on the control surfaces of the aircraft (Video 6.8.1).



Video* 6.8.1*: *Freezing point depression is exploited to remove ice from the control surfaces of aircraft.*

The decrease in vapor pressure, increase in boiling point, and decrease in freezing point of a solution versus a pure liquid all depend on the total number of dissolved nonvolatile solute particles.

Example 6.8.4

In colder regions of the United States, $\mathbf{NaCl}$ or $\mathbf{CaCl_2}$ is often sprinkled on icy roads in winter to melt the ice and make driving safer. Use the data in Figure 13.9 to estimate the concentrations of two saturated solutions at 0°C, one of $\mathbf{NaCl}$ and one of $\mathbf{CaCl_2}$, and calculate the freezing points of both solutions to see which salt is likely to be more effective at melting ice.

Given: solubilities of two compounds

Asked for: concentrations and freezing points

Strategy:

A. Estimate the solubility of each salt in 100 g of water from Figure 13.9. Determine the number of moles of each in 100 g and calculate the molalities.
B. Determine the concentrations of the dissolved salts in the solutions. Substitute these values into Equation **6.8.4** to calculate the freezing point depressions of the solutions.

Solution:

A From Figure 13.9, we can estimate the solubilities of $\mathbf{NaCl}$ and $\mathbf{CaCl_2}$ to be about 36 g and 60 g, respectively, per 100 g of water at 0°C. The corresponding concentrations in molality are

$$m_{NaCl} = \left(\frac{36\ \cancel{g\ NaCl}}{100\ \cancel{g}\ H_2O}\right)\left(\frac{1\ mol\ NaCl}{58.44\ \cancel{g\ NaCl}}\right)\left(\frac{1000\ \cancel{g}}{1\ kg}\right) = 6.2\ m \tag{6.8.7}$$

$$m_{CaCl_2} = \left(\frac{60\ \cancel{g\ CaCl_2}}{100\ \cancel{g}\ H_2O}\right)\left(\frac{1\ mol\ CaCl_2}{110.98\ \cancel{g\ CaCl_2}}\right)\left(\frac{1000\ \cancel{g}}{1 kg}\right) = 5.4\ m \tag{6.8.8}$$

The lower formula mass of $\mathbf{NaCl}$ more than compensates for its lower solubility, resulting in a saturated solution that has a slightly higher concentration than $\mathbf{CaCl_2}$.

B Because these salts are ionic compounds that dissociate in water to yield two and three ions per formula unit of $\mathbf{NaCl}$ and $\mathbf{CaCl_2}$, respectively, the actual concentrations of the dissolved species in the two saturated solutions are 2 × 6.2 m = 12 m for $\mathbf{NaCl}$ and 3 × 5.4 m = 16 m for $\mathbf{CaCl_2}$. The resulting freezing point depressions can be calculated using Equation **6.8.4**:

$$\mathrm{NaCl}: \Delta T_f = mK_f = (12\ \cancel{m})(1.86°C/\cancel{m}) = 22°C \tag{6.8.9}$$

$$\mathrm{CaCl_2}: \Delta T_f = mK_f = (16\ \cancel{m})(1.86°C/\cancel{m}) = 30°C \tag{6.8.10}$$

Because the freezing point of pure water is 0°C, the actual freezing points of the solutions are −22°C and −30°C, respectively. Note that $\mathbf{CaCl_2}$ is substantially more effective at lowering the freezing point of water because its solutions contain three ions per formula unit. In fact, $\mathbf{CaCl_2}$ is the salt usually sold for home use, and it is also often used on highways.

Because the solubilities of both salts decrease with decreasing temperature, the freezing point can be depressed by only a certain amount, regardless of how much salt is spread on an icy road. If the temperature is significantly below the minimum temperature at which one of these salts will cause ice to melt (say −35°C), there is no point in using salt until it gets warmer

Exercise 6.8.4

Calculate the freezing point of the 30.2% solution of ethylene glycol in water whose vapor pressure and boiling point we calculated in Example **6.8.6**.8 and Example **6.8.6**.10.

Answer

−13.0°C

Example 6.8.5

Arrange these aqueous solutions in order of decreasing freezing points: 0.1 m KCl, 0.1 m glucose, 0.1 m SrCl2, 0.1 m ethylene glycol, 0.1 m benzoic acid, and 0.1 m HCl.

Given: molalities of six solutions

Asked for: relative freezing points

Strategy:

A. Identify each solute as a strong, weak, or nonelectrolyte, and use this information to determine the number of solute particles produced.
B. Multiply this number by the concentration of the solution to obtain the effective concentration of solute particles. The solution with the highest effective concentration of solute particles has the largest freezing point depression.

Solution:

A Because the molal concentrations of all six solutions are the same, we must focus on which of the substances are strong electrolytes, which are weak electrolytes, and which are nonelectrolytes to determine the actual numbers of particles in solution. KCl, $SrCl_2$, and HCl are **strong electrolytes**, producing two, three, and two ions per formula unit, respectively. Benzoic acid is a weak electrolyte (approximately one particle per molecule), and glucose and ethylene glycol are both nonelectrolytes (one particle per molecule).

B The molalities of the solutions in terms of the total particles of solute are: KCl and HCl, 0.2 m; $SrCl_2$, 0.3 m; glucose and ethylene glycol, 0.1 m; and benzoic acid, 0.1–0.2 m. Because the magnitude of the decrease in freezing point is proportional to the concentration of dissolved particles, the order of freezing points of the solutions is: glucose and ethylene glycol (highest freezing point, smallest freezing point depression) > benzoic acid > HCl = KCl > $SrCl_2$.

Exercise 6.8.5

Arrange these aqueous solutions in order of increasing freezing points: 0.2 m $NaCl$, 0.3 m acetic acid, 0.1 m $CaCl_2$, and 0.2 m sucrose.

Answer

0.2 m $NaCl$ (lowest freezing point) < 0.3 m acetic acid ≈ 0.1 m $CaCl_2$ < 0.2 m sucrose (highest freezing point)



Boiling Point Elevation and Freezing Point Depression: https://youtu.be/0MZm1Ay6LhU

Determination of Molar Masses

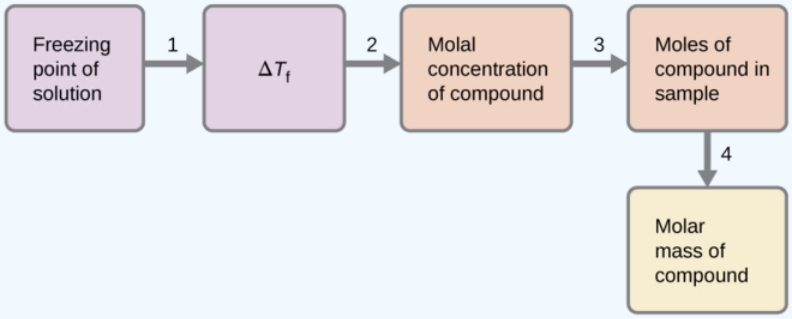
Osmotic pressure and changes in freezing point, boiling point, and vapor pressure are directly proportional to the concentration of solute present. Consequently, we can use a measurement of one of these properties to determine the molar mass of the solute from the measurements.

Determining Molar Mass from Freezing Point Depression

A solution of 4.00 g of a nonelectrolyte dissolved in 55.0 g of benzene is found to freeze at 2.32 °C. What is the molar mass of this compound?

Solution

We can solve this problem using the following steps.



1. *Determine the change in freezing point from the observed freezing point and the freezing point of pure benzene* (Table 6.8.1).

$$\Delta T_f = 5.5\ °C - 2.32\ °C = 3.2\ °C$$

- *Determine the molal concentration from K_f, the freezing point depression constant for benzene* (Table 6.8.1), *and* ΔT_f.

$$\Delta T_f = K_f m$$

$$m = \frac{\Delta T_f}{K_f} = \frac{3.2\ °C}{5.12\ °C m^{-1}} = 0.63\ m$$

- *Determine the number of moles of compound in the solution from the molal concentration and the mass of solvent used to make the solution.*

$$\text{Moles of solute} = \frac{0.62\ \text{mol solute}}{1.00\ \cancel{\text{kg solvent}}} \times 0.0550\ \cancel{\text{kg solvent}} = 0.035\ \text{mol}$$

- *Determine the molar mass from the mass of the solute and the number of moles in that mass.*

$$\text{Molar mass} = \frac{4.00\ \text{g}}{0.034\ \text{mol}} = 1.2 \times 10^2\ \text{g/mol}$$

Exercise 6.8.6

A solution of 35.7 g of a nonelectrolyte in 220.0 g of chloroform has a boiling point of 64.5 °C. What is the molar mass of this compound?

Answer

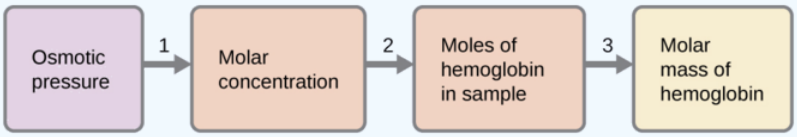
1.8×10^2 g/mol

Determination of a Molar Mass from Osmotic Pressure

A 0.500 L sample of an aqueous solution containing 10.0 g of hemoglobin has an osmotic pressure of 5.9 torr at 22 °C. What is the molar mass of hemoglobin?

Solution

Here is one set of steps that can be used to solve the problem:



1. *Convert the osmotic pressure to atmospheres, then determine the molar concentration from the osmotic pressure.*

$$\Pi = \frac{5.9 \text{ torr} \times 1 \text{ atm}}{760 \text{ torr}} = 7.8 \times 10^{-3} \text{ atm} \tag{6.8.11}$$

$$\Pi = MRT \tag{6.8.12}$$

$$M = \frac{\Pi}{RT} = \frac{7.8 \times 10^{-3} \text{ atm}}{(0.08206 \text{ L atm/mol K})(295 \text{ K})} = 3.2 \times 10^{-4} \text{ M}$$

- *Determine the number of moles of hemoglobin in the solution from the concentration and the volume of the solution.*

$$\text{moles of hemoglobin} = \frac{3.2 \times 10^{-4} \text{ mol}}{1 \cancel{\text{L solution}}} \times 0.500 \cancel{\text{L solution}} = 1.6 \times 10^{-4} \text{ mol}$$

- *Determine the molar mass from the mass of hemoglobin and the number of moles in that mass.*

$$\text{molar mass} = \frac{10.0 \text{ g}}{1.6 \times 10^{-4} \text{ mol}} = 6.2 \times 10^{4} \text{ g/mol}$$

Exercise 6.8.7

What is the molar mass of a protein if a solution of 0.02 g of the protein in 25.0 mL of solution has an osmotic pressure of 0.56 torr at 25 °C?

Answer

2.7×10^4 g/mol



Finding the Molecular Weight of an Unknown using Colligative Properties:

https://youtu.be/faSk2REYy74

Summary

- **vapor pressure lowering**:

$$P_A^0 - P_A = \Delta P_A = X_B P_A^0 \tag{6.8.13}$$

- **vapor pressure of a system containing two volatile components**:

$$P_T = X_A P_A^0 + (1 - X_A) P_B^0 \tag{6.8.14}$$

- **boiling point elevation**:

$$\Delta T_b = m K_b \tag{6.8.15}$$

- **freezing point depression:**

$$\Delta T_f = m K_f \tag{6.8.16}$$

The colligative properties of a solution depend on only the total number of dissolved particles in solution, not on their chemical identity. Colligative properties include vapor pressure, boiling point, freezing point, and osmotic pressure. The addition of a nonvolatile solute (one without a measurable vapor pressure) decreases the vapor pressure of the solvent. The vapor pressure of the solution is proportional to the mole fraction of solvent in the solution, a relationship known as **Raoult's law**. Solutions that obey Raoult's law are called ideal solutions. Most real solutions exhibit positive or negative deviations from Raoult's law. The boiling point elevation (ΔT_b) and freezing point depression (ΔT_f) of a solution are defined as the differences between the boiling and freezing points, respectively, of the solution and the pure solvent. Both are proportional to the molality of the solute.

6.8: Freezing-Point Depression and Boiling-Point Elevation of Nonelectrolyte Solutions is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

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6.9: Solutions of Electrolytes

Thus far we have assumed that we could simply multiply the molar concentration of a solute by the number of ions per formula unit to obtain the actual concentration of dissolved particles in an electrolyte solution. We have used this simple model to predict such properties as freezing points, melting points, vapor pressure, and osmotic pressure. If this model were perfectly correct, we would expect the freezing point depression of a 0.10 m solution of sodium chloride, with 2 mol of ions per mole of $NaCl$ in solution, to be exactly twice that of a 0.10 m solution of glucose, with only 1 mol of molecules per mole of glucose in solution. In reality, this is not always the case. Instead, the observed change in freezing points for 0.10 m aqueous solutions of $NaCl$ and KCl are significantly less than expected (−0.348°C and −0.344°C, respectively, rather than −0.372°C), which suggests that fewer particles than we expected are present in solution.

The relationship between the actual number of moles of solute added to form a solution and the apparent number as determined by colligative properties is called the van't Hoff factor (i) and is defined as follows:Named for Jacobus Hendricus van't Hoff (1852–1911), a Dutch chemistry professor at the University of Amsterdam who won the first Nobel Prize in Chemistry (1901) for his work on thermodynamics and solutions.

$$i = \frac{\text{apparent number of particles in solution}}{\text{number of moles of solute dissolved}} \tag{6.9.1}$$

> As the solute concentration increases the van't Hoff factor decreases.

The van't Hoff factor is therefore a measure of a deviation from ideal behavior. The lower the van 't Hoff factor, the greater the deviation. As the data in Table **6.9.1** show, the van't Hoff factors for ionic compounds are somewhat lower than expected; that is, their solutions apparently contain fewer particles than predicted by the number of ions per formula unit. As the concentration of the solute increases, the van't Hoff factor decreases because ionic compounds generally do not totally dissociate in aqueous solution.

Table **6.9.1**: van 't Hoff Factors for 0.0500 M Aqueous Solutions of Selected Compounds at 25°C

Compound	i (measured)	i (ideal)
glucose	1.0	1.0
sucrose	1.0	1.0
$NaCl$	1.9	2.0
HCl	1.9	2.0
$MgCl_2$	2.7	3.0
$FeCl_3$	3.4	4.0
$Ca(NO_3)_2$	2.5	3.0
$AlCl_3$	3.2	4.0
$MgSO_4$	1.4	2.0

Instead, some of the ions exist as ion pairs, a cation and an anion that for a brief time are associated with each other without an intervening shell of water molecules (Figure **6.9.1**). Each of these temporary units behaves like a single dissolved particle until it dissociates. Highly charged ions such as Mg^{2+}, Al^{3+}, SO_4^{2-}, and PO_4^{3-} have a greater tendency to form ion pairs because of their strong electrostatic interactions. The actual number of solvated ions present in a solution can be determined by measuring a colligative property at several solute concentrations.

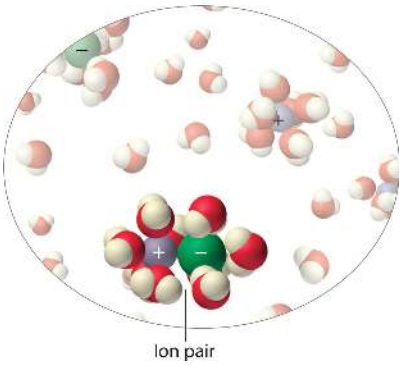


Figure **6.9.1**: Ion Pairs. In concentrated solutions of electrolytes like $NaCl$, some of the ions form neutral ion pairs that are not separated by solvent and diffuse as single particles.

Example 6.9.1: Iron Chloride in Water

A 0.0500 M aqueous solution of $FeCl_3$ has an osmotic pressure of 4.15 atm at 25°C. Calculate the van't Hoff factor i for the solution.

Given: solute concentration, osmotic pressure, and temperature

Asked for: van't Hoff factor

Strategy:

A. Use Equation 13.9.12 to calculate the expected osmotic pressure of the solution based on the effective concentration of dissolved particles in the solvent.
B. Calculate the ratio of the observed osmotic pressure to the expected value. Multiply this number by the number of ions of solute per formula unit, and then use Equation 13.9.1 to calculate the van't Hoff factor.

Solution:

A If $FeCl_3$ dissociated completely in aqueous solution, it would produce four ions per formula unit [Fe3+(aq) plus 3Cl−(aq)] for an effective concentration of dissolved particles of 4 × 0.0500 M = 0.200 M. The osmotic pressure would be

$$\Pi = MRT = (0.200\ mol/L)\,[0.0821\ (L \cdot atm)/(K \cdot mol)]\,(298\ K) = 4.89\ atm \tag{6.9.2}$$

B The observed osmotic pressure is only 4.15 atm, presumably due to ion pair formation. The ratio of the observed osmotic pressure to the calculated value is 4.15 atm/4.89 atm = 0.849, which indicates that the solution contains (0.849)(4) = 3.40 particles per mole of $FeCl_3$ dissolved. Alternatively, we can calculate the observed particle concentration from the osmotic pressure of 4.15 atm:

$$4.15\ atm = M\,[0.0821\ (L \cdot atm)/(K \cdot mol)]\,(298\ K) \tag{6.9.3}$$

$$0.170 mol/L = M \tag{6.9.4}$$

The ratio of this value to the expected value of 0.200 M is 0.170 M/0.200 M = 0.850, which again gives us (0.850)(4) = 3.40 particles per mole of $FeCl_3$ dissolved. From Equation 6.9.1, the van't Hoff factor for the solution is

$$i = \frac{3.40\ \text{particles observed}}{1\ \text{formula unit}\ FeCl_3} = 3.40 \tag{6.9.5}$$

Exercise 6.9.1: Magnesium Chloride in Water

Calculate the van't Hoff factor for a 0.050 m aqueous solution of $MgCl_2$ that has a measured freezing point of −0.25°C.

Answer:

2.7 (versus an ideal value of 3

Key Concepts and Summary

Ionic compounds may not completely dissociate in solution due to **activity** effects, in which case observed colligative effects may be less than predicted.

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6.10: Colloidal Mixtures

A suspension is a heterogeneous mixture of particles of one substance distributed throughout a second phase; the dispersed particles separate from the dispersing phase on standing. In contrast, the particles in a colloid are smaller and do not separate on standing. A colloid can be classified as a sol, a dispersion of solid particles in a liquid or solid; a gel, a semisolid sol in which all of the liquid phase has been absorbed by the solid particles; an aerosol, a dispersion of solid or liquid particles in a gas; or an emulsion, a dispersion of one liquid phase in another. A colloid can be distinguished from a true solution by its ability to scatter a beam of light, known as the Tyndall effect. Hydrophilic colloids contain an outer shell of groups that interact favorably with water, whereas hydrophobic colloids have an outer surface with little affinity for water. Emulsions are prepared by dispersing a hydrophobic liquid in water. In the absence of a dispersed hydrophobic liquid phase, solutions of detergents in water form organized spherical aggregates called micelles. Phospholipids are a class of detergent-like molecules that have two hydrophobic tails attached to a hydrophilic head. A bilayer is a two-dimensional sheet consisting of a double layer of phospholipid molecules arranged tail to tail with a hydrophobic interior and a hydrophilic exterior. Cells are collections of molecules that are surrounded by a phospholipid bilayer called a cell membrane and are able to reproduce themselves.

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SECTION OVERVIEW

6.11: Solubility and Complex-Ion Equilibria

In an aqueous solution, a complex ion exists in equilibrium with it's components, the central metallic ion and the ligands.

Topic hierarchy

6.11.1: Solubility Product Constant, Ksp

6.11.2: Relationship Between Solubility and Ksp

6.11.3: Common-Ion Effect in Solubility Equilibria

6.11.4: Limitations of the Ksp Concept

6.11.5: Criteria for Precipitation and its Completeness

6.11.6: Fractional Precipitation

6.11.7: Solubility and pH

6.11.8: Equilibria Involving Complex Ions

6.11.9: Qualitative Cation Analysis

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6.11.1: Solubility Product Constant, Ksp

Learning Objectives

- To calculate the solubility of an ionic compound from its K_{sp}

We begin our discussion of solubility and complexation equilibria—those associated with the formation of complex ions—by developing quantitative methods for describing dissolution and precipitation reactions of ionic compounds in aqueous solution. Just as with acid–base equilibria, we can describe the concentrations of ions in equilibrium with an ionic solid using an equilibrium constant expression.

The Solubility Product

When a slightly soluble ionic compound is added to water, some of it dissolves to form a solution, establishing an equilibrium between the pure solid and a solution of its ions. For the dissolution of calcium phosphate, one of the two main components of kidney stones, the equilibrium can be written as follows, with the solid salt on the left:

$$Ca_3(PO_4)_{2(s)} \rightleftharpoons 3Ca^{2+}_{(aq)} + 2PO^{3-}_{4(aq)} \tag{6.11.1.1}$$

As you will discover in Section 17.4 and in more advanced chemistry courses, basic anions, such as S^{2-}, PO_4^{3-}, and CO_3^{2-}, react with water to produce OH^- and the corresponding protonated anion. Consequently, their calculated molarities, assuming no protonation in aqueous solution, are only approximate.

The equilibrium constant for the dissolution of a sparingly soluble salt is the **solubility product (K_{sp})** of the salt. Because the concentration of a pure solid such as $Ca_3(PO_4)_2$ is a constant, it does not appear explicitly in the equilibrium constant expression. The equilibrium constant expression for the dissolution of calcium phosphate is therefore

$$K = \frac{[Ca^{2+}]^3[PO_4^{3-}]^2}{[Ca_3(PO_4)_2]} \tag{6.11.1.2}$$

$$[Ca_3(PO_4)_2]K = K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 \tag{6.11.1.3}$$

At 25°C and pH 7.00, Ksp for calcium phosphate is 2.07×10^{-33}, indicating that the concentrations of Ca^{2+} and PO_4^{3-} ions in solution that are in equilibrium with solid calcium phosphate are very low. The values of K_{sp} for some common salts are listed in Table **6.11.1.1**, which shows that the magnitude of K_{sp} varies dramatically for different compounds. Although K_{sp} is not a function of pH in Equations **6.11.1.2** and **6.11.1.3**, changes in pH can affect the solubility of a compound as discussed later.

> *As with any K, the concentration of a pure solid does not appear explicitly in K_{sp}.*

Table **6.11.1.1**: Solubility Products for Selected Ionic Substances at 25°C

Solid	Color	K_{sp}		Solid	Color	K_{sp}
Acetates				**Iodides**		
$Ca(O_2CCH_3)_2 \cdot 3H_2O$	white	4×10^{-3}		Hg_2I_2*	yellow	5.2×10^{-29}
Bromides				PbI_2	yellow	9.8×10^{-9}
AgBr	off-white	5.35×10^{-13}		**Oxalates**		
Hg_2Br_2*	yellow	6.40×10^{-23}		$Ag_2C_2O_4$	white	5.40×10^{-12}
Carbonates				$MgC_2O_4 \cdot 2H_2O$	white	4.83×10^{-6}
$CaCO_3$	white	3.36×10^{-9}		PbC_2O_4	white	4.8×10^{-10}
$PbCO_3$	white	7.40×10^{-14}		**Phosphates**		
Chlorides				Ag_3PO_4	white	8.89×10^{-17}
AgCl	white	1.77×10^{-10}		$Sr_3(PO_4)_2$	white	4.0×10^{-28}
Hg_2Cl_2*	white	1.43×10^{-18}		$FePO_4 \cdot 2H_2O$	pink	9.91×10^{-16}
$PbCl_2$	white	1.70×10^{-5}		**Sulfates**		
Chromates				Ag_2SO_4	white	1.20×10^{-5}
$CaCrO_4$	yellow	7.1×10^{-4}		$BaSO_4$	white	1.08×10^{-10}
$PbCrO_4$	yellow	2.8×10^{-13}		$PbSO_4$	white	2.53×10^{-8}
Fluorides				**Sulfides**		
BaF_2	white	1.84×10^{-7}		Ag_2S	black	6.3×10^{-50}
PbF_2	white	3.3×10^{-8}		CdS	yellow	8.0×10^{-27}
Hydroxides				PbS	black	8.0×10^{-28}
$Ca(OH)_2$	white	5.02×10^{-6}		ZnS	white	1.6×10^{-24}
$Cu(OH)_2$	pale blue	1×10^{-14}				
$Mn(OH)_2$	light pink	1.9×10^{-13}				
$Cr(OH)_3$	gray-green	6.3×10^{-31}				
$Fe(OH)_3$	rust red	2.79×10^{-39}				

*These contain the Hg_2^{2+} ion.



Definition of a Solubility Product: Definition of a Solubility Product(opens in new window) [youtu.be]

Solubility products are determined experimentally by directly measuring either the concentration of one of the component ions or the solubility of the compound in a given amount of water. However, whereas solubility is usually expressed in terms of mass of solute per 100 mL of solvent, K_{sp}, like K, is defined in terms of the molar concentrations of the component ions.



A color photograph of a kidney stone, 8 mm in length. Kidney stones form from sparingly soluble calcium salts and are largely composed of $Ca(O_2CCO_2)\cdot H_2O$ and $Ca_3(PO_4)_2$. from Wikipedia.

Example 6.11.1.1

Calcium oxalate monohydrate [$Ca(O_2CCO_2)\cdot H_2O$, also written as $CaC_2O_4\cdot H_2O$] is a sparingly soluble salt that is the other major component of kidney stones [along with $Ca_3(PO_4)_2$]. Its solubility in water at 25°C is 7.36×10^{-4} g/100 mL. Calculate its K_{sp}.

Given: solubility in g/100 mL

Asked for: K_{sp}

Strategy:

A. Write the balanced dissolution equilibrium and the corresponding solubility product expression.

B. Convert the solubility of the salt to moles per liter. From the balanced dissolution equilibrium, determine the equilibrium concentrations of the dissolved solute ions. Substitute these values into the solubility product expression to calculate K_{sp}.

Solution

A We need to write the solubility product expression in terms of the concentrations of the component ions. For calcium oxalate monohydrate, the balanced dissolution equilibrium and the solubility product expression (abbreviating oxalate as ox^{2-}) are as follows:

$$Ca(O_2CCO_2)\cdot H_2O(s) \rightleftharpoons Ca^{2+}(aq) + {}^{-}O_2CCO_2^{-}(aq) + H_2O(l) \quad K_{sp} = [Ca^{2+}][ox^{2-}]$$

Neither solid calcium oxalate monohydrate nor water appears in the solubility product expression because their concentrations are essentially constant.

B Next we need to determine [Ca^{2+}] and [ox^{2-}] at equilibrium. We can use the mass of calcium oxalate monohydrate that dissolves in 100 mL of water to calculate the number of moles that dissolve in 100 mL of water. From this we can determine the number of moles that dissolve in 1.00 L of water. For dilute solutions, the density of the solution is nearly the same as that of water, so dissolving the salt in 1.00 L of water gives essentially 1.00 L of solution. Because each 1 mol of dissolved calcium oxalate monohydrate dissociates to produce 1 mol of calcium ions and 1 mol of oxalate ions, we can obtain the equilibrium concentrations that must be inserted into the solubility product expression. The number of moles of calcium oxalate monohydrate that dissolve in 100 mL of water is as follows:

$$\frac{7.36 \times 10^{-4}\ \text{g}}{146.1\ \text{g/mol}} = 5.04 \times 10^{-6}\ \text{mol}\ \text{Ca}(\text{O}_2\text{CCO}_2) \cdot \text{H}_2\text{O}$$

The number of moles of calcium oxalate monohydrate that dissolve in 1.00 L of the saturated solution is as follows:

$$\left(\frac{5.04 \times 10^{-6}\ \text{mol}\ \text{Ca}(\text{O}_2\text{CCO}_2\cdot)\text{H}_2\text{O}}{100\ \text{mL}}\right)\left(\frac{1000\ \text{mL}}{1.00\ \text{L}}\right) = 5.04 \times 10^{-5}\ \text{mol/L} = 5.04 \times 10^{-5}\ \text{M}$$

Because of the stoichiometry of the reaction, the concentration of Ca^{2+} and ox^{2-} ions are both 5.04×10^{-5} M. Inserting these values into the solubility product expression,

$$K_{sp} = [Ca^{2+}][ox^{2-}] = (5.04 \times 10^{-5})(5.04 \times 10^{-5}) = 2.54 \times 10^{-9}$$

In our calculation, we have ignored the reaction of the weakly basic anion with water, which tends to make the actual solubility of many salts greater than the calculated value.

? Exercise 6.11.1.1: Calcite

One crystalline form of calcium carbonate ($CaCO_3$) is "calcite", found as both a mineral and a structural material in many organisms. Calcite is found in the teeth of sea urchins. The urchins create depressions in limestone that they can settle in by grinding the rock with their teeth. Limestone, however, also consists of calcite, so how can the urchins grind the rock without also grinding their teeth? Researchers have discovered that the teeth are shaped like needles and plates and contain magnesium. The concentration of magnesium increases toward the tip, which contributes to the hardness. Moreover, each tooth is composed of two blocks of the polycrystalline calcite matrix that are interleaved near the tip. This creates a corrugated surface that presumably increases grinding efficiency. Toolmakers are particularly interested in this approach to grinding.



A crystal of calcite ($CaCO_3$), illustrating the phenomenon of double refraction. When a transparent crystal of calcite is placed over a page, we see two images of the letters. from Wikipedia

The solubility of calcite in water is 0.67 mg/100 mL. Calcite its K_{sp}.

Answer

4.5×10^{-9}

> *The reaction of weakly basic anions with H_2O tends to make the actual solubility of many salts higher than predicted.*



Finding Ksp from Ion Concentrations: Finding Ksp from Ion Concentrations(opens in new window) [youtu.be]

Tabulated values of K_{sp} can also be used to estimate the solubility of a salt with a procedure that is essentially the reverse of the one used in Example 6.11.1.1. In this case, we treat the problem as a typical equilibrium problem and set up a table of initial concentrations, changes in concentration, and final concentrations (ICE Tables), remembering that the concentration of the pure solid is essentially constant.

Example 6.11.1.2

We saw that the K_{sp} for $Ca_3(PO_4)_2$ is 2.07×10^{-33} at 25°C. Calculate the aqueous solubility of $Ca_3(PO_4)_2$ in terms of the following:

a. the molarity of ions produced in solution
b. the mass of salt that dissolves in 100 mL of water at 25°C

Given: K_{sp}

Asked for: molar concentration and mass of salt that dissolves in 100 mL of water

Strategy:

A. Write the balanced equilibrium equation for the dissolution reaction and construct a table showing the concentrations of the species produced in solution. Insert the appropriate values into the solubility product expression and calculate the molar solubility at 25°C.
B. Calculate the mass of solute in 100 mL of solution from the molar solubility of the salt. Assume that the volume of the solution is the same as the volume of the solvent.

Solution:

A. **A** The dissolution equilibrium for $Ca_3(PO_4)_2$ (Equation 6.11.1.2) is shown in the following ICE table. Because we are starting with distilled water, the initial concentration of both calcium and phosphate ions is zero. For every 1 mol of $Ca_3(PO_4)_2$ that dissolves, 3 mol of Ca^{2+} and 2 mol of PO_4^{3-} ions are produced in solution. If we let x equal the solubility of $Ca_3(PO_4)_2$ in moles per liter, then the change in $[Ca^{2+}]$ will be $+3x$, and the change in $[PO_4^{3-}]$ will be $+2x$. We can insert these values into the table.

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$$

Solutions to Example 17.4.2

	Ca3(PO4)2	[Ca2+]	$[PO_4^{3-}]$
initial	pure solid	0	0
change	—	$+3x$	$+2x$
final	pure solid	$3x$	$2x$

Although the amount of solid $Ca_3(PO_4)_2$ changes as some of it dissolves, its molar concentration does not change. We now insert the expressions for the equilibrium concentrations of the ions into the solubility product expression (Equation 17.2):

$$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 = (3x)^3(2x)^2 \quad (6.11.1.4)$$

$$2.07 \times 10^{-33} = 108x^5 \quad (6.11.1.5)$$

$$1.92 \times 10^{-35} = x^5 \quad (6.11.1.6)$$

$$1.14 \times 10^{-7}\ \text{M} = x \quad (6.11.1.7)$$

This is the molar solubility of calcium phosphate at 25°C. However, the molarity of the ions is 2*x* and 3*x*, which means that $[PO_4^{3-}] = 2.28 \times 10^{-7}$ and $[Ca^{2+}] = 3.42 \times 10^{-7}$.

b. **B** To find the mass of solute in 100 mL of solution, we assume that the density of this dilute solution is the same as the density of water because of the low solubility of the salt, so that 100 mL of water gives 100 mL of solution. We can then determine the amount of salt that dissolves in 100 mL of water:

$$\left(\frac{1.14 \times 10^{-7}\ \text{mol}}{1\ \text{L}}\right) 100\ \text{mL} \left(\frac{1\ \text{L}}{1000\ \text{mL}}\right) \left(\frac{310.18\ \text{g}\ Ca_3(PO_4)_2}{1\ \text{mol}}\right) = 3.54 \times 10^{-6}\ \text{g}\ Ca_3(PO_4)_2$$

? Exercise 6.11.1.2

The solubility product of silver carbonate (Ag_2CO_3) is 8.46×10^{-12} at 25°C. Calculate the following:

a. the molarity of a saturated solution
b. the mass of silver carbonate that will dissolve in 100 mL of water at this temperature

Answer

a. 1.28×10^{-4} M
b. 3.54 mg



Finding the Solubility of a Salt: Finding the Solubility of a Salt (opens in new window) [youtu.be]

The Ion Product

The **ion product (*Q*)** of a salt is the product of the concentrations of the ions in solution raised to the same powers as in the solubility product expression. It is analogous to the reaction quotient (*Q*) discussed for gaseous equilibria. Whereas K_{sp} describes equilibrium concentrations, the ion product describes concentrations that are not necessarily equilibrium concentrations.

> *The ion product Q is analogous to the reaction quotient Q for gaseous equilibria.*

As summarized in Figure **6.11.1.1**, there are three possible conditions for an aqueous solution of an ionic solid:

- $Q < K_{sp}$. The solution is unsaturated, and more of the ionic solid, if available, will dissolve.
- $Q = K_{sp}$. The solution is saturated and at equilibrium.

- $Q > K_{sp}$. The solution is supersaturated, and ionic solid will precipitate.

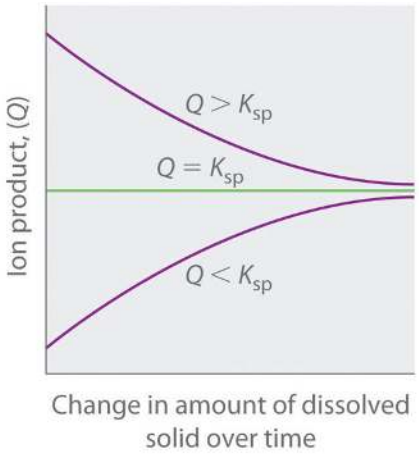


Figure **6.11.1.1**: The Relationship between Q and K_{sp}. If Q is less than K_{sp}, the solution is unsaturated and more solid will dissolve until the system reaches equilibrium ($Q = K_{sp}$). If Q is greater than K_{sp}, the solution is supersaturated and solid will precipitate until $Q = K_{sp}$. If $Q = K_{sp}$, the rate of dissolution is equal to the rate of precipitation; the solution is saturated, and no net change in the amount of dissolved solid will occur.

Graph of ion product against change in amount of dissolved solid over time. The purple curves are when Q is greater or less than Ksp. The green line is when Q is equal to Ksp.

The process of calculating the value of the ion product and comparing it with the magnitude of the solubility product is a straightforward way to determine whether a solution is unsaturated, saturated, or supersaturated. More important, the ion product tells chemists whether a precipitate will form when solutions of two soluble salts are mixed.

Example 6.11.1.3

We mentioned that barium sulfate is used in medical imaging of the gastrointestinal tract. Its solubility product is 1.08×10^{-10} at 25°C, so it is ideally suited for this purpose because of its low solubility when a "barium milkshake" is consumed by a patient. The pathway of the sparingly soluble salt can be easily monitored by x-rays. Will barium sulfate precipitate if 10.0 mL of 0.0020 M Na_2SO_4 is added to 100 mL of 3.2×10^{-4} M $BaCl_2$? Recall that NaCl is highly soluble in water.

Given: K_{sp} and volumes and concentrations of reactants

Asked for: whether precipitate will form

Strategy:

A. Write the balanced equilibrium equation for the precipitation reaction and the expression for K_{sp}.

B. Determine the concentrations of all ions in solution when the solutions are mixed and use them to calculate the ion product (Q).

C. Compare the values of Q and K_{sp} to decide whether a precipitate will form.

Solution

A The only slightly soluble salt that can be formed when these two solutions are mixed is $BaSO_4$ because NaCl is highly soluble. The equation for the precipitation of $BaSO_4$ is as follows:

$$BaSO_{4(s)} \rightleftharpoons Ba^{2+}_{(aq)} + SO^{2-}_{4(aq)}$$

The solubility product expression is as follows:

$$K_{sp} = [Ba^{2+}][SO_4^{2-}] = 1.08 \times 10^{-10}$$

B To solve this problem, we must first calculate the ion product—$Q = [Ba^{2+}][SO_4^{2-}]$—using the concentrations of the ions that are present after the solutions are mixed and before any reaction occurs. The concentration of Ba^{2+} when the solutions are mixed is the total number of moles of Ba^{2+} in the original 100 mL of $BaCl_2$ solution divided by the final volume (100 mL + 10.0 mL = 110 mL):

$$\text{moles } Ba^{2+} = 100 \text{ mL}\left(\frac{1 \text{ L}}{1000 \text{ mL}}\right)\left(\frac{3.2 \times 10^{-4} \text{ mol}}{1 \text{ L}}\right) = 3.2 \times 10^{-5} \text{ mol } Ba^{2+}$$

$$[Ba^{2+}] = \left(\frac{3.2 \times 10^{-5} \text{ mol } Ba^{2+}}{110 \text{ mL}}\right)\left(\frac{1000 \text{ mL}}{1 \text{ L}}\right) = 2.9 \times 10^{-4} \text{ M } Ba^{2+}$$

Similarly, the concentration of SO_4^{2-} after mixing is the total number of moles of SO_4^{2-} in the original 10.0 mL of Na_2SO_4 solution divided by the final volume (110 mL):

$$\text{moles } SO_4^{2-} = 10.0 \text{ mL}\left(\frac{1 \text{ L}}{1000 \text{ mL}}\right)\left(\frac{0.0020 \text{ mol}}{1 \text{ L}}\right) = 2.0 \times 10^{-5} \text{ mol } SO_4^{2-}$$

$$[SO_4^{2-}] = \left(\frac{2.0 \times 10^{-5} \text{ mol } SO_4^{2-}}{110 \text{ mL}}\right)\left(\frac{1000 \text{ mL}}{1 \text{ L}}\right) = 1.8 \times 10^{-4} \text{ M } SO_4^{2-}$$

We can now calculate Q:

$$Q = [Ba^{2+}][SO_4^{2-}] = (2.9\times10^{-4})(1.8\times10^{-4}) = 5.2\times10^{-8}$$

C We now compare Q with the K_{sp}. If $Q > K_{sp}$, then $BaSO_4$ will precipitate, but if $Q < K_{sp}$, it will not. Because $Q > K_{sp}$, we predict that $BaSO_4$ will precipitate when the two solutions are mixed. In fact, $BaSO_4$ will continue to precipitate until the system reaches equilibrium, which occurs when $[Ba^{2+}][SO_4^{2-}] = K_{sp} = 1.08 \times 10^{-10}$.

? Exercise 6.11.1.3

The solubility product of calcium fluoride (CaF_2) is 3.45×10^{-11}. If 2.0 mL of a 0.10 M solution of NaF is added to 128 mL of a 2.0×10^{-5}M solution of $Ca(NO_3)_2$, will CaF_2 precipitate?

Answer

yes ($Q = 4.7 \times 10^{-11} > K_{sp}$)



Determining if a Precipitate forms (The Ion Product): Determining if a Precipitate forms (The Ion Product)(opens in new window) [youtu.be]

The Common Ion Effect and Solubility

The solubility product expression tells us that the equilibrium concentrations of the cation and the anion are inversely related. That is, as the concentration of the anion increases, the maximum concentration of the cation needed for precipitation to occur decreases—and vice versa—so that K_{sp} is constant. Consequently, the solubility of an ionic compound depends on the concentrations of other salts that contain the same ions. Adding a common cation or anion shifts a solubility equilibrium in the direction predicted by Le Chatelier's principle. As a result, the solubility of any sparingly soluble salt is almost always decreased by the presence of a soluble salt that contains a common ion. The exceptions generally involve the formation of complex ions, which is discussed later.

Consider, for example, the effect of adding a soluble salt, such as $CaCl_2$, to a saturated solution of calcium phosphate [$Ca_3(PO_4)_2$]. We have seen that the solubility of $Ca_3(PO_4)_2$ in water at 25°C is 1.14×10^{-7} M ($K_{sp} = 2.07 \times 10^{-33}$). Thus a saturated solution of

$Ca_3(PO_4)_2$ in water contains $3 \times (1.14 \times 10^{-7}\ M) = 3.42 \times 10^{-7}\ M\ Ca^{2+}$ and $2 \times (1.14 \times 10^{-7}\ M) = 2.28 \times 10^{-7}\ M\ PO_4^{3-}$, according to the stoichiometry shown in Equation 6.11.1.1 (neglecting hydrolysis to form HPO_4^{2-} as described in Chapter 16). If $CaCl_2$ is added to a saturated solution of $Ca_3(PO_4)_2$, the Ca^{2+} ion concentration will increase such that $[Ca^{2+}] > 3.42 \times 10^{-7}\ M$, making $Q > K_{sp}$. The only way the system can return to equilibrium is for the reaction in Equation 6.11.1.1 to proceed to the left, resulting in precipitation of $Ca_3(PO_4)_2$. This will decrease the concentration of both Ca^{2+} and PO_4^{3-} until $Q = K_{sp}$.

> *The common ion effect usually **decreases** the solubility of a sparingly soluble salt.*

Example 6.11.1.4

Calculate the solubility of calcium phosphate [$Ca_3(PO_4)_2$] in 0.20 M $CaCl_2$.

Given: concentration of $CaCl_2$ solution

Asked for: solubility of $Ca_3(PO_4)_2$ in $CaCl_2$ solution

Strategy:

A. Write the balanced equilibrium equation for the dissolution of $Ca_3(PO_4)_2$. Tabulate the concentrations of all species produced in solution.

B. Substitute the appropriate values into the expression for the solubility product and calculate the solubility of $Ca_3(PO_4)_2$.

Solution

A The balanced equilibrium equation is given in the following table. If we let x equal the solubility of $Ca_3(PO_4)_2$ in moles per liter, then the change in $[Ca^{2+}]$ is once again $+3x$, and the change in $[PO_4^{3-}]$ is $+2x$. We can insert these values into the ICE table.

$$Ca_3(PO_4)_{2(s)} \rightleftharpoons 3Ca^{2+}_{(aq)} + 2PO^{3-}_{4(aq)}$$

Solutions to Example 17.4.4

	Ca3(PO4)2	$[Ca^{2+}]$	$[PO_4^{3-}]$
initial	pure solid	0.20	0
change	—	$+3x$	$+2x$
final	pure solid	$0.20 + 3x$	$2x$

B The K_{sp} expression is as follows:

$$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 = (0.20 + 3x)^3(2x)^2 = 2.07 \times 10^{-33}$$

Because $Ca_3(PO_4)_2$ is a sparingly soluble salt, we can reasonably expect that $x << 0.20$. Thus $(0.20 + 3x)$ M is approximately 0.20 M, which simplifies the K_{sp} expression as follows:

$$\begin{aligned} K_{sp} = (0.20)^3(2x)^2 &= 2.07 \times 10^{-33} \\ x^2 &= 6.5 \times 10^{-32} \\ x &= 2.5 \times 10^{-16}\ M \end{aligned}$$

This value is the solubility of $Ca_3(PO_4)_2$ in 0.20 M $CaCl_2$ at 25°C. It is approximately nine orders of magnitude less than its solubility in pure water, as we would expect based on Le Chatelier's principle. With one exception, this example is identical to Example **6.11.1.2**—here the initial $[Ca^{2+}]$ was 0.20 M rather than 0.

Exercise 6.11.1.4

Calculate the solubility of silver carbonate in a 0.25 M solution of sodium carbonate. The solubility of silver carbonate in pure water is 8.45×10^{-12} at 25°C.

Answer

2.9×10^{-6} M (versus 1.3×10^{-4} M in pure water)



The Common Ion Effect in Solubility Products: The Common Ion Effect in Solubility Products(opens in new window) [youtu.be]

Summary

The solubility product (K_{sp}) is used to calculate equilibrium concentrations of the ions in solution, whereas the ion product (Q) describes concentrations that are not necessarily at equilibrium. The equilibrium constant for a dissolution reaction, called the solubility product (K_{sp}), is a measure of the solubility of a compound. Whereas solubility is usually expressed in terms of mass of solute per 100 mL of solvent, K_{sp} is defined in terms of the molar concentrations of the component ions. In contrast, the ion product (Q) describes concentrations that are not necessarily equilibrium concentrations. Comparing Q and K_{sp} enables us to determine whether a precipitate will form when solutions of two soluble salts are mixed. Adding a common cation or common anion to a solution of a sparingly soluble salt shifts the solubility equilibrium in the direction predicted by Le Chatelier's principle. The solubility of the salt is almost always decreased by the presence of a common ion.

6.11.1: Solubility Product Constant, Ksp is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

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6.11.2: Relationship Between Solubility and Ksp

Learning Objectives

- Quantitatively related K_{sp} to solubility

Considering the relation between solubility and K_{sp} is important when describing the solubility of slightly ionic compounds. However, this article discusses ionic compounds that are difficult to dissolve; they are considered "slightly soluble" or "almost insoluble." Solubility product constants (K_{sq}) are given to those solutes, and these constants can be used to find the molar solubility of the compounds that make the solute. This relationship also facilitates finding the K_{sq} of a slightly soluble solute from its solubility.

Introduction

Recall that the definition of *solubility* is the maximum possible concentration of a solute in a solution at a given temperature and pressure. We can determine the solubility product of a slightly soluble solid from that measure of its solubility at a given temperature and pressure, provided that the only significant reaction that occurs when the solid dissolves is its dissociation into solvated ions, that is, the only equilibrium involved is:

$$\mathrm{M_pX_q}(s) \rightleftharpoons p\mathrm{M^{m+}}(aq) + q\mathrm{X^{n-}}(aq) \tag{6.11.2.1}$$

In this case, we calculate the solubility product by taking the solid's solubility expressed in units of moles per liter (mol/L), known as its **molar solubility**.

Calculation of K_{sp} from Equilibrium Concentrations

We began the chapter with an informal discussion of how the mineral fluorite is formed. Fluorite, $\mathrm{CaF_2}$, is a slightly soluble solid that dissolves according to the equation:

$$\mathrm{CaF_2}(s) \rightleftharpoons \mathrm{Ca^{2+}}(aq) + 2\,\mathrm{F^-}(aq)$$

The concentration of Ca^{2+} in a saturated solution of CaF_2 is 2.1×10^{-4} *M*; therefore, that of F^- is 4.2×10^{-4} *M*, that is, twice the concentration of $\mathrm{Ca^{2+}}$. What is the solubility product of fluorite?

Solution

First, write out the K_{sp} expression, then substitute in concentrations and solve for K_{sp}:

$$\mathrm{CaF_2\,(s) \rightleftharpoons Ca^{2+}\,(aq) + 2\,F^-\,(aq)}$$

A saturated solution is a solution at equilibrium with the solid. Thus:

$$\begin{aligned} K_{sp} &= [\mathrm{Ca^{2+}}][\mathrm{F^-}]^2 \\ &= (2.1 \times 10^{-4})(4.2 \times 10^{-4})^2 \\ &= 3.7 \times 10^{-11} \end{aligned}$$

As with other equilibrium constants, we do not include units with K_{sp}.

Exercise 6.11.2.1

In a saturated solution that is in contact with solid $Mg(OH)_2$, the concentration of Mg^{2+} is 3.7×10^{-5} *M*. What is the solubility product for $Mg(OH)_2$?

$$\mathrm{Mg(OH)_2}(s) \rightleftharpoons \mathrm{Mg^{2+}}(aq) + 2\,\mathrm{OH^-}(aq)$$

Answer

2.0×10^{-13}

Determination of Molar Solubility from K_{sp}

The K_{sp} of copper(I) bromide, **CuBr**, is 6.3×10^{-9}. Calculate the molar solubility of copper bromide.

Solution

The solubility product constant of copper(I) bromide is 6.3×10^{-9}.

The reaction is:

$$\mathrm{CuBr}(s) \rightleftharpoons \mathrm{Cu}^{+}(aq) + \mathrm{Br}^{-}(aq)$$

First, write out the solubility product equilibrium constant expression:

$$K_{sp} = [\mathrm{Cu}^{+}][\mathrm{Br}^{-}]$$

Create an ICE table (as introduced in the chapter on fundamental equilibrium concepts), leaving the **CuBr** column empty as it is a solid and does not contribute to the K_{sp}:

	CuBr $\rightleftharpoons$	Cu^+	+ Br^-
Initial concentration (*M*)		0	0
Change (*M*)		*x*	*x*
Equilibrium concentration (*M*)		0 + *x* = *x*	0 + *x* = *x*

At equilibrium:

$$K_{sp} = [\mathrm{Cu}^{+}][\mathrm{Br}^{-}]$$
$$6.3 \times 10^{-9} = (x)(x) = x^2$$
$$x = \sqrt{(6.3 \times 10^{-9})} = 7.9 \times 10^{-5}$$

Therefore, the molar solubility of **CuBr** is 7.9×10^{-5} *M*.



Finding the Solubility of a Salt: https://youtu.be/98BuldrICXM

Summary

Solubility is defined as the maximum amount of solute that can be dissolved in a solvent at equilibrium. Equilibrium is the state at which the concentrations of products and reactant are constant after the reaction has taken place. The solubility product constant (K_{sp}) describes the equilibrium between a solid and its constituent ions in a solution. The value of the constant identifies the degree to which the compound can dissociate in water. The higher the K_{sp}, the more soluble the compound is. K_{sq} is defined in terms of activity rather than concentration because it is a measure of a concentration that depends on certain conditions such as temperature, pressure, and composition. It is influenced by surroundings. K_{sp} is used to describe the saturated solution of ionic compounds. (A saturated solution is in a state of equilibrium between the dissolved, dissociated, undissolved solid, and the ionic compound.)

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6.11.3: Common-Ion Effect in Solubility Equilibria

Learning Objectives

- Recognize common ions from various salts, acids, and bases.
- Calculate concentrations involving common ions.
- Calculate ion concentrations involving chemical equilibrium.

The common-ion effect is used to describe the effect on an equilibrium involving a substance that adds an ion that is a part of the equilibrium.

Introduction

The solubility products K_{sp}'s are equilibrium constants in hetergeneous equilibria (i.e., between two different phases). If several salts are present in a system, they all ionize in the solution. If the salts contain a common cation or anion, these salts contribute to the concentration of the common ion. Contributions from all salts must be included in the calculation of concentration of the common ion. For example, a solution containing sodium chloride and potassium chloride will have the following relationship:

$$[\mathrm{Na^+}] + [\mathrm{K^+}] = [\mathrm{Cl^-}] \tag{6.11.3.1}$$

Consideration of *charge balance* or *mass balance* or both leads to the same conclusion. The solubility product expression tells us that the equilibrium concentrations of the cation and the anion are inversely related. That is, as the concentration of the anion increases, the maximum concentration of the cation needed for precipitation to occur decreases—and vice versa—so that K_{sp} is constant. Consequently, the solubility of an ionic compound depends on the concentrations of other salts that contain the same ions. Adding a common cation or anion shifts a solubility equilibrium in the direction predicted by Le Chatelier's principle. As a result, the solubility of any sparingly soluble salt is almost always decreased by the presence of a soluble salt that contains a common ion. The exceptions generally involve the formation of complex ions, which is discussed later.

Common Ions

When NaCl and KCl are dissolved in the same solution, the $\mathrm{Cl^-}$ ions are *common* to both salts. In a system containing NaCl and KCl, the $\mathrm{Cl^-}$ ions are common ions.

$$\mathrm{NaCl} \rightleftharpoons \mathrm{Na^+} + \mathrm{Cl^-}$$
$$\mathrm{KCl} \rightleftharpoons \mathrm{K^+} + \mathrm{Cl^-}$$
$$\mathrm{CaCl_2} \rightleftharpoons \mathrm{Ca^{2+}} + 2\mathrm{Cl^-}$$
$$\mathrm{AlCl_3} \rightleftharpoons \mathrm{Al^{3+}} + 3\mathrm{Cl^-}$$
$$\mathrm{AgCl} \rightleftharpoons \mathrm{Ag^+} + \mathrm{Cl^-}$$

For example, when AgCl is dissolved into a solution already containing NaCl (actually $\mathrm{Na^+}$ and $\mathrm{Cl^-}$ ions), the $\mathrm{Cl^-}$ ions come from the ionization of both AgCl and NaCl. Thus, $[\mathrm{Cl^-}]$ differs from $[\mathrm{Ag^+}]$. The following examples show how the concentration of the common ion is calculated.

Example 6.11.3.1

What are $[\mathrm{Na^+}]$, $[\mathrm{Cl^-}]$, $[\mathrm{Ca^{2+}}]$, and $[\mathrm{H^+}]$ in a solution containing 0.10 M each of NaCl, $\mathrm{CaCl_2}$, and HCl?

Solution

Due to the conservation of ions, we have

$$[\mathrm{Na^+}] = [\mathrm{Ca^{2+}}] = [\mathrm{H^+}] = 0.10\ \mathrm{M}.$$

but

$$\begin{aligned}[\mathrm{Cl^-}] = &\ 0.10\ (\text{due to NaCl}) \\ &+ 0.20\ (\text{due to } \mathrm{CaCl_2}) \\ &+ 0.10\ (\text{due to HCl}) \\ = &\ 0.40\ \mathrm{M}\end{aligned}$$

? Exercise 6.11.3.1

John poured 10.0 mL of 0.10 M **NaCl**, 10.0 mL of 0.10 M **KOH**, and 5.0 mL of 0.20 M **HCl** solutions together and then he made the total volume to be 100.0 mL. What is $[\mathrm{Cl^-}]$ in the final solution?

$$[\mathrm{Cl^-}] = \frac{0.1\ \mathrm{M} \times 10\ \mathrm{mL} + 0.2\ \mathrm{M} \times 5.0\ \mathrm{mL}}{100.0\ \mathrm{mL}} = 0.020\ \mathrm{M}$$

Le Châtelier's Principle states that if an equilibrium becomes unbalanced, the reaction will shift to restore the balance. If a common ion is added to a weak acid or weak base equilibrium, then the equilibrium will shift towards the reactants, in this case the weak acid or base.

✓ Example 6.11.3.2

Consider the lead(II) ion concentration in this *saturated* solution of $PbCl_2$. The balanced reaction is

$$PbCl_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2Cl^-_{(aq)}$$

Defining s as the concentration of dissolved lead(II) chloride, then:

$$[Pb^{2+}] = s$$

$$[Cl^-] = 2s$$

These values can be substituted into the solubility product expression, which can be solved for s:

$$\begin{aligned}K_{sp} &= [Pb^{2+}][Cl^-]^2 \\ &= s \times (2s)^2 \\ 1.7 \times 10^{-5} &= 4s^3 \\ s^3 &= \frac{1.7 \times 10^{-5}}{4} \\ &= 4.25 \times 10^{-6} \\ s &= \sqrt[3]{4.25 \times 10^{-6}} \\ &= 1.62 \times 10^{-2}\ mol\ dm^{-3}\end{aligned}$$

The concentration of lead(II) ions in the solution is 1.62 x 10^{-2} M. Consider what happens if sodium chloride is added to this saturated solution. Sodium chloride shares an ion with lead(II) chloride. The chloride ion is **common** to both of them; this is the origin of the term "common ion effect".

Look at the original equilibrium expression again:

$$PbCl_2\ (s) \rightleftharpoons Pb^{2+}\ (aq) + 2Cl^-\ (aq)$$

What happens to that equilibrium if extra chloride ions are added? According to *Le* Châtelier, the position of equilibrium will shift to counter the change, in this case, by removing the chloride ions by making extra solid lead(II) chloride.

Of course, the concentration of lead(II) ions in the solution is so small that only a tiny proportion of the extra chloride ions can be converted into solid lead(II) chloride. The lead(II) chloride becomes even *less soluble*, and the concentration of lead(II) ions in the solution *decreases*. This type of response occurs with any sparingly soluble substance: it is less soluble in a solution which contains any ion which it has in common. This is the common ion effect.

A Simple Example

If an attempt is made to dissolve some lead(II) chloride in some 0.100 M sodium chloride solution instead of in water, what is the equilibrium concentration of the lead(II) ions this time? As before, define s to be the concentration of the lead(II) ions.

$$[Pb^{2+}] = s \tag{6.11.3.2}$$

The calculations are different from before. This time the concentration of the chloride ions is governed by the concentration of the sodium chloride solution. The number of ions coming from the lead(II) chloride is going to be tiny compared with the 0.100 M coming from the sodium chloride solution. In calculations like this, it can be assumed that the concentration of the common ion is entirely due to the other solution. This simplifies the calculation.

So we assume:

$$[Cl^-] = 0.100\ M \tag{6.11.3.3}$$

The rest of the mathematics looks like this:

$$\begin{aligned} K_{sp} &= [Pb^{2+}][Cl^-]^2 \\ &= s \times (0.100)^2 \\ 1.7 \times 10^{-5} &= s \times 0.00100 \end{aligned} \tag{6.11.3.4}$$

therefore:

$$\begin{aligned} s &= \frac{1.7 \times 10^{-5}}{0.0100} \\ &= 1.7 \times 10^{-3}\ \text{M} \end{aligned} \tag{6.11.3.5}$$

Finally, compare that value with the simple saturated solution:

Original solution:

$$[Pb^{2+}] = 0.0162\ M \tag{6.11.3.6}$$

Solution in 0.100 M NaCl solution:

$$[Pb^{2+}] = 0.0017\ M \tag{6.11.3.7}$$

The concentration of the lead(II) ions has decreased by a factor of about 10. If more concentrated solutions of sodium chloride are used, the solubility decreases further.

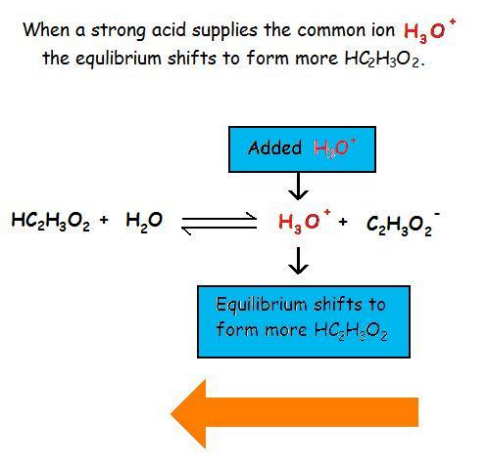
> Adding a common ion to a system at equilibrium affects the equilibrium composition, but **not** the ionization constant.

Common Ion Effect with Weak Acids and Bases

Adding a common ion prevents the weak acid or weak base from ionizing as much as it would without the added common ion. The common ion effect suppresses the ionization of a weak acid by adding more of an ion that is a product of this equilibrium.

Example 6.11.3.3

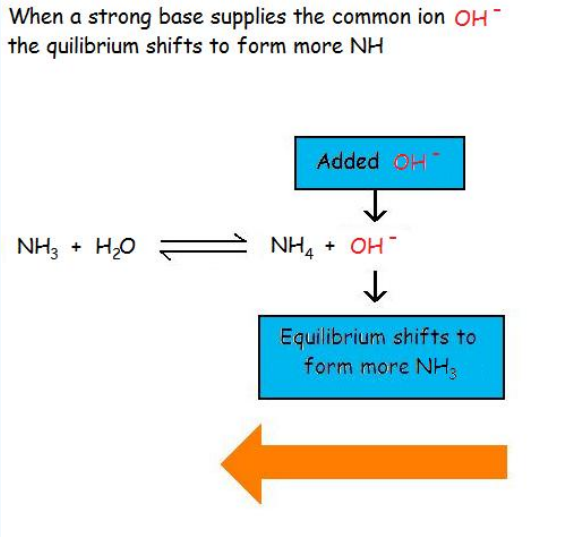
The common ion effect of H_3O^+ on the ionization of acetic acid



The common ion effect suppresses the ionization of a weak base by adding more of an ion that is a product of this equilibrium.

Example 6.11.3.4

Consider the common ion effect of OH^- on the ionization of ammonia



Adding the common ion of hydroxide shifts the reaction towards the left to decrease the stress (in accordance with Le Châtelier's Principle), forming more reactants. This decreases the reaction quotient, because the reaction is being pushed towards the left to reach equilibrium. The equilibrium constant, $K_b = 1.8 \times 10^{-5}$, does not change. The reaction is put out of balance, or equilibrium.

$$Q_a = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

At first, when more hydroxide is added, the quotient is greater than the equilibrium constant. The reaction then shifts right, causing the denominator to increase, decreasing the reaction quotient and pulling towards equilibrium and causing Q to decrease towards K.

Common Ion Effect on Solubility

Consider, for example, the effect of adding a soluble salt, such as $CaCl_2$, to a saturated solution of calcium phosphate [$Ca_3(PO_4)_2$].

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3\,Ca^{2+}(aq) + 2\,PO_4^{3-}(aq) \qquad (6.11.3.8)$$

We have seen that the solubility of $Ca_3(PO_4)_2$ in water at 25°C is 1.14×10^{-7} M ($K_{sp} = 2.07 \times 10^{-33}$). Thus a saturated solution of $Ca_3(PO_4)_2$ in water contains

$$3 \times (1.14 \times 10^{-7}\,M) = 3.42 \times 10^{-7}\,M\,Ca^{2+} \tag{6.11.3.9}$$

and

$$2 \times (1.14 \times 10^{-7}\,M) = 2.28 \times 10^{-7}\,M\,PO_4^{3-} \tag{6.11.3.10}$$

according to the stoichiometry shown in Equation 6.11.3.8 (neglecting hydrolysis to form HPO_4^{2-}). If $CaCl_2$ is added to a saturated solution of $Ca_3(PO_4)_2$, the Ca^{2+} ion concentration will increase such that $[Ca^{2+}] > 3.42 \times 10^{-7}$ M, making $Q > K_{sp}$. The only way the system can return to equilibrium is for the reaction in Equation 6.11.3.8 to proceed to the left, resulting in precipitation of $Ca_3(PO_4)_2$. This will decrease the concentration of both Ca^{2+} and PO_4^{3-} until $Q = K_{sp}$.

> *Adding a common ion decreases solubility, as the reaction shifts toward the left to relieve the stress of the excess product. Adding a common ion to a dissociation reaction causes the equilibrium to shift left, toward the reactants, causing precipitation.*

Example 6.11.3.5

Consider the reaction:

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$

What happens to the solubility of $PbCl_2$(s) when 0.1 M NaCl is added?

Solution

$$K_{sp} = 1.7 \times 10^{-5}$$

$$Q_{sp} = 1.8 \times 10^{-5}$$

Identify the common ion: Cl^-

Notice: $Q_{sp} > K_{sp}$ The addition of NaCl has caused the reaction to shift out of equilibrium because there are more dissociated ions. Typically, solving for the molarities requires the assumption that the solubility of $PbCl_2$ is equivalent to the concentration of Pb^{2+} produced because they are in a 1:1 ratio.

Because K_{sp} for the reaction is 1.7×10^{-5}, the overall reaction would be $(s)(2s)^2 = 1.7\times10^{-5}$. Solving the equation for s gives $s = 1.62\times10^{-2}$ M. The coefficient on Cl^- is 2, so it is assumed that twice as much Cl^- is produced as Pb^{2+}, hence the '2s.' The solubility equilibrium constant can be used to solve for the molarities of the ions at equilibrium.

The molarity of Cl^- added would be 0.1 M because Na^+ and Cl^- are in a 1:1 ration in the ionic salt, NaCl. Therefore, the overall molarity of Cl^- would be 2s + 0.1, with 2s referring to the contribution of the chloride ion from the dissociation of lead chloride.

$$\begin{aligned} Q_{sp} &= [Pb^{2+}][Cl^-]^2 \\ 1.8 \times 10^{-5} &= (s)(2s + 0.1)^2 \end{aligned} \tag{6.11.3.11}$$

$$\begin{aligned} s &= [Pb^{2+}] \\ &= 1.8 \times 10^{-3} M \\ 2s &= [Cl^-] \\ &\approx 0.1M \end{aligned} \tag{6.11.3.12}$$

Notice that the molarity of Pb^{2+} is lower when NaCl is added. The equilibrium constant remains the same because of the increased concentration of the chloride ion. To simplify the reaction, it can be assumed that $[Cl^-]$ is approximately 0.1M since the formation of the chloride ion from the dissociation of lead chloride is so small. The reaction quotient for $PbCl_2$ is greater than the equilibrium constant because of the added Cl^-. This therefore shift the reaction left towards equilibrium, causing precipitation and lowering the current solubility of the reaction. Overall, the solubility of the reaction decreases with the added sodium chloride.

The common ion effect usually decreases the solubility of a sparingly soluble salt.

Example 6.11.3.6

Calculate the solubility of calcium phosphate [$Ca_3(PO_4)_2$] in 0.20 M $CaCl_2$.

Given: concentration of $CaCl_2$ solution

Asked for: solubility of $Ca_3(PO_4)_2$ in $CaCl_2$ solution

Strategy:

A. Write the balanced equilibrium equation for the dissolution of $Ca_3(PO_4)_2$. Tabulate the concentrations of all species produced in solution.
B. Substitute the appropriate values into the expression for the solubility product and calculate the solubility of $Ca_3(PO_4)_2$.

Solution

A The balanced equilibrium equation is given in the following table. If we let x equal the solubility of $Ca_3(PO_4)_2$ in moles per liter, then the change in [Ca^{2+}] is once again +3x, and the change in [PO_4^{3-}] is +2x. We can insert these values into the ICE table.

$$Ca_3(PO_4)_{2(s)} \rightleftharpoons 3Ca^{2+}_{(aq)} + 2PO^{3-}_{4(aq)} \tag{6.11.3.13}$$

	$Ca_3(PO_4)_2$	[Ca^{2+}]	[PO_4^{3-}]
initial	pure solid	0.20	0
change	—	+3x	+2x
final	pure solid	0.20 + 3x	2x

B The K_{sp} expression is as follows:

$$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 = (0.20 + 3x)^3(2x)^2 = 2.07\times10^{-33}$$

Because $Ca_3(PO_4)_2$ is a sparingly soluble salt, we can reasonably expect that x << 0.20. Thus (0.20 + 3x) M is approximately 0.20 M, which simplifies the K_{sp} expression as follows:

$$K_{sp} = (0.20)^3(2x)^2 = 2.07 \times 10^{-33}$$
$$x^2 = 6.5 \times 10^{-32}$$
$$x = 2.5 \times 10^{-16}\ \text{M}$$

This value is the solubility of $Ca_3(PO_4)_2$ in 0.20 M $CaCl_2$ at 25°C. It is approximately nine orders of magnitude less than its solubility in pure water, as we would expect based on Le Chatelier's principle. With one exception, this example is identical to Example **6.11.3.2**—here the initial [Ca^{2+}] was 0.20 M rather than 0.

Exercise 6.11.3.4

Calculate the solubility of silver carbonate in a 0.25 M solution of sodium carbonate. The solubility of silver carbonate in pure water is 8.45×10^{-12} at 25°C.

Answer

2.9×10^{-6} M (versus 1.3×10^{-4} M in pure water)



The Common Ion Effect in Solubility Products: https://youtu.be/_P3wozLs0Tc

Summary

Adding a common cation or common anion to a solution of a sparingly soluble salt shifts the solubility equilibrium in the direction predicted by Le Chatelier's principle. The solubility of the salt is almost always **decreased** by the presence of a common ion.

Contributors and Attributions

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6.11.4: Limitations of the Ksp Concept

Solubility equilibria defined by a single, simple K_s expression are probably the exception rather than the rule. Such equilibria are often in competition with other reactions with such species as H^+or OH^-, complexing agents, oxidation-reduction, formation of other sparingly soluble species or, in the case of carbonates and sulfites, of gaseous products. The exact treatments of these systems can be extremely complicated, involving the solution of large sets of simultaneous equations. For most practical purposes it is sufficient to recognize the general trends, and to carry out approximate calculations.

The solubility product of an ionic compound describes the concentrations of ions in equilibrium with a solid, but what happens if some of the cations become associated with anions rather than being completely surrounded by solvent? Then predictions of the total solubility of the compound based on the assumption that the solute exists solely as discrete ions would differ substantially from the actual solubility, as would predictions of ionic concentrations. In general, four situations explain why the solubility of a compound may be other than expected: ion pair formation, the incomplete dissociation of molecular solutes, the formation of complex ions, and changes in pH.

The Diverse Ion Effect (The Salt Effect)

A sparingly-soluble salt will be more soluble in a solution that contains non-participating ions. This is just the opposite of the **common ion effect**, and it might at first seem rather counter-intuitive: why would adding more ions of any kind make a salt more likely to dissolve?

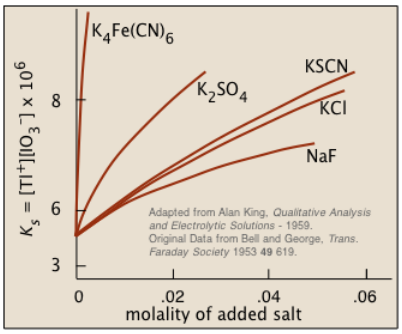


Figure **6.11.4.1**: Solubility of thallium iodate in solutions containing dissolved salts

Although the concentrations of ions in equilibrium with a sparingly soluble solid are so low that they are essentially the same as the activities, the presence of other ions at concentrations of about 0.001 M or greater can materially reduce the activities of the dissolution products, permitting the solubilities to be greater than what simple equilibrium calculations would predict.

> *The Diverse Ion Effect typically has the opposite effect on solubility than the common ion effect.*

The higher the charge of the foreign ion, the more pronounced is the salt effect. This tells us that inter-ionic (and thus electrostatic) interactions must play a role. The details are rather complicated, but the general idea is that all ions in solution, besides possessing tightly-held waters of hydration, tend to attract oppositely-charged ions ("*counter-ions*") around them. This "atmosphere" of counterions is always rather diffuse, but much less so (and more tightly bound) when one or both kinds of ions have greater charges. From a distance, these ion-counterion pairs (or ion pairs) bodies appear to be almost electrically neutral, which keeps them from interacting with each other (as to form a precipitate).

✔ Example 6.11.4.1

How does the solubility of $AgCl$ change in absence and presence of $NaNO_3$, given that the molar solubility product of $AgCl$ is 1.76×10^{-10}.

Solution

The Uncommon Ion Effect is a "real" effect and requires the activity definition of K_{sp} to address. The exact definition of the solubility constant is:

$$K_{sp} = a\{Ag^+\} \cdot a\{Cl^-\} = [Ag+]\gamma(Ag^+)[Cl^-]\gamma(Cl^-)$$

Where $a\{Ag^+\}$ and $a\{Cl^-\}$ are the activities of these ions in the presence of the $NaNO_3$. The γ values are the are the corresponding activity coefficients for the ions.

- In dilute solutions (i.e. absence of $NaNO_3$\)

$$\gamma(Ag^+) = \gamma(Cl^-) = 1$$

So, the solubility of $AgCl$ is then

$$[Ag^+] = \sqrt{K_{sp}} = 1.33 \times 10^{-5} \tag{6.11.4.1}$$

- In the presence of $NaNO_3$, the activity coefficients deviate from unity. So

$$[Ag^+] = \frac{\sqrt{K_{sp}}}{\sqrt{\gamma(Ag^+)\gamma(Cl^-)}} \tag{6.11.4.2}$$

. The denominator has to evaluated from an activity table and is 0.769 so \([Ag^+] = \dfrac{\sqrt{K_{sp}}}{0.769} = 1.73 \times 10^{-5}\].

Hence, in the presence of the $NaNO_3$ soluble salt, the molar solubility of the slightly soluble $AgCl$ salt *increases*. An opposite effect is expected if there were a common ions between the two salts.

Incomplete Dissociation of Solutes into Ions

An **ion pair** consists of a cation and an anion that are in intimate contact in solution, rather than separated by solvent (Figure 6.11.4.1). The ions in an ion pair are held together by the same attractive electrostatic force in ionic solids. As a result, the ions in an ion pair migrate as a single unit, whose net charge is the sum of the charges on the ions. In many ways, we can view an ion pair as a species intermediate between the ionic solid (in which each ion participates in many cation–anion interactions that hold the ions in a rigid array) and the completely dissociated ions in solution (where each is fully surrounded by water molecules and free to migrate independently).

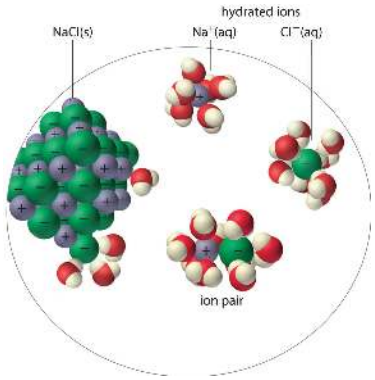


Figure 6.11.4.2: Ion-Pair Formation. In an ion pair, the cation and the anion are in intimate contact in solution and migrate as a single unit. They are not completely dissociated and individually surrounded by solvent molecules, as are the hydrated ions, which are free to migrate independently.

The overall effect is to reduce the concentrations of the less-shielded ions that are available to combine to form a precipitate. We say that the *thermodynamically-effective concentrations* of these ions are less than their "analytical" concentrations. Chemists refer to these effective concentrations as ionic *activities*, and they denote them by curly brackets $\{Ag^+\}$ as opposed to square brackets $[Ag^+]$ which refer to the nominal or analytical concentrations.

As illustrated for calcium sulfate in the following equation, a second equilibrium must be included to describe the solubility of salts that form ion pairs:

$$\underset{\text{ion pair}}{CaSO_4(s) \rightleftharpoons Ca^{2+} \cdot SO_4^{2-}(aq)} \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq) \tag{6.11.4.3}$$

The ion pair is represented by the symbols of the individual ions separated by a dot, which indicates that they are associated in solution. The formation of an ion pair is a dynamic process, just like any other equilibrium, so a particular ion pair may exist only briefly before dissociating into the free ions, each of which may later associate briefly with other ions.

Ion-pair formation can have a major effect on the measured solubility of a salt. For example, the measured K_{sp} for calcium sulfate is 4.93×10^{-5} at 25°C. The solubility of $CaSO_4$ should be 7.02×10^{-3} M if the only equilibrium involved were as follows:

$$CaSO_{4(s)} \rightleftharpoons Ca^{2+}_{(aq)} + SO^{2-}_{4(aq)} \tag{6.11.4.4}$$

In fact, the experimentally measured solubility of calcium sulfate at 25°C is 1.6×10^{-2} M, almost twice the value predicted from its K_{sp}. The reason for the discrepancy is that the concentration of ion pairs in a saturated $CaSO_4$ solution is almost as high as the concentration of the hydrated ions. Recall that the magnitude of attractive electrostatic interactions is greatest for small, highly charged ions. Hence ion pair formation is most important for salts that contain M^{2+} and M^{3+} ions, such as Ca^{2+} and La^{3+}, and is relatively unimportant for salts that contain monopositive cations, except for the smallest, Li^+. We therefore expect a saturated solution of $CaSO_4$ to contain a high concentration of ion pairs and its solubility to be greater than predicted from its K_{sp}.

Simultaneous Equilibria (Side Reactions)

A molecular solute may also be more soluble than predicted by the measured concentrations of ions in solution due to incomplete dissociation. This is particularly common with weak organic acids. Although strong acids (HA) dissociate completely into their constituent ions (H^+ and A^-) in water, weak acids such as carboxylic acids do not ($K_a = 1.5 \times 10^{-5}$). However, the molecular (undissociated) form of a weak acid (HA) is often quite soluble in water; for example, acetic acid (CH_3CO_2H) is completely miscible with water. Many carboxylic acids, however, have only limited solubility in water, such as benzoic acid ($C_6H_5CO_2H$), with $K_a = 6.25 \times 10^{-5}$. Just as with calcium sulfate, we need to include an additional equilibrium to describe the solubility of benzoic acid:

$$C_6H_5CO_2H_{(s)} \rightleftharpoons C_6H_5CO_2H_{(aq)} \rightleftharpoons C_6H_5CO^-_{2(aq)} + H^+_{(aq)} \tag{6.11.4.5}$$

In a case like this, measuring only the concentration of the ions grossly underestimates the total concentration of the organic acid in solution. In the case of benzoic acid, for example, the pH of a saturated solution at 25°C is 2.85, corresponding to $[H^+] = [C_6H_5CO_2^-] = 1.4 \times 10^{-3}$ M. The total concentration of benzoic acid in the solution, however, is 2.8×10^{-2} M. Thus approximately 95% of the benzoic acid in solution is in the form of hydrated neutral molecules—$C_6H_5CO_2H_{(aq)}$—and only about 5% is present as the dissociated ions (Figure **6.11.4.3**).

> *Incomplete dissociation of a molecular solute that is miscible with water can increase the solubility of the solute.*

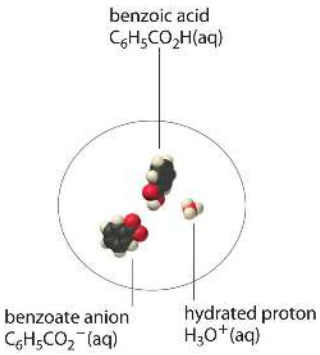


Figure **6.11.4.3**: Incomplete Dissociation of a Molecular Solute. In a saturated solution of benzoic acid in water at 25°C, only about 5% of the dissolved benzoic acid molecules are dissociated to form benzoate anions and hydrated protons. The remaining 95% exists in solution in the form of hydrated neutral molecules. (H_2O molecules are omitted for clarity.)

Although ion pairs, such as $Ca^{2+} \cdot SO_4^{2-}$, and undissociated electrolytes, such as $C_6H_5CO_2H$, are both electrically neutral, there is a major difference in the forces responsible for their formation. Simple electrostatic attractive forces between the cation and the anion hold the ion pair together, whereas a polar covalent O−H bond holds together the undissociated electrolyte.

Example 6.11.4.2: CdI_2 Solubility

The dissolution of cadmium iodide is water is commonly represented as

$$CdI_{2(s)} \rightleftharpoons Cd^{2+} + 2I^{-} \tag{6.11.4.6}$$

What you were likely taught about the dissociation of salts in water is wrong! To most students (and to most of their teachers!), this would imply that a 0.1$\underline{M}$ solution of this salt would contain 0.1$\underline{M}$ of $Cd^{2+}(aq)$ — and this would be seriously in error because it fails to take into account that the two ions react with each other.

Firstly, they combine to form neutral, largely-covalent molecular species:

$$Cd^{2+}_{(aq)} + 2I^{-}_{(aq)} \rightarrow CdI_{2(aq)} \tag{6.11.4.7}$$

This non-ionic form accounts for 78% of the Cd present in the solution! In addition, they form a molecular ion $CdI^{-}_{(aq)}$ according to the following scheme:

Table **6.11.4.1**: CdI2 species in solution

$CdI_{2(s)} \rightleftharpoons Cd^{2+} + 2I^{-}$	$K_1 = 10^{-3.9}$
$Cd^{2+} + I^{-} \rightleftharpoons CdI^{+}$	$K_2 = 10^{+2.3}$
$CdI2_{(s)} \rightleftharpoons CdI^{+} + I^{-}$	$K = 10^{-1.6} = 0.023$

As a consequence, the concentration of "free" Cd^{2+}(aq) in an aqueous cadmium iodide solution is only about 2% of the value you would calculate by taking K_1 as the solubility product. The principal component of such as solution is actually [covalently-bound] CdI_2(aq). It turns out that

Many salts, especially those of metals beyond Group 2, are similarly only partially ionized in aqueous solution:

Table **6.11.4.2**: Incomplete Dissociation of Select Salts

salt	molarity	% cation	other species
KCl	0.52	95	KCl(aq) 5%
$MgSO_4$	0.04	58	$MgSO_4$(aq) 42%
$CaCl_2$	0.44	70	$CaCl^{+}$(aq) 30%
$CuSO_4$	0.045	56	$CuSO_4$(aq) 44%
CdI_2	0.50	2	CdI_2(aq) 76%, CdI^{-}(aq) 22%
$FeCl_3$	0.1	10	$FeCl^{2+}$(aq) 42%, $FeCl_2$(aq) 40%, $FeOH^{2+}$(aq) 6%, $Fe(OH)_2^{+}$(aq) 2%

The data shown Tables **6.11.4.1** and **6.11.4.2** are taken from the article *Salts are Mostly NOT Ionized* by Stephen Hawkes: 1996 *J Chem Educ.* 73(5) 421-423. This fact was stated by Arrhenius in 1887, but has been largely ignored and is rarely mentioned in standard textbooks.

Summary

The solubility constant, as with all equilibrium constants, are properly defined in terms of *effective concentrations* (activities) and the use of true concentrations to approximate activities in equilibrium constants can often fail. As with all approximations, it is important to understand the conditions that it will fail. three examples are discussed. The salt effect refers to the fact that the presence of a salt which has no ion in common with the solute, has an effect on the ionic strength of the solution and hence on activity coefficients, so that the equilibrium constant, expressed as a concentration quotient, changes.

Contributors and Attributions

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6.11.5: Criteria for Precipitation and its Completeness

The equation that describes the equilibrium between solid calcium carbonate and its solvated ions is:

$$\mathrm{CaCO_3}(s) \rightleftharpoons \mathrm{Ca^{2+}}(aq) + \mathrm{CO_3^{2-}}(aq) \tag{6.11.5.1}$$

We can establish this equilibrium either by adding solid calcium carbonate to water or by mixing a solution that contains calcium ions with a solution that contains carbonate ions. If we add calcium carbonate to water, the solid will dissolve until the concentrations are such that the value of the reaction quotient ($Q = [\mathrm{Ca^{2+}}][\mathrm{CO_3^{2-}}]$) is equal to the solubility product ($K_{sp} = 4.8 \times 10^{-9}$). If we mix a solution of calcium nitrate, which contains Ca^{2+} ions, with a solution of sodium carbonate, which contains $\mathrm{CO_3^{2-}}$ ions, the slightly soluble ionic solid $CaCO_3$ will precipitate, provided that the concentrations of Ca^{2+} and $\mathrm{CO_3^{2-}}$ ions are such that Q is greater than K_{sp} for the mixture. The reaction shifts to the left and the concentrations of the ions are reduced by formation of the solid until the value of Q equals K_{sp}. A saturated solution in equilibrium with the undissolved solid will result. If the concentrations are such that Q is less than K_{sp}, then the solution is not saturated and no precipitate will form.

We can compare numerical values of Q with K_{sp} to predict whether precipitation will occur, as Example **6.11.5.7** shows. (Note: Since all forms of equilibrium constants are temperature dependent, we will assume a room temperature environment going forward in this chapter unless a different temperature value is explicitly specified.)

The first step in the preparation of magnesium metal is the precipitation of $Mg(OH)_2$ from sea water by the addition of lime, $Ca(OH)_2$, a readily available inexpensive source of OH^- ion:

$$\mathrm{Mg(OH)_2}(s) \rightleftharpoons \mathrm{Mg^{2+}}(aq) + 2\,\mathrm{OH^-}(aq) \quad K_{sp} = 2.1 \times 10^{-13} \tag{6.11.5.2}$$

The concentration of $Mg^{2+}(aq)$ in sea water is 0.0537 *M*. Will $Mg(OH)_2$ precipitate when enough $Ca(OH)_2$ is added to give a $[OH^-]$ of 0.0010 *M*?

Solution

This problem asks whether the reaction:

$$\mathrm{Mg(OH)_2}(s) \rightleftharpoons \mathrm{Mg^{2+}}(aq) + 2\,\mathrm{OH^-}(aq) \tag{6.11.5.3}$$

shifts to the left and forms solid $Mg(OH)_2$ when $[Mg^{2+}] = 0.0537$ *M* and $[OH^-] = 0.0010$ *M*. The reaction shifts to the left if Q is greater than K_{sp}. Calculation of the reaction quotient under these conditions is shown here:

$$Q = [\mathrm{Mg^{2+}}][\mathrm{OH^-}]^2 = (0.0537)(0.0010)^2 = 5.4 \times 10^{-8} \tag{6.11.5.4}$$

Because Q is greater than K_{sp} ($Q = 5.4 \times 10^{-8}$ is larger than $K_{sp} = 2.1 \times 10^{-13}$), we can expect the reaction to shift to the left and form solid magnesium hydroxide. $Mg(OH)_2(s)$ forms until the concentrations of magnesium ion and hydroxide ion are reduced sufficiently so that the value of Q is equal to K_{sp}.

? Exercise 6.11.5.1

Use the solubility products in Appendix J to determine whether $CaHPO_4$ will precipitate from a solution with $[Ca^{2+}] = 0.0001$ *M* and $[\mathrm{HPO_4^{2-}}] = 0.001$ *M*.

Answer

No precipitation of $CaHPO_4$; $Q = 1 \times 10^{-7}$, which is less than K_{sp}

✔ Precipitation of AgCl upon Mixing Solutions

Does silver chloride precipitate when equal volumes of a 2.0×10^{-4}-*M* solution of $AgNO_3$ and a 2.0×10^{-4}-*M* solution of NaCl are mixed?

(Note: The solution also contains Na^+ and $\mathrm{NO_3^-}$ ions, but when referring to solubility rules, one can see that sodium nitrate is very soluble and cannot form a precipitate.)

Solution

The equation for the equilibrium between solid silver chloride, silver ion, and chloride ion is:

$$\mathrm{AgCl}(s) \rightleftharpoons \mathrm{Ag^+}(aq) + \mathrm{Cl^-}(aq)$$

The solubility product is 1.8×10^{-10} (see Appendix J).

AgCl will precipitate if the reaction quotient calculated from the concentrations in the mixture of $AgNO_3$ and NaCl is greater than K_{sp}. The volume doubles when we mix equal volumes of $AgNO_3$ and NaCl solutions, so each concentration is reduced to half its initial value. Consequently, immediately upon mixing, $[Ag^+]$ and $[Cl^-]$ are both equal to:

$$\frac{1}{2}(2.0 \times 10^{-4})\ M = 1.0 \times 10^{-4}\ M$$

The reaction quotient, Q, is *momentarily* greater than K_{sp} for AgCl, so a supersaturated solution is formed:

$$Q = [\mathrm{Ag^+}][\mathrm{Cl^-}] = (1.0 \times 10^{-4})(1.0 \times 10^{-4}) = 1.0 \times 10^{-8} > K_{sp}$$

Since supersaturated solutions are unstable, AgCl will precipitate from the mixture until the solution returns to equilibrium, with Q equal to K_{sp}.

Exercise 6.11.5.2

Will $KClO_4$ precipitate when 20 mL of a 0.050-*M* solution of K^+ is added to 80 mL of a 0.50-*M* solution of ClO_4^-? (Remember to calculate the new concentration of each ion after mixing the solutions before plugging into the reaction quotient expression.)

Answer

No, $Q = 4.0 \times 10^{-3}$, which is less than $K_{sp} = 1.07 \times 10^{-2}$

In the previous two examples, we have seen that $Mg(OH)_2$ or AgCl precipitate when Q is greater than K_{sp}. In general, when a solution of a soluble salt of the M^{m+} ion is mixed with a solution of a soluble salt of the X^{n-} ion, the solid, M_pX_q precipitates if the value of Q for the mixture of M^{m+} and X^{n-} is greater than K_{sp} for M_pX_q. Thus, if we know the concentration of one of the ions of a slightly soluble ionic solid and the value for the solubility product of the solid, then we can calculate the concentration that the other ion must exceed for precipitation to begin. To simplify the calculation, we will assume that precipitation begins when the reaction quotient becomes equal to the solubility product constant.

Precipitation of Calcium Oxalate

Blood will not clot if calcium ions are removed from its plasma. Some blood collection tubes contain salts of the oxalate ion, $C_2O_4^{2-}$, for this purpose (Figure 6.11.5.4). At sufficiently high concentrations, the calcium and oxalate ions form solid, $CaC_2O_4{\cdot}H_2O$ (which also contains water bound in the solid). The concentration of Ca^{2+} in a sample of blood serum is 2.2×10^{-3} *M*. What concentration of $C_2O_4^{2-}$ ion must be established before $CaC_2O_4{\cdot}H_2O$ begins to precipitate?



Figure 6.11.5.4: Anticoagulants can be added to blood that will combine with the Ca^{2+} ions in blood serum and prevent the blood from clotting. (credit: modification of work by Neeta Lind)

Solution

The equilibrium expression is:

$$\mathrm{CaC_2O_4}(s) \rightleftharpoons \mathrm{Ca^{2+}}(aq) + \mathrm{C_2O_4^{2-}}(aq) \tag{6.11.5.5}$$

For this reaction:

$$K_{sp} = [\mathrm{Ca^{2+}}][\mathrm{C_2O_4^{2-}}] = 2.27 \times 10^{-9} \tag{6.11.5.6}$$

(see Appendix J)

CaC_2O_4 does not appear in this expression because it is a solid. Water does not appear because it is the solvent.

Solid CaC_2O_4 does not begin to form until Q equals K_{sp}. Because we know K_{sp} and $[Ca^{2+}]$, we can solve for the concentration of $\mathrm{C_2O_4^{2-}}$ that is necessary to produce the first trace of solid:

$$\begin{gathered} Q = K_{sp} = [\mathrm{Ca^{2+}}][\mathrm{C_2O_4^{2-}}] = 2.27 \times 10^{-9} \\ (2.2 \times 10^{-3})[\mathrm{C_2O_4^{2-}}] = 2.27 \times 10^{-9} \\ [\mathrm{C_2O_4^{2-}}] = \frac{2.27 \times 10^{-9}}{2.2 \times 10^{-3}} = 1.0 \times 10^{-6} \end{gathered}$$

A concentration of $[\mathrm{C_2O_4^{2-}}] = 1.0 \times 10^{-6}\ M$ is necessary to initiate the precipitation of CaC_2O_4 under these conditions.

Exercise 6.11.5.3

If a solution contains 0.0020 mol of $\mathrm{CrO_4^{2-}}$ per liter, what concentration of Ag^+ ion must be reached by adding solid $AgNO_3$ before Ag_2CrO_4 begins to precipitate? Neglect any increase in volume upon adding the solid silver nitrate.

Answer:

$7.0 \times 10^{-5}\ M$

It is sometimes useful to know the concentration of an ion that remains in solution after precipitation. We can use the solubility product for this calculation too: If we know the value of K_{sp} and the concentration of one ion in solution, we can calculate the concentration of the second ion remaining in solution. The calculation is of the same type as that in Example—calculation of the concentration of a species in an equilibrium mixture from the concentrations of the other species and the equilibrium constant. However, the concentrations are different; we are calculating concentrations after precipitation is complete, rather than at the start of precipitation.

Concentrations Following Precipitation

Clothing washed in water that has a manganese $[Mn^{2+}(aq)]$ concentration exceeding 0.1 mg/L ($1.8 \times 10^{-6}\ M$) may be stained by the manganese upon oxidation, but the amount of Mn^{2+} in the water can be reduced by adding a base. If a person doing laundry wishes to add a buffer to keep the pH high enough to precipitate the manganese as the hydroxide, $Mn(OH)_2$, what pH is required to keep $[Mn^{2+}]$ equal to $1.8 \times 10^{-6}\ M$?

Solution The dissolution of $Mn(OH)_2$ is described by the equation:

$$\mathrm{Mn(OH)_2}(s) \rightleftharpoons \mathrm{Mn^{2+}}(aq) + 2\,\mathrm{OH^-}(aq) \quad K_{sp} = 4.5 \times 10^{-14} \tag{6.11.5.7}$$

We need to calculate the concentration of OH^- when the concentration of Mn^{2+} is $1.8 \times 10^{-6}\ M$. From that, we calculate the pH. At equilibrium:

$$K_{sp} = [\mathrm{Mn^{2+}}][\mathrm{OH^-}]^2 \tag{6.11.5.8}$$

or

$$(1.8 \times 10^{-6})[\mathrm{OH^-}]^2 = 4.5 \times 10^{-14} \tag{6.11.5.9}$$

so

$$[\mathrm{OH^-}] = 1.6 \times 10^{-4}\ M \tag{6.11.5.10}$$

Now we calculate the pH from the pOH:

$$\mathrm{pOH} = -\log[\mathrm{OH^-}] = -\log(1.6 \times 10^{-4}) = 3.80$$
$$\mathrm{pH} = 14.00 - \mathrm{pOH} = 14.00 - 3.80 = 10.20$$

If the person doing laundry adds a base, such as the sodium silicate (Na_4SiO_4) in some detergents, to the wash water until the pH is raised to 10.20, the manganese ion will be reduced to a concentration of 1.8×10^{-6} *M*; at that concentration or less, the ion will not stain clothing.

? Exercise 6.11.5.4

The first step in the preparation of magnesium metal is the precipitation of $Mg(OH)_2$ from sea water by the addition of $Ca(OH)_2$. The concentration of $Mg^{2+}(aq)$ in sea water is 5.37×10^{-2} *M*. Calculate the pH at which $[Mg^{2+}]$ is diminished to 1.0×10^{-5} *M* by the addition of $Ca(OH)_2$.

Answer

11.09

Due to their light sensitivity, mixtures of silver halides are used in fiber optics for medical lasers, in photochromic eyeglass lenses (glass lenses that automatically darken when exposed to sunlight), and—before the advent of digital photography—in photographic film. Even though AgCl ($K_{sp} = 1.6 \times 10^{-10}$), AgBr ($K_{sp} = 7.7 \times 10^{-13}$), and AgI ($K_{sp} = 8.3 \times 10^{-17}$) are each quite insoluble, we cannot prepare a homogeneous solid mixture of them by adding Ag^+ to a solution of Cl^-, Br^-, and I^-; essentially all of the AgI will precipitate before any of the other solid halides form because of its smaller value for K_{sp}. However, we can prepare a homogeneous mixture of the solids by slowly adding a solution of Cl^-, Br^-, and I^- to a solution of Ag^+.

When two anions form slightly soluble compounds with the same cation, or when two cations form slightly soluble compounds with the same anion, the less soluble compound (usually, the compound with the smaller K_{sp}) generally precipitates first when we add a precipitating agent to a solution containing both anions (or both cations). When the K_{sp} values of the two compounds differ by two orders of magnitude or more (e.g., 10^{-2} vs. 10^{-4}), almost all of the less soluble compound precipitates before any of the more soluble one does. This is an example of selective precipitation, where a reagent is added to a solution of dissolved ions causing one of the ions to precipitate out before the rest.



Determining if a Precipitate forms (The Ion Product): https://youtu.be/Naf7PoHPz8Y

Summary

A slightly soluble electrolyte begins to precipitate when the magnitude of the reaction quotient for the dissolution reaction exceeds the magnitude of the solubility product. Precipitation continues until the reaction quotient equals the solubility product. A reagent can be added to a solution of ions to allow one ion to selectively precipitate out of solution. The common ion effect can also play a role in precipitation reactions. In the presence of an ion in common with one of the ions in the solution, Le Chatelier's principle applies and more precipitate comes out of solution so that the molar solubility is reduced.

Glossary

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

molar solubility

solubility of a compound expressed in units of moles per liter (mol/L)

selective precipitation

process in which ions are separated using differences in their solubility with a given precipitating reagent

solubility product (K_{sp})

equilibrium constant for the dissolution of a slightly soluble electrolyte

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6.11.6: Fractional Precipitation

Learning Objectives

- Calculate ion concentrations to maintain a heterogeneous equilibrium.
- Calculate pH required to precipitate a metal hydroxide.
- Design experiments to separate metal ions in a solution of mixtures of metals.

A mixture of metal ions in a solution can be separated by precipitation with anions such as Cl^-, Br^-, SO_4^{2-}, CO_3^{2-}, S^{2-}, $Cr_2O_4^{2-}$, PO_4^{2-}, OH^- etc. When a metal ion or a group of metal ions form insoluble salts with a particular anion, they can be separated from others by precipitation. We can also separate the anions by precipitating them with appropriate metal ions. There are no definite dividing lines between **insoluble salts, sparingly soluble**, and **soluble salts**, but concentrations of their saturated solutions are small, medium, and large. Solubility products are usually listed for insoluble and sparingly soluble salts, but they are not given for soluble salts. Solubility products for soluble salts are very large.

What type of salts are usually soluble, sparingly soluble and insoluble? The following are some general guidelines, but these are not precise laws.

- All nitrates are soluble. The singly charged large NO_3^- ions form salts with high solubilities. So do ClO_4^-, ClO_3^-, NO_2^-, $HCOO^-$, and CH_3COO^-.
- All chlorides, bromides, and iodides are soluble except those of Ag^+, Hg_2^{2+}, and Pb^{2+}. CaF_2, BaF_2, and PbF_2 are also insoluble.
- All sulfates are soluble, except those of Ba^{2+}, Sr^{2+}, and Pb^{2+}. The doubly charged sulfates are usually less soluble than halides and nitrates.
- Most singly charge cations K^+, Na^+, NH_4^+ form soluble salts. However, $K_3Co(NO_2)_6$ and $(NH_4)_3Co(NO_2)_6$ are insoluble.

These are handy rules for us to have if we deal with salts often. On the other hand, solubility is an important physical property of a substance, and these properties are listed in handbooks.

Chemical Separation of Metal Ions

Formation of crystals from a saturated solution is a **heterogeneous equilibrium** phenomenon, and it can be applied to separate various chemicals or ions in a solution. When solubilities of two metal salts are very different, they can be separated by precipitation. The K_{sp} values for various salts are valuable information, and some data are given in Table E3. In the first two examples, we show how barium and strontium can be separated as chromate.

Example 6.11.6.1

The K_{sp} for strontium chromate is 3.6×10^{-5} and the K_{sp} for barium chromate is 1.2×10^{-10}. What concentration of potassium chromate will precipitate the maximum amount of either the barium or the strontium chromate from an equimolar 0.30 M solution of barium and strontium ions without precipitating the other?

Solution

Since the K_{sp} for barium chromate is smaller, we know that $BaCrO_4$ will form a precipitate first as $[CrO_4^{2-}]$ increases so that Q_{sp} for $BaCrO_4$ also increases from zero to K_{sp} of $BaCrO_4$, at which point, $BaCrO_4$ precipitates. As $[CrO_4^{2-}]$ increases, $[Ba^{2+}]$ decreases. Further increase of $[CrO_4^{2-}]$ till Q_{sp} for $SrCrO_4$ increases to K_{sp} of $SrCrO_4$; it then precipitates.

Let us write the equilibrium equations and data down to help us think. Let x be the concentration of chromate to precipitate Sr^{2+}, and y be that to precipitate Ba^{2+}:

$$SrCrO_4(s) \rightarrow Sr^{2+}(aq) + CrO_4^{2-}(aq)$$

According to the definition of K_{sp} we have we have $K_{sp} = (0.30)(x) = 3.6 \times 10^{-5}$. Solving for x gives

$$x = \frac{3.6 \times 10^{-5}}{0.30} = 1.2 \times 10^{-4} M$$

Further, let y be the concentration of chromate to precipitate precipitate Ba^{2+}:

$$BaCrO_4(s) \rightarrow Ba^{2+}(aq) + CrO_4{}^{2-}(aq)$$

with $K_{sp} = (0.30)(y) = 1.2 \times 10^{-10}$. Solving for y gives

$$y = \frac{1.2 \times 10^{-10}}{0.30} = 4.0 \times 10^{-10}\ M$$

The K_{sp}'s for the two salts indicate $BaCrO_4$ to be much less soluble, and it will precipitate before any $SrCrO_4$ precipitates. If chromate concentration is maintained less than $1.2 \times 10^{-4} M$, then all Sr^{2+} ions will remain in the solution.

Discussion

In reality, controling the increase of $[CrO_4{}^{2-}]$ is very difficult.

Example 6.11.6.2

The K_{sp} for strontium chromate is 3.6×10^{-5} and the K_{sp} for barium chromate is 1.2×10^{-10}. Potassium chromate is added a small amount at a time to first precipitate $BaCrO_4$. Calculate $[Ba^{2+}]$ when the first trace of $SrCrO_4$ precipitate starts to form in a solution that contains 0.30 M each of Ba^{2+} and Sr^{2+} ions.

Solution

From the solution given in Example 6.11.6.1, $[CrO_4{}^{2-}] = 3.6 \times 10^{-4}\ M$ when $SrCrO_4$ starts to form. At this concentration, the $[Ba^{2+}]$ is estimated at $3.6 \times 10^{-4} = 1.2 \times 10^{-10}$.

The K_{sp} of $BaCrO_4$.

Thus,

$$[Ba^{2+}] = 3.33 \times 10^{-7}\ M$$

Very small indeed, compared to 0.30. In the fresh precipitate of $SrCrO_4$, the molar ratio of $SrCrO_4$ to $BaCrO_4$ is

$$\frac{0.30}{3.33 \times 10^{-7}} = 9.0 \times 10^{5}.$$

Hence, the amount of Ba^{2+} ion in the solid is only 1×10^{-6} (i.e., 1 ppm) of all metal ions, providing that all the solid was removed when

$$[CrO_4{}^{2-}] = 3.6 \times 10^{-4} M.$$

Discussion

The calculation shown here indicates that the separation of Sr and Ba is pretty good. In practice, an impurity level of 1 ppm is a very small value.

Example 6.11.6.3

What reagent should you use to separate silver and lead ions that are present in a solution? What data or information will be required for this task?

Solution

The K_{sp}'s for salts of silver and lead are required. We list the K_{sp}'s for chlorides and sulfates in a table here. These value are found in the Handbook Menu of our website as Salts K_{sp}.

Solutions to Example 17.6.3

Because the K_{sp}'s $AgCl$ and $PbCl_2$ are very different, chloride, Cl^-, apppears a good choice of negative ions for their separation.

The literature also indicates that $PbCl_2$ is rather soluble in warm water, and by heating the solution to 350 K (80°C), you can keep Pb^{2+} ions in solution and precipitate $AgCl$ as a solid. The solubility of $AgCl$ is very small even at high temperatures.

Discussion

Find more detailed information about the solubility of lead chloride as a function of temperature.

Salt	K_{sp}	Salt	K_{sp}
$AgCl$	1.8×10^{-10}	Ag_2SO_4	1.4×10^{-5}
Hg_2Cl_2	1.3×10^{-18}	$BaSO_4$	1.1×10^{-10}
$PbCl_2$	1.7×10^{-5}	$CaSO_4$	2.4×10^{-5}
		$PbSO_4$	6.3×10^{-7}
		$SrSO_4$	3.2×10^{-7}

Can sulfate be used to separate silver and lead ions? Which one will form a precipitate first as the sulfate ion concentration increases? What is the $[Pb^{2+}]$ when Ag_2SO_4 begins to precipitate in a solution that contains 0.10 M Ag^+?



The Separation of Two Ions by a Difference in Solubility: The Separation of Two Ions by a Difference in Solubility(opens in new window) [youtu.be]

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6.11.7: Solubility and pH

Learning Objectives

- To understand why the solubility of many compounds depends on pH.

The solubility of many compounds depends strongly on the pH of the solution. For example, the anion in many sparingly soluble salts is the conjugate base of a weak acid that may become protonated in solution. In addition, the solubility of simple binary compounds such as oxides and sulfides, both strong bases, is often dependent on pH. In this section, we discuss the relationship between the solubility of these classes of compounds and pH.

The Effect of Acid–Base Equilibria the Solubility of Salts

We begin our discussion by examining the effect of pH on the solubility of a representative salt, $\mathbf{M^+A^-}$, where $\mathbf{A^-}$ is the conjugate base of the weak acid **HA**. When the salt dissolves in water, the following reaction occurs:

$$\mathbf{MA\,(s)} \rightleftharpoons \mathbf{M^+\,(aq) + A^-\,(aq)}$$

with

$$K_{sp} = [\mathrm{M^+}][\mathrm{A^-}]$$

The anion can also react with water in a hydrolysis reaction:

$$\mathbf{A^-\,(aq) + H_2O\,(l)} \rightleftharpoons \mathbf{OH^-\,(aq) + HA\,(aq)} \tag{6.11.7.1}$$

Because of the reaction described in Equation 6.11.7.1, the predicted solubility of a sparingly soluble salt that has a basic anion such as S^{2-}, PO_4^{3-}, or CO_3^{2-} is increased. If instead a strong acid is added to the solution, the added H^+ will react essentially completely with A^- to form HA. This reaction decreases $[A^-]$, which decreases the magnitude of the ion product

$$Q = [\mathrm{M^+}][\mathrm{A^-}] \tag{6.11.7.2}$$

According to Le Chatelier's principle, more MA will dissolve until $Q = K_{sp}$. Hence an acidic pH dramatically increases the solubility of virtually all sparingly soluble salts whose anion is the conjugate base of a weak acid. In contrast, pH has little to no effect on the solubility of salts whose anion is the conjugate base of a stronger weak acid or a strong acid, respectively (e.g., chlorides, bromides, iodides, and sulfates). For example, the hydroxide salt $Mg(OH)_2$ is relatively insoluble in water:

$$Mg(OH)_{2(s)} \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq) \tag{6.11.7.3}$$

with

$$K_{sp} = 5.61 \times 10^{-12} \tag{6.11.7.4}$$

When acid is added to a saturated solution that contains excess solid $Mg(OH)_2$, the following reaction occurs, removing OH^- from solution:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l) \tag{6.11.7.5}$$

The overall equation for the reaction of $Mg(OH)_2$ with acid is thus

$$Mg(OH)_{2(s)} + 2H^+(aq) \rightleftharpoons Mg^{2+}(aq) + 2H_2O(l) \tag{6.11.7.6}$$

As more acid is added to a suspension of $Mg(OH)_2$, the equilibrium shown in Equation 6.11.7.6 is driven to the right, so more $Mg(OH)_2$ dissolves.

Such pH-dependent solubility is not restricted to salts that contain anions derived from water. For example, CaF_2 is a sparingly soluble salt:

$$CaF_{2(s)} \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq) \tag{6.11.7.7}$$

with

$$K_{sp} = 3.45 \times 10^{-11} \tag{6.11.7.8}$$

When strong acid is added to a saturated solution of CaF_2, the following reaction occurs:

$$H^+(aq) + F^-(aq) \rightleftharpoons HF(aq) \tag{6.11.7.9}$$

Because the forward reaction decreases the fluoride ion concentration, more CaF_2 dissolves to relieve the stress on the system. The net reaction of CaF_2 with strong acid is thus

$$CaF_{2(s)} + 2H^+(aq) \rightarrow Ca^{2+}(aq) + 2HF(aq) \tag{6.11.7.10}$$

Example **6.11.7.1** shows how to calculate the solubility effect of adding a strong acid to a solution of a sparingly soluble salt.

> *Sparingly soluble salts derived from weak acids tend to be more soluble in an acidic solution.*

Example 6.11.7.1

Lead oxalate (PbC_2O_4), lead iodide (PbI_2), and lead sulfate ($PbSO_4$) are all rather insoluble, with K_{sp} values of 4.8×10^{-10}, 9.8×10^{-9}, and 2.53×10^{-8}, respectively. What effect does adding a strong acid, such as perchloric acid, have on their relative solubilities?

Given: K_{sp} values for three compounds

Asked for: relative solubilities in acid solution

Strategy:

Write the balanced chemical equation for the dissolution of each salt. Because the strongest conjugate base will be most affected by the addition of strong acid, determine the relative solubilities from the relative basicity of the anions.

Solution

The solubility Equilibria for the three salts are as follows:

$$PbC_2O_{4(s)} \rightleftharpoons Pb^{2+}(aq) + C_2O^{2-}_{4(aq)}$$

$$PbI_{2(s)} \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$$

$$PbSO_{4(s)} \rightleftharpoons Pb^{2+}(aq) + SO^{2-}_{4(aq)}$$

The addition of a strong acid will have the greatest effect on the solubility of a salt that contains the conjugate base of a weak acid as the anion. Because HI is a strong acid, we predict that adding a strong acid to a saturated solution of PbI_2 will not greatly affect its solubility; the acid will simply dissociate to form H^+(aq) and the corresponding anion. In contrast, oxalate is the fully deprotonated form of oxalic acid (HO_2CCO_2H), which is a weak diprotic acid (pK_{a1} = 1.23 and pK_{a2} = 4.19). Consequently, the oxalate ion has a significant affinity for one proton and a lower affinity for a second proton. Adding a strong acid to a saturated solution of lead oxalate will result in the following reactions:

$$C_2O^{2-}_{4(aq)} + H^+(aq) \rightarrow HO_2CCO^-_{2(aq)}$$

$$HO_2CCO^-_{2(aq)} + H^+(aq) \rightarrow HO_2CCO_2H(aq)$$

These reactions will decrease $[C_2O_4{}^{2-}]$, causing more lead oxalate to dissolve to relieve the stress on the system. The pK_a of $HSO_4{}^-$ (1.99) is similar in magnitude to the pK_{a1} of oxalic acid, so adding a strong acid to a saturated solution of $PbSO_4$ will result in the following reaction:

$$SO^{2-}_{4(aq)} + H^+(aq) \rightleftharpoons HSO^-_{4(aq)}$$

Because $HSO_4{}^-$ has a pKa of 1.99, this reaction will lie largely to the left as written. Consequently, we predict that the effect of added strong acid on the solubility of $PbSO_4$ will be significantly less than for PbC_2O_4.

? Exercise 6.11.7.1

Which of the following insoluble salts—AgCl, Ag_2CO_3, Ag_3PO_4, and/or AgBr—will be substantially more soluble in 1.0 M HNO_3 than in pure water?

Answer

Ag_2CO_3 and Ag_3PO_4



Solubility Products and pH: https://youtu.be/XJ0s5SATZgQ

Caves and their associated pinnacles and spires of stone provide one of the most impressive examples of pH-dependent solubility Equilbria(part (a) in Figure 6.11.7.1:). Perhaps the most familiar caves are formed from limestone, such as Carlsbad Caverns in New Mexico, Mammoth Cave in Kentucky, and Luray Caverns in Virginia. The primary reactions that are responsible for the formation of limestone caves are as follows:

$$\mathrm{CO_2\,(aq) + H_2O\,(l) \rightleftharpoons H^+\,(aq) + HCO_3^-\,(aq)} \tag{6.11.7.11}$$

$$\mathrm{HCO_3^-\,(aq) \rightleftharpoons H^+\,(aq) + CO_3^{2-}\,(aq)} \tag{6.11.7.12}$$

$$\mathrm{Ca^{2+}\,(aq) + CO_3^{2-}\,(aq) \rightleftharpoons CaCO_3\,(s)} \tag{6.11.7.13}$$

Limestone deposits that form caves consist primarily of $CaCO_3$ from the remains of living creatures such as clams and corals, which used it for making structures such as shells. When a saturated solution of $CaCO_3$ in CO_2-rich water rises toward Earth's surface or is otherwise heated, CO_2 gas is released as the water warms. $CaCO_3$ then precipitates from the solution according to the following equation (part (b) in Figure 6.11.7.1:):

$$Ca^{2+}(aq) + 2HCO_{3(aq)}^- \rightleftharpoons CaCO_{3(s)} + CO_{2(g)} + H_2O(l) \tag{6.11.7.14}$$

The forward direction is the same reaction that produces the solid called scale in teapots, coffee makers, water heaters, boilers, and other places where hard water is repeatedly heated.



Figure **6.11.7.1**: The Chemistry of Cave Formation. (a) This cave in Campanet, Mallorca, Spain, and its associated formations are examples of pH-dependent solubility equilibriums. (b) A cave forms when groundwater containing atmospheric CO_2, forming an acidic solution, dissolves limestone ($CaCO_3$) in a process that may take tens of thousands of years. As groundwater seeps into a cave, water evaporates from the solution of $CaCO_3$ in CO_2-rich water, producing a supersaturated solution and a shift in equilibrium that causes precipitation of the $CaCO_3$. The deposited limestone eventually forms stalactites and stalagmites.

When groundwater-containing atmospheric CO_2 (Equations **6.11.7.11** and **6.11.7.12**) finds its way into microscopic cracks in the limestone deposits, $CaCO_3$ dissolves in the acidic solution in the reverse direction of Equation **6.11.7.14**. The cracks gradually enlarge from 10–50 µm to 5–10 mm, a process that can take as long as 10,000 yr. Eventually, after about another 10,000 yr, a cave forms. Groundwater from the surface seeps into the cave and clings to the ceiling, where the water evaporates and causes the equilibrium in Equation **6.11.7.14** to shift to the right. A circular layer of solid $CaCO_3$ is deposited, which eventually produces a long, hollow spire of limestone called a stalactite that grows down from the ceiling. Below, where the droplets land when they fall from the ceiling, a similar process causes another spire, called a stalagmite, to grow up. The same processes that carve out hollows below ground are also at work above ground, in some cases producing fantastically convoluted landscapes like that of Yunnan Province in China (Figure **6.11.7.2**).

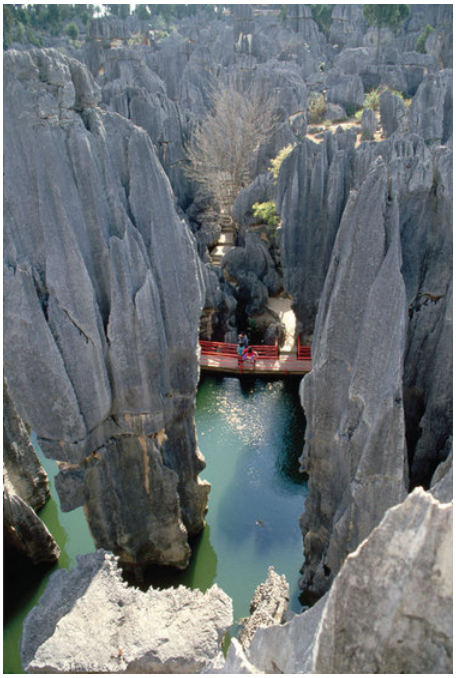


Figure **6.11.7.2**: Solubility Equilbriain the Formation of Karst Landscapes. Landscapes such as the steep limestone pinnacles of the Stone Forest in Yunnan Province, China, are formed from the same process that produces caves and their associated formations.

Acidic, Basic, and Amphoteric Oxides and Hydroxides

One of the earliest classifications of substances was based on their solubility in acidic versus basic solution, which led to the classification of oxides and hydroxides as being either basic or acidic. **Basic oxides** and hydroxides either react with water to produce a basic solution or dissolve readily in aqueous acid. **Acidic oxides** or hydroxides either react with water to produce an acidic solution or are soluble in aqueous base. There is a clear correlation between the acidic or the basic character of an oxide and the position of the element combined with oxygen in the periodic table. Oxides of metallic elements are generally basic oxides, and oxides of nonmetallic elements are acidic oxides. Compare, for example, the reactions of a typical metal oxide, cesium oxide, and a typical nonmetal oxide, sulfur trioxide, with water:

$$Cs_2O(s) + H_2O(l) \rightarrow 2Cs^+(aq) + 2OH^-(aq) \tag{6.11.7.15}$$

$$SO_{3(g)} + H_2O(l) \rightarrow H_2SO_{4(aq)} \tag{6.11.7.16}$$

Cesium oxide reacts with water to produce a basic solution of cesium hydroxide, whereas sulfur trioxide reacts with water to produce a solution of sulfuric acid—very different behaviors indeed

> *Metal oxides generally react with water to produce basic solutions, whereas nonmetal oxides produce acidic solutions.*

The difference in reactivity is due to the difference in bonding in the two kinds of oxides. Because of the low electronegativity of the metals at the far left in the periodic table, their oxides are best viewed as containing discrete M^{n+} cations and O^{2-} anions. At the other end of the spectrum are nonmetal oxides; due to their higher electronegativities, nonmetals form oxides with covalent bonds to oxygen. Because of the high electronegativity of oxygen, however, the covalent bond between oxygen and the other atom, E, is usually polarized: $E^{\delta+}$–$O^{\delta-}$. The atom E in these oxides acts as a Lewis acid that reacts with the oxygen atom of water to produce an oxoacid. Oxides of metals in high oxidation states also tend to be acidic oxides for the same reason: they contain covalent bonds to oxygen. An example of an acidic metal oxide is MoO_3, which is insoluble in both water and acid but dissolves in strong base to give solutions of the molybdate ion (MoO_4^{2-}):

$$MoO_{3(s)} + 2OH^-(aq) \rightarrow MoO^{2-}_{4(aq)} + H_2O(l) \tag{6.11.7.17}$$

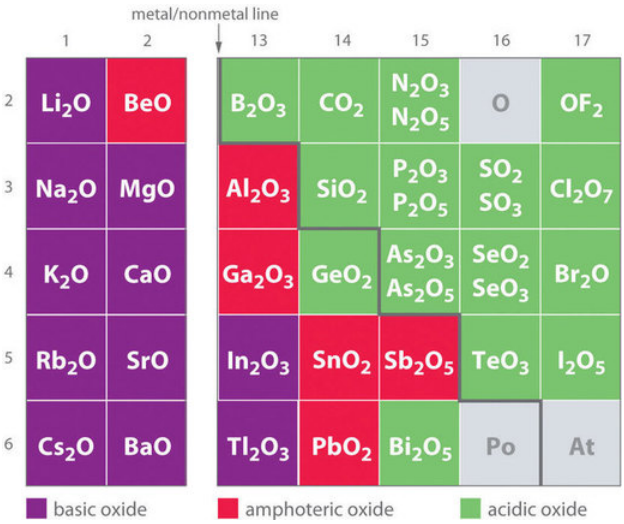


Figure **6.11.7.3**: Classification of the Oxides of the Main Group Elements According to Their Acidic or Basic Character. There is a gradual transition from basic oxides to acidic oxides from the lower left to the upper right in the periodic table. Oxides of metallic elements are generally basic oxides, which either react with water to form a basic solution or dissolve in aqueous acid. In contrast, oxides of nonmetallic elements are acidic oxides, which either react with water to form an acidic solution or are soluble in aqueous base. Oxides of intermediate character, called amphoteric oxides, are located along a diagonal line between the two extremes. Amphoteric oxides either dissolve in acid to produce water or dissolve in base to produce a soluble complex ion. (Radioactive elements are not classified.)

As shown in Figure **6.11.7.3**, there is a gradual transition from basic metal oxides to acidic nonmetal oxides as we go from the lower left to the upper right in the periodic table, with a broad diagonal band of oxides of intermediate character separating the two

extremes. Many of the oxides of the elements in this diagonal region of the periodic table are soluble in both acidic and basic solutions; consequently, they are called **amphoteric oxides** (from the Greek ampho, meaning "both," as in amphiprotic). Amphoteric oxides either dissolve in acid to produce water or dissolve in base to produce a soluble complex. As shown in Video **6.11.7.1**, for example, mixing the amphoteric oxide $Cr(OH)_3$ (also written as Cr_2O_3•$3H_2O$) with water gives a muddy, purple-brown suspension. Adding acid causes the $Cr(OH)_3$ to dissolve to give a bright violet solution of $Cr^{3+}(aq)$, which contains the $[Cr(H_2O)_6]^{3+}$ ion, whereas adding strong base gives a green solution of the $[Cr(OH)_4]^-$ ion. The chemical equations for the reactions are as follows:

$$\underset{\text{violet}}{Cr(OH)_3(s) + 3H^+(aq) \rightarrow Cr^{3+}(aq)} + 3H_2O(l) \tag{6.11.7.18}$$

$$\underset{\text{green}}{Cr(OH)_3(s) + OH^-(aq) \rightarrow [Cr(OH)_4]^-(aq)} \tag{6.11.7.19}$$



***Video* 6.11.7.1:** *Chromium(III) Hydroxide [$Cr(OH)_3$ or Cr_2O_3•$3H_2O$] is an Example of an Amphoteric Oxide. All three beakers originally contained a suspension of brownish purple $Cr(OH)_3(s)$ (center). When concentrated acid (6 M H_2SO_4) was added to the beaker on the left, $Cr(OH)_3$ dissolved to produce violet $[Cr(H_2O)_6]^{3+}$ ions and water. The addition of concentrated base (6 M NaOH) to the beaker on the right caused $Cr(OH)_3$ to dissolve, producing green $[Cr(OH)_4]^-$ ions. For a more complete description, see https://www.youtube.com/watch?v=IQNcLH6OZK0*

Example 6.11.7.2

Aluminum hydroxide, written as either $Al(OH)_3$ or Al_2O_3•$3H_2O$, is amphoteric. Write chemical equations to describe the dissolution of aluminum hydroxide in (a) acid and (b) base.

Given: amphoteric compound

Asked for: dissolution reactions in acid and base

Strategy:

Using Equations **6.11.7.18** and **6.11.7.19** as a guide, write the dissolution reactions in acid and base solutions.

Solution

a. An acid donates protons to hydroxide to give water and the hydrated metal ion, so aluminum hydroxide, which contains three OH^- ions per Al, needs three H^+ ions:

$$Al(OH)_{3(s)} + 3H^+(aq) \rightarrow Al^{3+}(aq) + 3H_2O(l)$$

In aqueous solution, Al^{3+} forms the complex ion $[Al(H_2O)_6]^{3+}$.

b. In basic solution, OH^- is added to the compound to produce a soluble and stable poly(hydroxo) complex:

$$Al(OH)_{3(s)} + OH^-(aq) \rightarrow [Al(OH)_4]^-(aq)$$

? Exercise 6.11.7.2

Copper(II) hydroxide, written as either $Cu(OH)_2$ or $CuO{\bullet}H_2O$, is *amphoteric*. Write chemical equations that describe the dissolution of cupric hydroxide both in an acid and in a base.

Answer

$$Cu(OH)_{2(s)} + 2H^+(aq) \rightarrow Cu^{2+}(aq) + 2H_2O(l)$$

$$Cu(OH)_{2(s)} + 2OH^-(aq) \rightarrow [Cu(OH)_4]^2_{-(aq)}$$

Selective Precipitation Using pH

Many dissolved metal ions can be separated by the selective precipitation of the cations from solution under specific conditions. In this technique, pH is often used to control the concentration of the anion in solution, which controls which cations precipitate.

> *The concentration of anions in solution can often be controlled by adjusting the pH, thereby allowing the selective precipitation of cations.*

Suppose, for example, we have a solution that contains 1.0 mM Zn^{2+} and 1.0 mM Cd^{2+} and want to separate the two metals by selective precipitation as the insoluble sulfide salts, ZnS and CdS. The relevant solubility equilbria can be written as follows:

$$ZnS(s) \rightleftharpoons Zn^{2+}(aq) + S^{2-}(aq) \tag{6.11.7.20}$$

with

$$K_{sp} = 1.6 \times 10^{-24} \tag{6.11.7.21}$$

and

$$CdS(s) \rightleftharpoons Cd^{2+}(aq) + S^{2-}(aq) \tag{6.11.7.22}$$

with

$$K_{sp} = 8.0 \times 10^{-27} \tag{6.11.7.23}$$

Because the S^{2-} ion is quite basic and reacts extensively with water to give HS^- and OH^-, the solubility equilbria are more accurately written as $MS(s) \rightleftharpoons M^{2+}(aq) + HS^-(aq) + OH^-$ rather than $MS(s) \rightleftharpoons M^{2+}(aq) + S^{2-}(aq)$. Here we use the simpler form involving S^{2-}, which is justified because we take the reaction of S^{2-} with water into account later in the solution, arriving at the same answer using either equilibrium equation.

The sulfide concentrations needed to cause ZnS and CdS to precipitate are as follows:

$$K_{sp} = [Zn^{2+}][S^{2-}] \tag{6.11.7.24}$$

$$1.6 \times 10^{-24} = (0.0010\ M)[S^{2-}] \tag{6.11.7.25}$$

$$1.6 \times 10^{-21}\ M = [S^{2-}] \tag{6.11.7.26}$$

and

$$K_{sp} = [Cd^{2+}][S^{2-}] \tag{6.11.7.27}$$

$$8.0 \times 10^{-27} = (0.0010\ M)[S^{2-}] \tag{6.11.7.28}$$

$$8.0 \times 10^{-24}\ M = [S^{2-}] \tag{6.11.7.29}$$

Thus sulfide concentrations between 1.6×10^{-21} M and 8.0×10^{-24} M will precipitate CdS from solution but not ZnS. How do we obtain such low concentrations of sulfide? A saturated aqueous solution of H_2S contains 0.10 M H_2S at 20°C. The $pK_{a1}$for H_2S is 6.97, and pK_{a2} corresponding to the formation of $[S^{2-}]$ is 12.90. The equations for these reactions are as follows:

$$H_2S(aq) \rightleftharpoons H^+(aq) + HS^-(aq) \tag{6.11.7.30}$$

with

$$pK_{a1} = 6.97 \text{ and hence } K_{a1} = 1.1 \times 10^{-7} \tag{6.11.7.31}$$

$$HS^-(aq) \rightleftharpoons H^+(aq) + S^{2-}(aq) \tag{6.11.7.32}$$

with

$$pK_{a2} = 12.90 \text{ and hence } K_{a2} = 1.3 \times 10^{-13} \tag{6.11.7.33}$$

We can show that the concentration of S^{2-} is 1.3×10^{-13} by comparing K_{a1} and K_{a2} and recognizing that the contribution to $[H^+]$ from the dissociation of HS^- is negligible compared with $[H^+]$ from the dissociation of H_2S. Thus substituting 0.10 M in the equation for K_{a1} for the concentration of H_2S, which is essentially constant regardless of the pH, gives the following:

$$K_{a1} = 1.1 \times 10^{-7} = \frac{[H^+][HS^-]}{[H_2S]} = \frac{x^2}{0.10\ M} \tag{6.11.7.34}$$

$$x = 1.1 \times 10^{-4}\ M = [H^+] = [HS^-]$$

Substituting this value for $[H^+]$ and $[HS^-]$ into the equation for K_{a2},

$$K_{a2} = 1.3 \times 10^{-13} = \frac{[H^+][S^{2-}]}{[HS^-]} = \frac{(1.1 \times 10^{-4}\ M)x}{1.1 \times 10^{-4}\ M} = x = [S^{2-}] \tag{6.11.7.35}$$

Although $[S^{2-}]$ in an H_2S solution is very low (1.3×10^{-13} M), bubbling H_2S through the solution until it is saturated would precipitate both metal ions because the concentration of S^{2-} would then be much greater than 1.6×10^{-21} M. Thus we must adjust $[S^{2-}]$ to stay within the desired range. The most direct way to do this is to adjust $[H^+]$ by adding acid to the H_2S solution (recall Le Chatelier's principle), thereby driving the equilibrium in Equation 6.11.7.33 to the left. The overall equation for the dissociation of H_2S is as follows:

$$H_2S(aq) \rightleftharpoons 2H^+(aq) + S^{2-}(aq) \tag{6.11.7.36}$$

Now we can use the equilibrium constant K for the overall reaction, which is the product of K_{a1} and K_{a2}, and the concentration of H_2S in a saturated solution to calculate the H^+ concentration needed to produce $[S^{2-}]$ of 1.6×10^{-21} M:

$$K = K_{a1}K_{a2} = (1.1 \times 10^{-7})(1.3 \times 10^{-13}) = 1.4 \times 10^{-20} = \frac{[H^+]^2[S^{2-}]}{[H_2S]} \tag{6.11.7.37}$$

$$[H^+]^2 = \frac{K[H_2S]}{[S^{2-}]} = \frac{(1.4 \times 10^{-20})(0.10\ M)}{1.6 \times 10^{-21}\ M} = 0.88 \tag{6.11.7.38}$$

$$[H^+] = 0.94 \tag{6.11.7.39}$$

Thus adding a strong acid such as HCl to make the solution 0.94 M in H^+ will prevent the more soluble ZnS from precipitating while ensuring that the less soluble CdS will precipitate when the solution is saturated with H_2S.

Example 6.11.7.3

A solution contains 0.010 M Ca^{2+} and 0.010 M La^{3+}. What concentration of HCl is needed to precipitate $La_2(C_2O_4)_3{\cdot}9H_2O$ but not $Ca(C_2O_4){\cdot}H_2O$ if the concentration of oxalic acid is 1.0 M? K_{sp} values are 2.32×10^{-9} for $Ca(C_2O_4)$ and 2.5×10^{-27} for $La_2(C_2O_4)_3$; $pK_{a1} = 1.25$ and $pK_{a2} = 3.81$ for oxalic acid.

Given: concentrations of cations, K_{sp} values, and concentration and pK_a values for oxalic acid

Asked for: concentration of HCl needed for selective precipitation of $La_2(C_2O_4)_3$

Strategy:

A. Write each solubility product expression and calculate the oxalate concentration needed for precipitation to occur. Determine the concentration range needed for selective precipitation of $La_2(C_2O_4)_3{\cdot}9H_2O$.

B. Add the equations for the first and second dissociations of oxalic acid to get an overall equation for the dissociation of oxalic acid to oxalate. Substitute the $[ox^{2-}]$ needed to precipitate $La_2(C_2O_4)_3{\cdot}9H_2O$ into the overall equation for the dissociation of oxalic acid to calculate the required $[H^+]$.

Solution

A Because the salts have different stoichiometries, we cannot directly compare the magnitudes of the solubility products. Instead, we must use the equilibrium constant expression for each solubility product to calculate the concentration of oxalate needed for precipitation to occur. Using ox^{2-} for oxalate, we write the solubility product expression for calcium oxalate as follows:

$$K_{sp} = [Ca^{2+}][ox^{2-}] = (0.010)[ox^{2-}] = 2.32 \times 10^{-9}$$

$$[ox^{2-}] = 2.32 \times 10^{-7}\ M$$

The expression for lanthanum oxalate is as follows:

$$K_{sp} = [La^{3+}]^2[ox^{2-}]^3 = (0.010)^2[ox^{2-}]^3 = 2.5 \times 10^{-27}$$

$$[ox^{2-}] = 2.9 \times 10^{-8}\ M$$

Thus lanthanum oxalate is less soluble and will selectively precipitate when the oxalate concentration is between $2.9 \times 10^{-8} M$ and $2.32 \times 10^{-7} M$.

B To prevent Ca^{2+} from precipitating as calcium oxalate, we must add enough H^+ to give a maximum oxalate concentration of 2.32×10^{-7} M. We can calculate the required $[H^+]$ by using the overall equation for the dissociation of oxalic acid to oxalate:

$$HO_2CCO_2H(aq) \rightleftharpoons 2H^+(aq) + C_2O_{4(aq)}^{2-} \tag{6.11.7.40}$$

$$K = K_{a1}K_{a2} = (10^{-1.25})(10^{-3.81}) = 10^{-5.06} = 8.7{\times}10^{-6}$$

Substituting the desired oxalate concentration into the equilibrium constant expression,

$$8.7 \times 10^{-6} = \frac{[H^+]^2[ox^{2-}]}{[HO_2CCO_2H]} = \frac{[H^+]^2(2.32 \times 10^{-7})}{1.0} \tag{6.11.7.41}$$

$$[H^+] = 6.1\ M \tag{6.11.7.42}$$

Thus adding enough HCl to give $[H^+]$ = 6.1 M will cause only $La_2(C_2O_4)_3{\bullet}9H_2O$ to precipitate from the solution.

? Exercise 6.11.7.3

A solution contains 0.015 M Fe^{2+} and 0.015 M Pb^{2+}. What concentration of acid is needed to ensure that Pb^{2+} precipitates as PbS in a saturated solution of H_2S, but Fe^{2+} does not precipitate as FeS? K_{sp} values are 6.3×10^{-18} for FeS and 8.0×10^{-28} for PbS.

Answer

0.018 M H^+

Summary

The anion in sparingly soluble salts is often the conjugate base of a weak acid that may become protonated in solution, so the solubility of simple oxides and sulfides, both strong bases, often depends on pH. The anion in many sparingly soluble salts is the conjugate base of a weak acid. At low pH, protonation of the anion can dramatically increase the solubility of the salt. Oxides can be classified as acidic oxides or basic oxides. Acidic oxides either react with water to give an acidic solution or dissolve in strong base; most acidic oxides are nonmetal oxides or oxides of metals in high oxidation states. Basic oxides either react with water to give a basic solution or dissolve in strong acid; most basic oxides are oxides of metallic elements. Oxides or hydroxides that are soluble in both acidic and basic solutions are called amphoteric oxides. Most elements whose oxides exhibit amphoteric behavior are located along the diagonal line separating metals and nonmetals in the periodic table. In solutions that contain mixtures of dissolved metal ions, the pH can be used to control the anion concentration needed to selectively precipitate the desired cation.

Contributors and Attributions

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6.11.8: Equilibria Involving Complex Ions

Learning Objectives

- To be introduced to complex ions, including ligands.

Previously, you learned that metal ions in aqueous solution are hydrated—that is, surrounded by a shell of usually four or six water molecules. A hydrated ion is one kind of a **complex ion** (or, simply, complex), a species formed between a central metal ion and one or more surrounding **ligands**, molecules or ions that contain at least one lone pair of electrons, such as the $[Al(H_2O)_6]^{3+}$ ion.

A complex ion forms from a metal ion and a ligand because of a Lewis acid–base interaction. The positively charged metal ion acts as a Lewis acid, and the ligand, with one or more lone pairs of electrons, acts as a Lewis base. Small, highly charged metal ions, such as Cu^{2+} or Ru^{3+}, have the greatest tendency to act as Lewis acids, and consequently, they have the greatest tendency to form complex ions.

As an example of the formation of complex ions, consider the addition of ammonia to an aqueous solution of the hydrated Cu^{2+} ion $\{[Cu(H_2O)_6]^{2+}\}$. Because it is a stronger base than H_2O, ammonia replaces the water molecules in the hydrated ion to form the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ion. Formation of the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex is accompanied by a dramatic color change, as shown in Figure **6.11.8.1**. The solution changes from the light blue of $[Cu(H_2O)_6]^{2+}$ to the blue-violet characteristic of the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ion.



Figure **6.11.8.1**: The Formation of Complex Ions. An aqueous solution of $CuSO_4$ consists of hydrated Cu^{2+} ions in the form of pale blue $[Cu(H_2O)_6]^{2+}$ (left). The addition of aqueous ammonia to the solution results in the formation of the intensely blue-violet $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ions, usually written as $[Cu(NH_3)_4]^{2+}$ ion (right) because ammonia, a stronger base than H_2O, replaces water molecules from the hydrated Cu^{2+} ion. For a more complete description, see https://www.youtube.com/watch?v=IQNcLH6OZK0.

The Formation Constant

The replacement of water molecules from $[Cu(H_2O)_6]^{2+}$ by ammonia occurs in sequential steps. Omitting the water molecules bound to Cu^{2+} for simplicity, we can write the equilibrium reactions as follows:

$$Cu^{2+}(aq) + NH_{3(aq)} \rightleftharpoons [Cu(NH_3)]^{2+}_{(aq)} \quad K_1 \tag{6.11.8.1}$$

$$[Cu(NH_3)]^{2+}_{(aq)} + NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_2]^{2+}_{(aq)} \quad K_2 \tag{6.11.8.2}$$

$$[Cu(NH_3)_2]^{2+}_{(aq)} + NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_3]^{2+}_{(aq)} \quad K_3 \tag{6.11.8.3}$$

$$[Cu(NH_3)_3]^{2+}_{(aq)} + NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_4]^{2+}_{(aq)} \quad K_4 \tag{6.11.8.4}$$

The sum of the stepwise reactions is the overall equation for the formation of the complex ion: The hydrated Cu^{2+} ion contains six H_2O ligands, but the complex ion that is produced contains only four NH_3 ligands, not six.

$$Cu^{2+}_{(aq)} + 4NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_4]^{2+}_{(aq)} \tag{6.11.8.5}$$

The equilibrium constant for the formation of the complex ion from the hydrated ion is called the **formation constant (K_f)**. The equilibrium constant expression for K_f has the same general form as any other equilibrium constant expression. In this case, the expression is as follows:

$$K_f = \frac{[[Cu(NH_3)_4]^{2+}]}{[Cu^{2+}][NH_3]^4} = 2.1 \times 10^{13} = K_1K_2K_3K_4 \tag{6.11.8.6}$$

> *The formation constant (K_f) has the same general form as any other equilibrium constant expression.*

Water, a pure liquid, does not appear explicitly in the equilibrium constant expression, and the hydrated $Cu^{2+}(aq)$ ion is represented as Cu^{2+} for simplicity. As for any equilibrium, the larger the value of the equilibrium constant (in this case, K_f), the more stable the product. With $K_f = 2.1 \times 10^{13}$, the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex ion is very stable. The formation constants for some common complex ions are listed in Table **6.11.8.1**.

Table **6.11.8.1**: Formation Constants for Selected Complex Ions in Aqueous Solution*

	Complex Ion	Equilibrium Equation	K_f
Ammonia Complexes	$[Ag(NH_3)_2]^+$	$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$	1.1×10^7
	$[Cu(NH_3)_4]^{2+}$	$Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$	2.1×10^{13}
	$[Ni(NH_3)_6]^{2+}$	$Ni^{2+} + 6NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+}$	5.5×10^8
Cyanide Complexes	$[Ag(CN)_2]^-$	$Ag^+ + 2CN^- \rightleftharpoons [Ag(CN)_2]^-$	1.1×10^{18}
	$[Ni(CN)_4]^{2-}$	$Ni^{2+} + 4CN^- \rightleftharpoons [Ni(CN)_4]^{2-}$	2.2×10^{31}
	$[Fe(CN)_6]^{3-}$	$Fe^{3+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{3-}$	1×10^{42}
Hydroxide Complexes	$[Zn(OH)_4]^{2-}$	$Zn^{2+} + 4OH^- \rightleftharpoons [Zn(OH)_4]^{2-}$	4.6×10^{17}
	$[Cr(OH)_4]^-$	$Cr^{3+} + 4OH^- \rightleftharpoons [Cr(OH)_4]^-$	8.0×10^{29}
Halide Complexes	$[HgCl_4]^{2-}$	$Hg^{2+} + 4Cl^- \rightleftharpoons [HgCl_4]^{2-}$	1.2×10^{15}
	$[CdI_4]^{2-}$	$Cd^{2+} + 4I \rightleftharpoons [CdI_4]^{2-}$	2.6×10^5
	$[AlF_6]^{3-}$	$Al^{3+} + 6F^- \rightleftharpoons [AlF_6]^{3-}$	6.9×10^{19}
Other Complexes	$[Ag(S_2O_3)_2]^{3-}$	$Ag^+ + 2S_2O_3^{2-} \rightleftharpoons [Ag(S_2O_3)_2]^{3-}$	2.9×10^{13}
	$[Fe(C_2O_4)_3]^{3-}$	$Fe^{3+} + 3C_2O_4^{2-} \rightleftharpoons [Fe(C_2O_4)_3]^{3-}$	2.0×10^{20}

*Reported values are overall formation constants. Source: Data from *Lange's Handbook of Chemistry*, 15th ed. (1999).

Example 6.11.8.1

If 12.5 g of $Cu(NO_3)_2 \cdot 6H_2O$ is added to 500 mL of 1.00 M aqueous ammonia, what is the equilibrium concentration of $Cu^{2+}(aq)$?

Given: mass of Cu^{2+} salt and volume and concentration of ammonia solution

Asked for: equilibrium concentration of $Cu^{2+}(aq)$

Strategy:

A. Calculate the initial concentration of Cu^{2+} due to the addition of copper(II) nitrate hexahydrate. Use the stoichiometry of the reaction shown in Equation 6.11.8.5 to construct a table showing the initial concentrations, the changes in concentrations, and the final concentrations of all species in solution.

B. Substitute the final concentrations into the expression for the formation constant (Equation 6.11.8.6) to calculate the equilibrium concentration of $Cu^{2+}(aq)$.

Solution

Adding an ionic compound that contains Cu^{2+} to an aqueous ammonia solution will result in the formation of $[Cu(NH_3)_4]^{2+}(aq)$, as shown in Equation 6.11.8.5. We assume that the volume change caused by adding solid copper(II) nitrate to aqueous ammonia is negligible.

A The initial concentration of Cu^{2+} from the amount of added copper nitrate prior to any reaction is as follows:

$$12.5\ \cancel{g}\ Cu(NO_3)_2 \cdot 6H_2O \left(\frac{1\ mol}{295.65\ \cancel{g}}\right)\left(\frac{1}{500\ \cancel{mL}}\right)\left(\frac{1000\ \cancel{mL}}{1\ L}\right) = 0.0846\ M \tag{6.11.8.7}$$

Because the stoichiometry of the reaction is four NH_3 to one Cu^{2+}, the amount of NH_3 required to react completely with the Cu^{2+} is 4(0.0846) = 0.338 M. The concentration of ammonia after complete reaction is 1.00 M − 0.338 M = 0.66 M. These results are summarized in the first two lines of the following table. Because the equilibrium constant for the reaction is large (2.1×10^{13}), the equilibrium will lie far to the right. Thus we will assume that the formation of $[Cu(NH_3)_4]^{2+}$ in the first step is complete and allow some of it to dissociate into Cu^{2+} and NH_3 until equilibrium has been reached. If we define x as the amount of Cu^{2+} produced by the dissociation reaction, then the stoichiometry of the reaction tells us that the change in the concentration of $[Cu(NH_3)_4]^{2+}$ is $-x$, and the change in the concentration of ammonia is $+4x$, as indicated in the table. The final concentrations of all species (in the bottom row of the table) are the sums of the concentrations after complete reaction and the changes in concentrations.

$$Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$$

	$[Cu^{2+}]$	$[NH_3]$	$[[Cu(NH_3)_4]^{2+}]$
initial	0.0846	1.00	0
after complete reaction	0	0.66	0.0846
change	$+x$	$+4x$	$-x$
final	x	$0.66 + 4x$	$0.0846 - x$

B Substituting the final concentrations into the expression for the formation constant (Equation 6.11.8.6) and assuming that x << 0.0846, which allows us to remove x from the sum and difference,

$$K_f = \frac{[[Cu(NH_3)_4]^{2+}]}{[Cu^{2+}][NH_3]^4} = \frac{0.0846 - x}{x(0.66 + 4x)^4} \approx \frac{0.0846}{x(0.66)^4} = 2.1 \times 10^{13} \tag{6.11.8.8}$$

$$x = 2.1 \times 10^{-14} \tag{6.11.8.9}$$

The value of x indicates that our assumption was justified. The equilibrium concentration of $Cu^{2+}(aq)$ in a 1.00 M ammonia solution is therefore 2.1×10^{-14} M.

? Exercise 6.11.8.1

The ferrocyanide ion $\{[Fe(CN)_6]^{4-}\}$ is very stable, with a K_f of 1×10^{35}. Calculate the concentration of cyanide ion in equilibrium with a 0.65 M solution of $K_4[Fe(CN)_6]$.

Answer 2×10^{-6} M

The Effect of the Formation of Complex Ions on Solubility

What happens to the solubility of a sparingly soluble salt if a ligand that forms a stable complex ion is added to the solution? One such example occurs in conventional black-and-white photography. Recall that black-and-white photographic film contains light-sensitive microcrystals of AgBr, or mixtures of AgBr and other silver halides. AgBr is a sparingly soluble salt, with a K_{sp} of 5.35×10^{-13} at 25°C. When the shutter of the camera opens, the light from the object being photographed strikes some of the crystals on the film and initiates a photochemical reaction that converts AgBr to black Ag metal. Well-formed, stable negative images appear in tones of gray, corresponding to the number of grains of AgBr converted, with the areas exposed to the most light being darkest. To fix the image and prevent more AgBr crystals from being converted to Ag metal during processing of the film, the unreacted AgBr on the film is removed using a complexation reaction to dissolve the sparingly soluble salt.

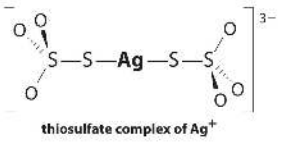
The reaction for the dissolution of silver bromide is as follows:

$$AgBr_{(s)} \rightleftharpoons Ag^+_{(aq)} + Br^-_{(aq)} \tag{6.11.8.10}$$

with

$$K_{sp} = 5.35 \times 10^{-13} \text{ at } 25°C \tag{6.11.8.11}$$

The equilibrium lies far to the left, and the equilibrium concentrations of Ag^+ and Br^- ions are very low (7.31×10^{-7} M). As a result, removing unreacted AgBr from even a single roll of film using pure water would require tens of thousands of liters of water and a great deal of time. Le Chatelier's principle tells us, however, that we can drive the reaction to the right by removing one of the products, which will cause more AgBr to dissolve. Bromide ion is difficult to remove chemically, but silver ion forms a variety of stable two-coordinate complexes with neutral ligands, such as ammonia, or with anionic ligands, such as cyanide or thiosulfate ($S_2O_3^{2-}$). In photographic processing, excess AgBr is dissolved using a concentrated solution of sodium thiosulfate.



thiosulfate complex of Ag^+

The reaction of Ag^+ with thiosulfate is as follows:

$$Ag^+_{(aq)} + 2S_2O^{2-}_{3(aq)} \rightleftharpoons [Ag(S_2O_3)_2]^{3-}_{(aq)} \tag{6.11.8.12}$$

with

$$K_f = 2.9 \times 10^{13} \tag{6.11.8.13}$$

The magnitude of the equilibrium constant indicates that almost all Ag^+ ions in solution will be immediately complexed by thiosulfate to form $[Ag(S_2O_3)_2]^{3-}$. We can see the effect of thiosulfate on the solubility of AgBr by writing the appropriate reactions and adding them together:

$$\mathrm{AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq) \quad K_{sp} = 5.35 \times 10^{-13}} \tag{6.11.8.14}$$

$$\mathrm{Ag^+(aq) + 2S_2O_3^{2-}(aq) \rightleftharpoons [Ag(S_2O_3)_2]^{3-}(aq) \quad K_f = 2.9 \times 10^{13}} \tag{6.11.8.15}$$

$$\mathrm{AgBr(s) + 2S_2O_3^{2-}(aq) \rightleftharpoons [Ag(S_2O_3)_2]^{3-}(aq) + Br^-(aq) \quad K = K_{sp}K_f = 15} \tag{6.11.8.16}$$

Comparing K with K_{sp} shows that the formation of the complex ion increases the solubility of AgBr by approximately 3×10^{13}. The dramatic increase in solubility combined with the low cost and the low toxicity explains why sodium thiosulfate is almost universally used for developing black-and-white film. If desired, the silver can be recovered from the thiosulfate solution using any of several methods and recycled.

> *If a complex ion has a large K_f, the formation of a complex ion can dramatically increase the solubility of sparingly soluble salts.*

Example 6.11.8.2

Due to the common ion effect, we might expect a salt such as AgCl to be much less soluble in a concentrated solution of KCl than in water. Such an assumption would be incorrect, however, because it ignores the fact that silver ion tends to form a two-coordinate complex with chloride ions ($AgCl_2^-$). Calculate the solubility of AgCl in each situation:

a. in pure water
b. in 1.0 M KCl solution, ignoring the formation of any complex ions
c. the same solution as in part (b) except taking the formation of complex ions into account, assuming that $AgCl_2^-$ is the only Ag^+ complex that forms in significant concentrations

At 25°C, $K_{sp} = 1.77 \times 10^{-10}$ for AgCl and $K_f = 1.1 \times 10^5$ for $AgCl_2^-$.

Given: K_{sp} of AgCl, K_f of $AgCl_2^-$, and KCl concentration

Asked for: solubility of AgCl in water and in KCl solution with and without the formation of complex ions

Strategy:

A. Write the solubility product expression for AgCl and calculate the concentration of Ag^+ and Cl^- in water.
B. Calculate the concentration of Ag^+ in the KCl solution.
C. Write balanced chemical equations for the dissolution of AgCl and for the formation of the $AgCl_2^-$ complex. Add the two equations and calculate the equilibrium constant for the overall equilibrium.
D. Write the equilibrium constant expression for the overall reaction. Solve for the concentration of the complex ion.

Solution

a. **A** If we let x equal the solubility of AgCl, then at equilibrium $[Ag+] = [Cl^-] = x$ M. Substituting this value into the solubility product expression,

$$K_{sp} = [Ag^+][Cl^-] = (x)(x) = x^2 = 1.77\times10^{-10}$$
$$x = 1.33\times10^{-5}$$

Thus the solubility of AgCl in pure water at 25°C is 1.33×10^{-5} M.

b. **B** If x equals the solubility of AgCl in the KCl solution, then at equilibrium $[Ag^+] = x$ M and $[Cl^-] = (1.0 + x)$ M. Substituting these values into the solubility product expression and assuming that $x << 1.0$,

$$K_{sp} = [Ag^+][Cl^-] = (x)(1.0 + x) \approx x(1.0) = 1.77\times10^{-10} = x$$

If the common ion effect were the only important factor, we would predict that AgCl is approximately five orders of magnitude less soluble in a 1.0 M KCl solution than in water.

c. **C** To account for the effects of the formation of complex ions, we must first write the equilibrium equations for both the dissolution and the formation of complex ions. Adding the equations corresponding to K_{sp} and K_f gives us an equation that describes the dissolution of AgCl in a KCl solution. The equilibrium constant for the reaction is therefore the product of K_{sp} and K_f:

$$\mathrm{AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)} \quad K_{sp} = 1.77 \times 10^{-10} \tag{6.11.8.17}$$
$$\mathrm{Ag^+(aq) + 2Cl^- \rightleftharpoons [AgCl_2]^-} \quad K_f = 1.1 \times 10^5 \tag{6.11.8.18}$$
$$\mathrm{AgCl(s) + Cl^- \rightleftharpoons [AgCl_2]^-} \quad K = K_{sp}K_f = 1.9 \times 10^{-5} \tag{6.11.8.19}$$

D If we let x equal the solubility of AgCl in the KCl solution, then at equilibrium $[AgCl_2^-] = x$ and $[Cl^-] = 1.0 - x$. Substituting these quantities into the equilibrium constant expression for the net reaction and assuming that $x << 1.0$,

$$K = \frac{[\mathrm{AgCl_2^-}]}{[\mathrm{Cl^-}]} = \frac{x}{1.0 - x} \approx 1.9 \times 10^{-5} = x$$

That is, AgCl dissolves in 1.0 M KCl to produce a 1.9×10^{-5} M solution of the $AgCl_2^-$ complex ion. Thus we predict that AgCl has approximately the same solubility in a 1.0 M KCl solution as it does in pure water, which is 10^5 times greater than that predicted based on the common ion effect. (In fact, the measured solubility of AgCl in 1.0 M KCl is almost a factor of 10 greater than that in pure water, largely due to the formation of other chloride-containing complexes.)

? Exercise 6.11.8.2

Calculate the solubility of mercury(II) iodide (HgI_2) in each situation:

a. pure water
b. a 3.0 M solution of NaI, assuming $[HgI_4]^{2-}$ is the only Hg-containing species present in significant amounts

$$K_{sp} = 2.9 \times 10^{-29} \text{ for } HgI_2 \text{ and } K_f = 6.8 \times 10^{29} \text{ for } [HgI_4]^{2-}.$$

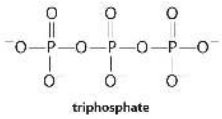
Answer

a. 1.9×10^{-10} M
b. 1.4 M



Solubility of Complex Ions: https://youtu.be/f4pkKDg2XTA

Complexing agents, molecules or ions that increase the solubility of metal salts by forming soluble metal complexes, are common components of laundry detergents. Long-chain carboxylic acids, the major components of soaps, form insoluble salts with Ca^{2+} and Mg^{2+}, which are present in high concentrations in "hard" water. The precipitation of these salts produces a bathtub ring and gives a gray tinge to clothing. Adding a complexing agent such as pyrophosphate ($O_3POPO_3^{4-}$, or $P_2O_7^{4-}$) or triphosphate ($P_3O_{10}^{5-}$) to detergents prevents the magnesium and calcium salts from precipitating because the equilibrium constant for complex-ion formation is large:



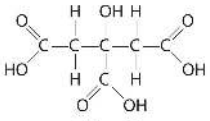
triphosphate

$$Ca^{2+}_{(aq)} + O_3POPO^{4-}_{4(aq)} \rightleftharpoons [Ca(O_3POPO_3)]^{2-}_{(aq)} \tag{6.11.8.20}$$

with

$$K_f = 4 \times 10^4 \tag{6.11.8.21}$$

However, phosphates can cause environmental damage by promoting eutrophication, the growth of excessive amounts of algae in a body of water, which can eventually lead to large decreases in levels of dissolved oxygen that kill fish and other aquatic organisms. Consequently, many states in the United States have banned the use of phosphate-containing detergents, and France has banned their use beginning in 2007. "Phosphate-free" detergents contain different kinds of complexing agents, such as derivatives of acetic acid or other carboxylic acids. The development of phosphate substitutes is an area of intense research.



Citric acid,
a hydroxy polycarboxylic acid

Commercial water softeners also use a complexing agent to treat hard water by passing the water over ion-exchange resins, which are complex sodium salts. When water flows over the resin, sodium ion is dissolved, and insoluble salts precipitate onto the resin surface. Water treated in this way has a saltier taste due to the presence of Na^+, but it contains fewer dissolved minerals.

Another application of complexing agents is found in medicine. Unlike x-rays, magnetic resonance imaging (MRI) can give relatively good images of soft tissues such as internal organs. MRI is based on the magnetic properties of the ^1H nucleus of hydrogen atoms in water, which is a major component of soft tissues. Because the properties of water do not depend very much on whether it is inside a cell or in the blood, it is hard to get detailed images of these tissues that have good contrast. To solve this problem, scientists have developed a class of metal complexes known as "MRI contrast agents." Injecting an MRI contrast agent into a patient selectively affects the magnetic properties of water in cells of normal tissues, in tumors, or in blood vessels and

allows doctors to “see” each of these separately (Figure **6.11.8.2**). One of the most important metal ions for this application is Gd^{3+}, which with seven unpaired electrons is highly paramagnetic. Because $Gd^{3+}(aq)$ is quite toxic, it must be administered as a very stable complex that does not dissociate in the body and can be excreted intact by the kidneys. The complexing agents used for gadolinium are ligands such as $DTPA^{5-}$ (diethylene triamine pentaacetic acid), whose fully protonated form is shown here.

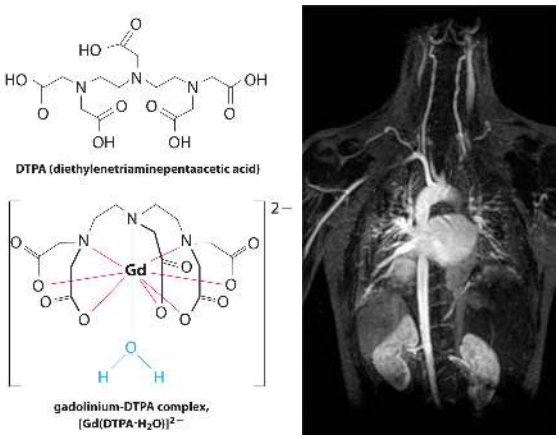


Figure **6.11.8.2**: An MRI Image of the Heart, Arteries, and Veins. When a patient is injected with a paramagnetic metal cation in the form of a stable complex known as an MRI contrast agent, the magnetic properties of water in cells are altered. Because the different environments in different types of cells respond differently, a physician can obtain detailed images of soft tissues.

Summary

The formation of complex ions can substantially increase the solubility of sparingly soluble salts if the complex ion has a large K_f. A complex ion is a species formed between a central metal ion and one or more surrounding ligands, molecules or ions that contain at least one lone pair of electrons. Small, highly charged metal ions have the greatest tendency to act as Lewis acids and form complex ions. The equilibrium constant for the formation of the complex ion is the formation constant (K_f). The formation of a complex ion by adding a complexing agent increases the solubility of a compound.

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6.11.9: Qualitative Cation Analysis

Learning Objectives

- To know how to separate metal ions by selective precipitation.
- To understand how several common metal cations can be identified in a solution using selective precipitation.

The composition of relatively complex mixtures of metal ions can be determined using **qualitative analysis**, a procedure for discovering the identity of metal ions present in the mixture (rather than quantitative information about their amounts). The procedure used to separate and identify more than 20 common metal cations from a single solution consists of selectively precipitating only a few kinds of metal ions at a time under given sets of conditions. Consecutive precipitation steps become progressively less selective until almost all of the metal ions are precipitated, as illustrated in Figure **6.11.9.1**.

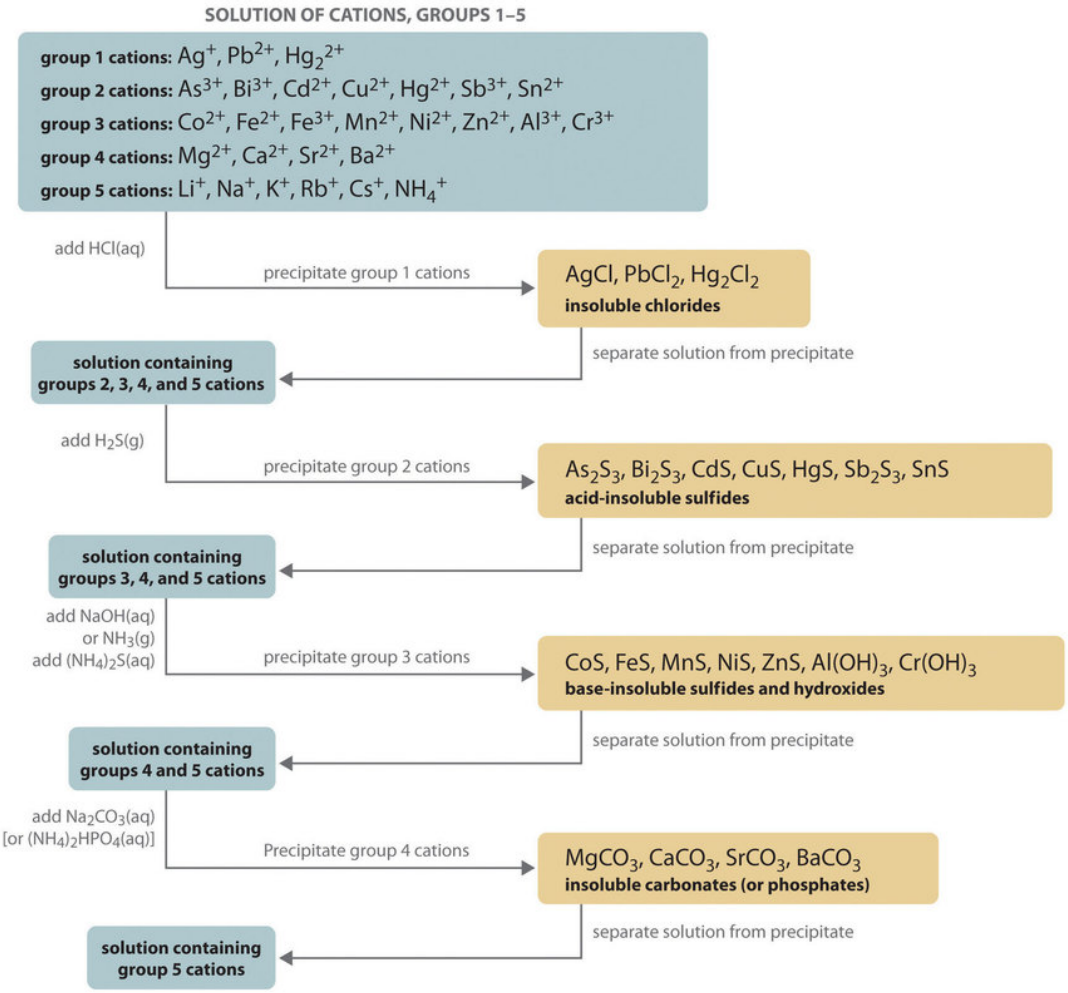


Figure **6.11.9.1**: Steps in a Typical Qualitative Analysis Scheme for a Solution That Contains Several Metal Ions

Group 1: Insoluble Chlorides

Most metal chloride salts are soluble in water; only Ag^+, Pb^{2+}, and Hg_2^{2+} form chlorides that precipitate from water. Thus the first step in a qualitative analysis is to add about 6 M HCl, thereby causing AgCl, $PbCl_2$, and/or Hg_2Cl_2 to precipitate. If no precipitate forms, then these cations are not present in significant amounts. The precipitate can be collected by filtration or centrifugation.

Group 2: Acid-Insoluble Sulfides

Next, the acidic solution is saturated with H_2S gas. Only those metal ions that form very insoluble sulfides, such as As^{3+}, Bi^{3+}, Cd^{2+}, Cu^{2+}, Hg^{2+}, Sb^{3+}, and Sn^{2+}, precipitate as their sulfide salts under these acidic conditions. All others, such as Fe^{2+} and Zn^{2+}, remain in solution. Once again, the precipitates are collected by filtration or centrifugation.

Group 3: Base-Insoluble Sulfides (and Hydroxides)

Ammonia or $NaOH$ is now added to the solution until it is basic, and then $(NH_4)_2S$ is added. This treatment removes any remaining cations that form insoluble hydroxides or sulfides. The divalent metal ions Co^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, and Zn^{2+} precipitate as their sulfides, and the trivalent metal ions Al^{3+} and Cr^{3+} precipitate as their hydroxides: $Al(OH)_3$ and $Cr(OH)_3$. If the mixture contains Fe^{3+}, sulfide reduces the cation to Fe^{2+}, which precipitates as FeS.

Group 4: Insoluble Carbonates or Phosphates

The next metal ions to be removed from solution are those that form insoluble carbonates and phosphates. When Na_2CO_3 is added to the basic solution that remains after the precipitated metal ions are removed, insoluble carbonates precipitate and are collected. Alternatively, adding $(NH_4)_2HPO_4$ causes the same metal ions to precipitate as insoluble phosphates.

Group 5: Alkali Metals

At this point, we have removed all the metal ions that form water-insoluble chlorides, sulfides, carbonates, or phosphates. The only common ions that might remain are any alkali metals (Li^+, Na^+, K^+, Rb^+, and Cs^+) and ammonium (NH_4^+). We now take a second sample from the original solution and add a small amount of $NaOH$ to neutralize the ammonium ion and produce NH_3. (We cannot use the same sample we used for the first four groups because we added ammonium to that sample in earlier steps.) Any ammonia produced can be detected by either its odor or a litmus paper test. A flame test on another original sample is used to detect sodium, which produces a characteristic bright yellow color. The other alkali metal ions also give characteristic colors in flame tests, which allows them to be identified if only one is present.

Metal ions that precipitate together are separated by various additional techniques, such as forming complex ions, changing the pH of the solution, or increasing the temperature to redissolve some of the solids. For example, the precipitated metal chlorides of group 1 cations, containing Ag^+, Pb^{2+}, and Hg_2^{2+}, are all quite insoluble in water. Because $PbCl_2$ is much more soluble in hot water than are the other two chloride salts, however, adding water to the precipitate and heating the resulting slurry will dissolve any $PbCl_2$ present. Isolating the solution and adding a small amount of Na_2CrO_4 solution to it will produce a bright yellow precipitate of $PbCrO_4$ if Pb^{2+} were in the original sample (Figure 6.11.9.2).



Figure 6.11.9.2: When a small amount of Na_2CrO_4 solution is added to a sample containing Pb^{2+} ions in water, a bright yellow precipitate of $PbCrO_4$ forms. (CC BY-SA 3.0 Unported; PRHaney via Wikipedia).

As another example, treating the precipitates from group 1 cations with aqueous ammonia will dissolve any $AgCl$ because Ag^+ forms a stable complex with ammonia: $[Ag(NH_3)_2]^+$. In addition, Hg_2Cl_2 disproportionates in ammonia.

$$2\,Hg_2^{2+} \rightarrow Hg + Hg^{2+}$$

to form a black solid that is a mixture of finely divided metallic mercury and an insoluble mercury(II) compound, which is separated from solution:

$$Hg_2Cl_2\,(s) + 2\,NH_3\,(aq) \rightarrow Hg\,(l) + Hg(NH_2)Cl\,(s) + NH_4^+\,(aq) + Cl^-\,(aq)$$

Any silver ion in the solution is then detected by adding **HCl**, which reverses the reaction and gives a precipitate of white **AgCl** that slowly darkens when exposed to light:

$$[Ag(NH_3)_2]^+(aq) + 2\,H^+(aq) + Cl^-(aq) \rightarrow AgCl(s) + 2\,NH_4^+(aq)$$

Similar but slightly more complex reactions are also used to separate and identify the individual components of the other groups.

Summary

In qualitative analysis, the identity, not the amount, of metal ions present in a mixture is determined. The technique consists of selectively precipitating only a few kinds of metal ions at a time under given sets of conditions. Consecutive precipitation steps become progressively less selective until almost all the metal ions are precipitated. Other additional steps are needed to separate metal ions that precipitate together.

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CHAPTER OVERVIEW

7: Acids and Bases

UC Davis CHE 2B: General Chemistry II

Reading Assignments • Homework

Template:HideTOC

It is not a revelation to know that matter or chemicals can convert from one species or state of matter to another. Often the general properties that govern this transformation can be described in terms of an equilibrium. That is, a situation whereby the quantity or quality of the sample does not change in time. Such a situation is intimately connected to "thermodynamics" as discussed later. As you will learn in Chem 2C, electrochemistry is the third member of this troika.

- 7.1: Acids and Bases
  - 7.1.1: Arrhenius Theory- A Brief Review
  - 7.1.2: Brønsted-Lowry Theory of Acids and Bases
  - 7.1.3: Self-Ionization of Water and the pH Scale
  - 7.1.4: Strong Acids and Strong Bases
  - 7.1.5: Weak Acids and Weak Bases
  - 7.1.6: Polyprotic Acids
  - 7.1.7: Ions as Acids and Bases
  - 7.1.8: Molecular Structure and Acid-Base Behavior
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- 7.2: Additional Aspects of Acid-Base Equilibria
  - 7.2.1: Common-Ion Effect in Acid–Base Equilibria
  - 7.2.2: Buffer Solutions
  - 7.2.3: Acid–Base Indicators
  - 7.2.4: Neutralization Reactions and Titration Curves
  - 7.2.5: Solutions of Salts of Polyprotic Acids
  - 7.2.6: Acid–Base Equilibrium Calculations- ASummary
- 7.3: Hard and Soft Acids and Bases
  - 7.3.1: Theory of Hard and Soft Acids and Bases
  - 7.3.2: HSAB Quantitative Measures

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SECTION OVERVIEW

7.1: Acids and Bases

Topic hierarchy

7.1.1: Arrhenius Theory- A Brief Review

7.1.2: Brønsted-Lowry Theory of Acids and Bases

7.1.3: Self-Ionization of Water and the pH Scale

7.1.4: Strong Acids and Strong Bases

7.1.5: Weak Acids and Weak Bases

7.1.6: Polyprotic Acids

7.1.7: Ions as Acids and Bases

7.1.8: Molecular Structure and Acid-Base Behavior

7.1.9: Lewis Acids and Bases

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7.1.1: Arrhenius Theory- A Brief Review

Acids and bases have been known for a long time. When Robert Boyle characterized them in 1680, he noted that acids dissolve many substances, change the color of certain natural dyes (for example, they change litmus from blue to red), and lose these characteristic properties after coming into contact with alkalis (bases). In the eighteenth century, it was recognized that acids have a sour taste, react with limestone to liberate a gaseous substance (now known to be CO_2), and interact with alkalis to form neutral substances. In 1815, Humphry Davy contributed greatly to the development of the modern acid-base concept by demonstrating that hydrogen is the essential constituent of acids. Around that same time, Joseph Louis Gay-Lussac concluded that acids are substances that can neutralize bases and that these two classes of substances can be defined only in terms of each other. The significance of hydrogen was reemphasized in 1884 when Svante Arrhenius defined an acid as a compound that dissolves in water to yield hydrogen cations (now recognized to be hydronium ions) and a base as a compound that dissolves in water to yield hydroxide anions.

Acids and bases are common solutions that exist everywhere. Almost every liquid that we encounter in our daily lives consists of acidic and basic properties, with the exception of water. They have completely different properties and are able to neutralize to form H_2O, which will be discussed later in a subsection. Acids and bases can be defined by their physical and chemical observations (Table **7.1.1.1**).

Table **7.1.1.1**: General Properties of Acids and Bases

ACIDS	BASES
produce a piercing pain in a wound.	give a slippery feel.
taste sour.	taste bitter.
are colorless when placed in phenolphthalein (an indicator).	are pink when placed in phenolphthalein (an indicator).
are red on blue litmus paper (a pH indicator).	are blue on red litmus paper (a pH indicator).
have a pH<7.	have a pH>7.
produce hydrogen gas when reacted with metals.	
produce carbon dioxide when reacted with carbonates.	
Common examples: Lemons, oranges, vinegar, urine, sulfuric acid, hydrochloric acid	Common Examples: Soap, toothpaste, bleach, cleaning agents, limewater, ammonia water, sodium hydroxide.

Acids and bases in aqueous solutions will conduct electricity because they contain dissolved ions. Therefore, acids and bases are **electrolytes**. Strong acids and bases will be strong electrolytes. Weak acids and bases will be weak electrolytes. This affects the amount of conductivity.

The Arrhenius Definition of Acids and Bases

In 1884, the Swedish chemist Svante Arrhenius proposed two specific classifications of compounds, termed acids and bases. When dissolved in an aqueous solution, certain ions were released into the solution. The Arrhenius definition of acid-base reactions is a development of the "hydrogen theory of acids". It was used to provide a modern definition of acids and bases, and followed from Arrhenius's work with Friedrich Wilhelm Ostwald in establishing the presence of ions in aqueous solution in 1884. This led to Arrhenius receiving the Nobel Prize in Chemistry in 1903.

An Arrhenius acid is a compound that increases the concentration of H^+ ions that are present when added to water. These H^+ ions form the hydronium ion (H_3O^+) when they combine with water molecules. This process is represented in a chemical equation by adding H_2O to the reactants side.

$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

In this reaction, hydrochloric acid (HCl) dissociates into hydrogen (H^+) and chlorine (Cl^-) ions when dissolved in water, thereby releasing H^+ ions into solution. Formation of the hydronium ion equation:

$$HCl_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$$

The Arrhenius definitions of acidity and alkalinity are restricted to aqueous solutions and refer to the concentration of the solvated ions. Under this definition, pure H_2SO_4 or HCl dissolved in toluene are not acidic, despite the fact that both of these acids will donate a proton to toluene. In addition, under the Arrhenius definition, a solution of sodium amide ($NaNH_2$) in liquid ammonia is not alkaline, despite the fact that the amide ion (NH_2^-) will readily deprotonate ammonia. Thus, the Arrhenius definition can only describe acids and bases in an aqueous environment.

Limitation of the Arrhenius Definition of Acids and Bases

The Arrhenius definition can **only** describe acids and bases in an aqueous environment.

In chemistry, acids and bases have been defined differently by three sets of theories: One is the Arrhenius definition defined above, which revolves around the idea that acids are substances that ionize (break off) in an aqueous solution to produce hydrogen (H^+) ions while bases produce hydroxide (OH^-) ions in solution. The other two definitions are discussed in detail alter in the chapter and include the Brønsted-Lowry definition the defines acids as substances that donate protons (H^+) whereas bases are substances that accept protons and the Lewis theory of acids and bases states that acids are electron pair acceptors while bases are electron pair donors.

Contributors and Attributions

- Anonymous

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7.1.2: Brønsted-Lowry Theory of Acids and Bases

Learning Objectives

- Identify acids, bases, and conjugate acid-base pairs according to the Brønsted-Lowry definition
- Write equations for acid and base ionization reactions
- Use the ion-product constant for water to calculate hydronium and hydroxide ion concentrations
- Describe the acid-base behavior of amphiprotic substances

The Arrhenius definition of an acid as a compound that dissolves in water to yield hydronium ions (H_3O^+) and a base as a compound that dissolves in water to yield hydroxide ions (OH^-). This definition is not wrong; it is simply limited. We extended the definition of an acid or a base using the more general definition proposed in 1923 by the Danish chemist Johannes Brønsted and the English chemist Thomas Lowry. Their definition centers on the proton, H^+. A proton is what remains when a normal hydrogen atom, ${}^1_1H$, loses an electron. A compound that donates a proton to another compound is called a Brønsted-Lowry acid, and a compound that accepts a proton is called a Brønsted-Lowry base. An acid-base reaction is the transfer of a proton from a proton donor (acid) to a proton acceptor (base). In a subsequent chapter of this text we will introduce the most general model of acid-base behavior introduced by the American chemist G. N. Lewis.

Brønsted-Lowry Defintions

- A compound that **donates** a proton to another compound is called a Brønsted-Lowry acid.
- A compound that **accepts** a proton is called a Brønsted-Lowry base.



Definitions of Acids and Bases: https://youtu.be/r8reN0CSIHw

Acids may be compounds such as HCl or H_2SO_4, organic acids like acetic acid (CH_3COOH) or ascorbic acid (vitamin C), or H_2O. Anions (such as HSO_4^-, $H_2PO_4^-$, HS^-, and HCO_3^-) and cations (such as H_3O^+, NH_4^+, and $[Al(H_2O)_6]^{3+}$) may also act as acids. Bases fall into the same three categories. Bases may be neutral molecules (such as H_2O, NH_3, and CH_3NH_2), anions (such as OH^-, HS^-, HCO_3^-, CO_3^{2-}, F^-, and PO_4^{3-}), or cations (such as $[Al(H_2O)_5OH]^{2+}$). The most familiar bases are ionic compounds such as $NaOH$ and $Ca(OH)_2$, which contain the hydroxide ion, OH^-. The hydroxide ion in these compounds accepts a proton from acids to form water:

$$H^+ + OH^- \rightarrow H_2O \tag{7.1.2.1}$$

We call the product that remains after an acid donates a proton the **conjugate base** of the acid. This species is a base because it can accept a proton (to re-form the acid):

$$\text{acid} \rightleftharpoons \text{proton} + \text{conjugate base} \tag{7.1.2.2}$$

$$HF \rightleftharpoons H^+ + F^-$$

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$$

$$NH_4^+ \rightleftharpoons H^+ + NH_3$$

We call the product that results when a base accepts a proton the base's **conjugate acid**. This species is an acid because it can give up a proton (and thus re-form the base):

$$\text{base} + \text{proton} \rightleftharpoons \text{conjugate acid} \tag{7.1.2.3}$$

$$OH^- + H^+ \rightleftharpoons H_2O$$

$$H_2O + H^+ \rightleftharpoons H_3O^+$$

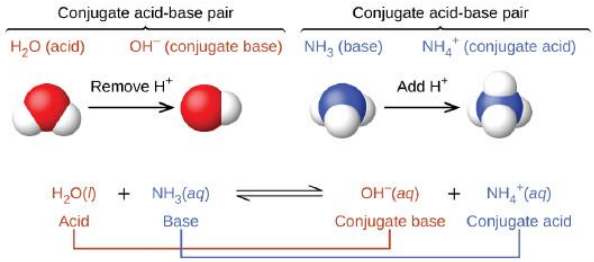
$$NH_3 + H^+ \rightleftharpoons NH_4^+$$

$$S^{2-} + H^+ \rightleftharpoons HS^-$$

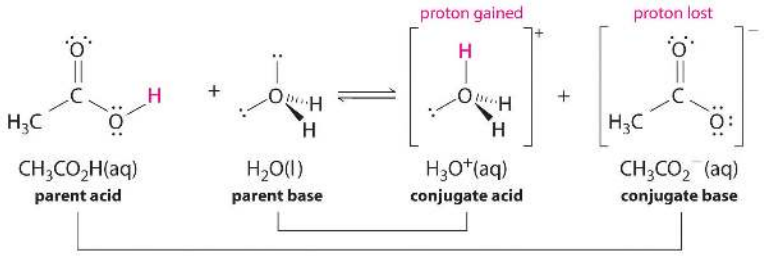
$$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^-$$

$$F^- + H^+ \rightleftharpoons HF$$

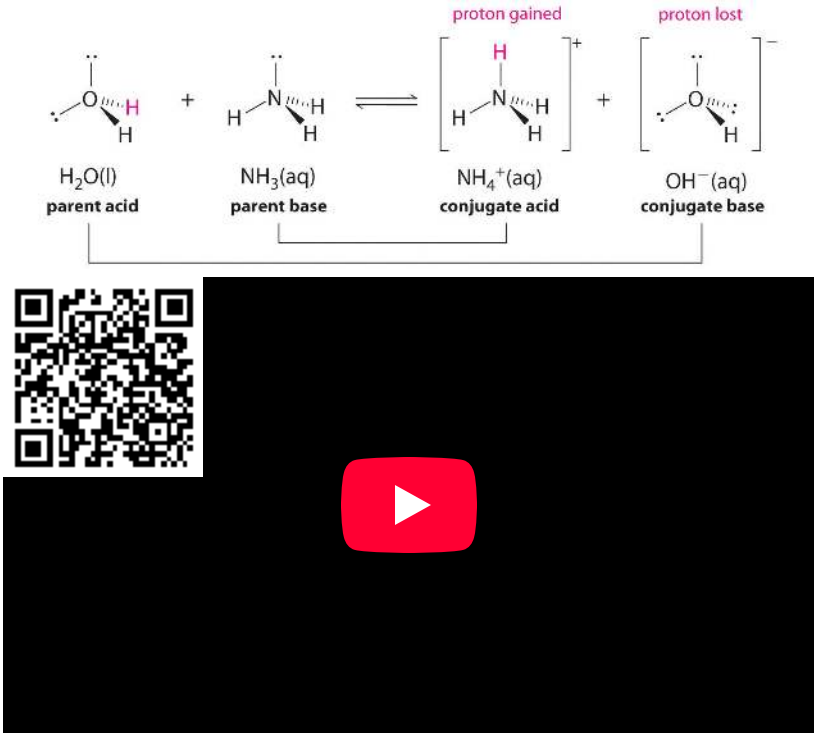
In these two sets of equations, the behaviors of acids as proton donors and bases as proton acceptors are represented in isolation. In reality, all acid-base reactions involve the transfer of protons between acids and bases. For example, consider the acid-base reaction that takes place when ammonia is dissolved in water. A water molecule (functioning as an acid) transfers a proton to an ammonia molecule (functioning as a base), yielding the conjugate base of water, OH^-, and the conjugate acid of ammonia, NH_4^+:



Similarly, in the reaction of acetic acid with water, acetic acid donates a proton to water, which acts as the base. In the reverse reaction, H_3O^+ is the acid that donates a proton to the acetate ion, which acts as the base. Once again, we have two conjugate acid–base pairs: the parent acid and its conjugate base ($CH_3CO_2H/CH_3CO_2^-$) and the parent base and its conjugate acid (H_3O^+/H_2O).



In the reaction of ammonia with water to give ammonium ions and hydroxide ions, ammonia acts as a base by accepting a proton from a water molecule, which in this case means that water is acting as an acid. In the reverse reaction, an ammonium ion acts as an acid by donating a proton to a hydroxide ion, and the hydroxide ion acts as a base. The conjugate acid–base pairs for this reaction are NH_4^+/NH_3 and H_2O/OH^-.



Conjugate Acid-Base Pairs: https://youtu.be/pPrp3xEQef4

Amphiprotic Species

Like water, many molecules and ions may either gain or lose a proton under the appropriate conditions. Such species are said to be amphiprotic. Another term used to describe such species is amphoteric, which is a more general term for a species that may act either as an acid or a base by any definition (not just the Brønsted-Lowry one). Consider for example the bicarbonate ion, which may either donate or accept a proton as shown here:

$$\mathrm{HCO_3^-\,(aq) + H_2O\,(l) \rightleftharpoons CO_3^{2-}\,(aq) + H_3O^+\,(aq)}$$

$$\mathrm{HCO_3^-\,(aq) + H_2O\,(l) \rightleftharpoons H_2CO_3\,(aq) + OH^-\,(aq)}$$

Water is the most important amphiprotic species. It can form both the hydronium ion, $\mathrm{H_3O^+}$, and the hydroxide ion, $\mathrm{OH^-}$ when it undergoes **autoionization**:

$$\mathrm{2\,H_2O_{(l)} \rightleftharpoons H_3O^+(aq) + OH^-(aq)}$$

✔ Example 7.1.2.1: The Acid-Base Behavior of an Amphoteric Substance

Write separate equations representing the reaction of $\mathrm{HSO_3^-}$

a. as an acid with $\mathrm{OH^-}$
b. as a base with HI

Solution

a. $\mathrm{HSO_3^-\,(aq) + OH^-\,(aq) \rightleftharpoons SO_3^{2-}\,(aq) + H_2O\,(l)}$
b. $\mathrm{HSO_3^-\,(aq) + HI\,(aq) \rightleftharpoons H_2SO_3\,(aq) + I^-\,(aq)}$

? Exercise 7.1.2.1

Write separate equations representing the reaction of $\mathrm{H_2PO_4^-}$

a. as a base with HBr

b. as an acid with OH^-

Answer a

$$H_2PO_4^-(aq) + HBr(aq) \rightleftharpoons H_3PO_4(aq) + Br^-(aq)$$

Answer b

$$H_2PO_4^-(aq) + OH^-(aq) \rightleftharpoons HPO_4^{2-}(aq) + H_2O_{(l)}$$

Key Concepts and Summary

A compound that can donate a proton (a hydrogen ion) to another compound is called a Brønsted-Lowry acid. The compound that accepts the proton is called a Brønsted-Lowry base. The species remaining after a Brønsted-Lowry acid has lost a proton is the conjugate base of the acid. The species formed when a Brønsted-Lowry base gains a proton is the conjugate acid of the base. Thus, an acid-base reaction occurs when a proton is transferred from an acid to a base, with formation of the conjugate base of the reactant acid and formation of the conjugate acid of the reactant base. Amphiprotic species can act as both proton donors and proton acceptors. Water is the most important amphiprotic species. It can form both the hydronium ion, H_3O^+, and the hydroxide ion, OH^- when it undergoes autoionization:

$$2\,H_2O_{(l)} \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

Glossary

acid ionization
reaction involving the transfer of a proton from an acid to water, yielding hydronium ions and the conjugate base of the acid

amphiprotic
species that may either gain or lose a proton in a reaction

amphoteric
species that can act as either an acid or a base

autoionization
reaction between identical species yielding ionic products; for water, this reaction involves transfer of protons to yield hydronium and hydroxide ions

base ionization
reaction involving the transfer of a proton from water to a base, yielding hydroxide ions and the conjugate acid of the base

Brønsted-Lowry acid
proton donor

Brønsted-Lowry base
proton acceptor

conjugate acid
substance formed when a base gains a proton

conjugate base
substance formed when an acid loses a proton

ion-product constant for water (K_w)
equilibrium constant for the autoionization of water

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7.1.3: Self-Ionization of Water and the pH Scale

Learning Objectives

- To understand the autoionization reaction of liquid water.
- To know the relationship among pH, pOH, and pK_w.

Because of its highly polar structure, liquid water can act as either an acid (by donating a proton to a base) or a base (by using a lone pair of electrons to accept a proton). For example, when a strong acid such as HCl dissolves in water, it dissociates into chloride ions (Cl^-) and protons (H^+). The proton, in turn, reacts with a water molecule to form the hydronium ion (H_3O^+):

$$\underset{acid}{HCl\,(aq)} + \underset{base}{H_2O\,(l)} \rightarrow \underset{acid}{H_3O^+\,(aq)} + \underset{base}{Cl^-\,(aq)} \tag{7.1.3.1}$$

In this reaction, HCl is the acid, and water acts as a base by accepting an H^+ ion. The reaction in Equation 7.1.3.1 is often written in a simpler form by removing H_2O from each side:

$$HCl\,(aq) \rightarrow H^+\,(aq) + Cl^-\,(aq) \tag{7.1.3.2}$$

In Equation 7.1.3.2, the hydronium ion is represented by $H^+\,(aq)$, although free H^+ ions do not exist in liquid water as this reaction demonstrates:

$$H^+\,(aq) + H_2O\,(l) \rightarrow H_3O^+\,(aq) \tag{7.1.3.3}$$

Water can also act as an acid, as shown in Equation 7.1.3.4. In this equilibrium reaction, H_2O donates a proton to NH_3, which acts as a base:

$$\underset{acid}{H_2O\,(aq)} + \underset{base}{NH_3\,(aq)} \rightleftharpoons \underset{acid}{NH_4^+\,(aq)} + \underset{base}{OH^-\,(aq)} \tag{7.1.3.4}$$

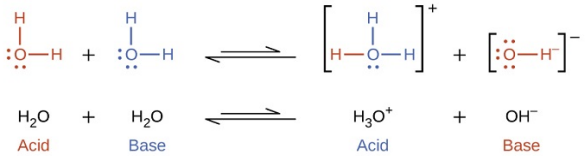
Water is thus termed **amphiprotic**, meaning that it can behave as either an acid or a base, depending on the nature of the other reactant. Notice that Equation 7.1.3.4 is an equilibrium reaction as indicated by the double arrow and hence has an equilibrium constant associated with it.

The Ion-Product Constant of Pure Water

Because water is amphiprotic, one water molecule can react with another to form an OH^- ion and an H_3O^+ ion in an autoionization process:

$$2\,H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + OH^-\,(aq) \tag{7.1.3.5}$$

In pure water, a very small fraction of water molecules donate protons to other water molecules to form hydronium ions and hydroxide ions:



The equilibrium constant K for this reaction can be written as follows:

$$K_a = \frac{a_{H_3O^+} \cdot a_{OH^-}}{a_{H_2O}^2} \approx \frac{[H_3O^+][HO^-]}{(1)^2} = [H_3O^+][HO^-] \tag{7.1.3.6}$$

where a is the activity of a species. Because water is the solvent, and the solution is assumed to be dilute, the activity of the water is approximated by the activity of pure liquid water, which is defined as having a value of 1. The activity of each solute is approximated by the molarity of the solute.

Note

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

In this reaction, one water molecule acts as an acid and one water molecule acts as a base. Thus, this reaction actually can be designated as the K_a of water and as the K_b of water. It is most common, however, to designate this reaction and the associated law of mass action as the K_w of water:

$$K_w = [H_3O^+][HO^-] \tag{7.1.3.7}$$

When pure liquid water is in equilibrium with hydronium and hydroxide ions at 25 °C, the concentrations of the hydronium ion and the hydroxide ion are equal:

$$[H_3O^+] = [OH^-] = 1.003 \times 10^{-7}\ M \tag{7.1.3.8}$$

Thus the number of dissociated water molecules is very small indeed, approximately 2 ppb.

Substituting the values for $[H_3O^+]$ and $[OH^-]$ at 25°C into this expression

$$K_w = (1.003 \times 10^{-7})(1.003 \times 10^{-7}) = 1.006 \times 10^{-14} \tag{7.1.3.9}$$

The slight ionization of pure water is reflected in the small value of the equilibrium constant; at 25 °C.Thus, to three significant figures, $K_w = 1.01 \times 10^{-14}\ M$ *at room temperature*. Like any other equilibrium constant, K_w varies with temperature, ranging from 1.15×10^{-15} at 0°C to 4.99×10^{-13} at 100°C.

In pure water, the concentrations of the hydronium ion and the hydroxide ion are equal, and the solution is therefore neutral. If $[H_3O^+] > [OH^-]$, however, the solution is acidic, whereas if $[H_3O^+] < [OH^-]$, the solution is basic. For an aqueous solution, the H_3O^+ concentration is a quantitative measure of acidity: the higher the H_3O^+ concentration, the more acidic the solution. Conversely, the higher the OH^- concentration, the more basic the solution. In most situations that you will encounter, the H_3O^+ and OH^- concentrations from the dissociation of water are so small ($1.003 \times 10^{-7} M$) that they can be ignored in calculating the H_3O^+ or OH^- concentrations of solutions of acids and bases, but this is not always the case.

Example 7.1.3.1: Ion Concentrations in Pure Water

What are the hydronium ion concentration and the hydroxide ion concentration in pure water at 25 °C?

Solution

The autoionization of water yields the same number of hydronium and hydroxide ions. Therefore, in pure water, $[H_3O^+] = [OH^-]$. At 25 °C:

$$\begin{aligned} K_w &= [H_3O^+][OH^-] \\ &= [H_3O^+]^2 \\ &= [OH^-]^2 \\ &= 1.0 \times 10^{-14} \end{aligned}$$

So:

$$[H_3O^+] = [OH^-] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7}\ M$$

The hydronium ion concentration and the hydroxide ion concentration are the same, and we find that both equal $1.0 \times 10^{-7}\ M$.

? Exercise 7.1.3.1

The ion product of water at 80 °C is 2.4×10^{-13}. What are the concentrations of hydronium and hydroxide ions in pure water at 80 °C?

Answer

$[H_3O^+] = [OH^-] = 4.9 \times 10^{-7}\ M$

It is important to realize that the autoionization equilibrium for water is established in all aqueous solutions. Adding an acid or base to water will not change the position of the equilibrium. Example 7.1.3.2 demonstrates the quantitative aspects of this relation between hydronium and hydroxide ion concentrations.

✓ Example 7.1.3.2: The Inverse Proportionality of Hydronium and Hydroxide Concentrations

A solution of carbon dioxide in water has a hydronium ion concentration of $2.0 \times 10^{-6}\ M$. What is the concentration of hydroxide ion at 25 °C?

Solution

We know the value of the ion-product constant for water at 25 °C:

$$2\,H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + OH^-{}_{(aq)}$$

and

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

Thus, we can calculate the missing equilibrium concentration.

Rearrangement of the k_w expression yields that $[OH^-]$ is directly proportional to the inverse of $[H_3O^+]$:

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-6}} = 5.0 \times 10^{-9}$$

The hydroxide ion concentration in water is reduced to $5.0 \times 10^{-9}\ M$ as the hydrogen ion concentration increases to $2.0 \times 10^{-6}\ M$. This is expected from Le Chatelier's principle; the autoionization reaction shifts to the left to reduce the stress of the increased hydronium ion concentration and the $[OH^-]$ is reduced relative to that in pure water.

A check of these concentrations confirms that our arithmetic is correct:

$$K_w = [H_3O^+][OH^-] = (2.0 \times 10^{-6})(5.0 \times 10^{-9}) = 1.0 \times 10^{-14}$$

? Exercise 7.1.3.2

What is the hydronium ion concentration in an aqueous solution with a hydroxide ion concentration of 0.001 M at 25 °C?

Answer

$$[H_3O^+] = 1 \times 10^{-11} M$$



Self-Ionization of Water (Kw): https://youtu.be/RMpO0rqUnFg

The Relationship among pH, pOH, and pK_w

The pH scale is a concise way of describing the H_3O^+ concentration and hence the acidity or basicity of a solution. Recall that pH and the H^+ (H_3O^+) concentration are related as follows:

$$pH = -\log_{10}[\mathrm{H^+}] \tag{7.1.3.10}$$

$$[\mathrm{H^+}] = 10^{-pH} \tag{7.1.3.11}$$

Because the scale is logarithmic, a pH difference of 1 between two solutions corresponds to a difference of a factor of 10 in their hydronium ion concentrations. Recall also that the pH of a neutral solution is 7.00 ($[H_3O^+] = 1.0 \times 10^{-7}\ M$), whereas acidic solutions have pH < 7.00 (corresponding to $[\mathrm{H_3O^+}] > 1.0 \times 10^{-7}$) and basic solutions have pH > 7.00 (corresponding to $[\mathrm{H_3O^+}] < 1.0 \times 10^{-7}$).

Similar notation systems are used to describe many other chemical quantities that contain a large negative exponent. For example, chemists use an analogous pOH scale to describe the hydroxide ion concentration of a solution. The pOH and $[\mathrm{OH^-}]$ are related as follows:

$$pOH = -\log_{10}[\mathrm{OH^-}] \tag{7.1.3.12}$$

$$[\mathrm{OH^-}] = 10^{-pOH} \tag{7.1.3.13}$$

The constant K_w can also be expressed using this notation, where $pK_w = -\log\ K_w$.

Because a neutral solution has $[OH^-] = 1.0 \times 10^{-7}$, the pOH of a neutral solution is 7.00. Consequently, the sum of the pH and the pOH for a neutral solution at 25°C is 7.00 + 7.00 = 14.00. We can show that the sum of pH and pOH is equal to 14.00 for any aqueous solution at 25°C by taking the negative logarithm of both sides of Equation ???:

$$-\log K_w = pK_w \tag{7.1.3.14}$$

$$= -\log([H_3O^+][OH^-]) \tag{7.1.3.15}$$

$$= (-\log[H_3O^+]) + (-\log[OH^-]) \tag{7.1.3.16}$$

$$= pH + pOH \tag{7.1.3.17}$$

Thus at any temperature, $pH + pOH = pK_w$, so at 25°C, where $K_w = 1.0 \times 10^{-14}$ and $pH + pOH = 14.00$. More generally, the pH of any neutral solution is half of the pK_w at that temperature. The relationship among pH, pOH, and the acidity or basicity of a solution is summarized graphically in Figure **7.1.3.1** over the common pH range of 0 to 14. Notice the inverse relationship between the pH and pOH scales.

> For any neutral solution, pH + pOH = 14.00 (at 25°C) with pH=pOH=7.

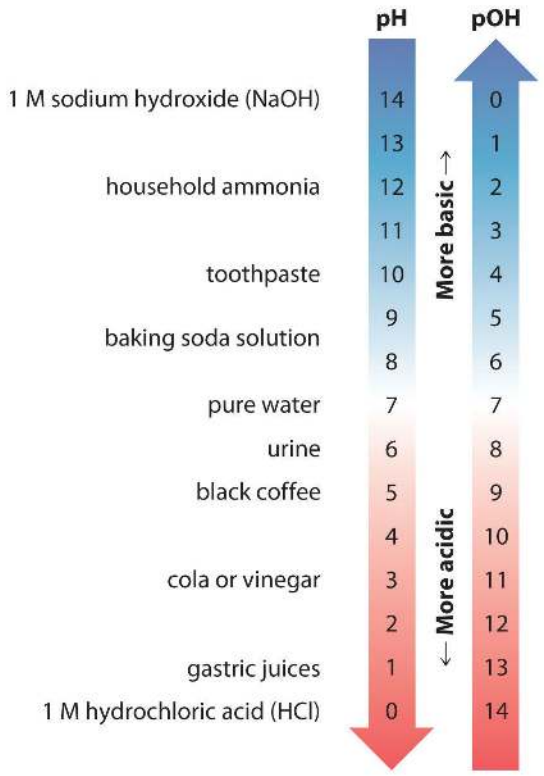


Figure **7.1.3.1**: The Inverse Relationship between the pH and pOH Scales. As pH decreases, $[H^+]$ and the acidity increase. As pOH increases, $[OH^-]$ and the basicity decrease. Common substances have pH values that range from extremely acidic to extremely basic. (CC BY; OpenStax)

Example 7.1.3.3

The k_w for water at 100°C is 4.99×10^{-13}. Calculate pK_w for water at this temperature and the pH and the pOH for a neutral aqueous solution at 100°C. Report pH and pOH values to two decimal places.

Given: K_w

Asked for: pK_w, pH, and pOH

Strategy:

A. Calculate pKw by taking the negative logarithm of K_w.

B. For a neutral aqueous solution, $[H_3O^+] = [OH^-]$. Use this relationship and Equation ??? to calculate $[H_3O^+]$ and $[OH^-]$. Then determine the pH and the pOH for the solution.

Solution:

A Because pK_w is the negative logarithm of Kw, we can write

$$pK_w = -\log K_w = -\log(4.99 \times 10^{-13}) = 12.302$$

The answer is reasonable: K_w is between 10^{-13} and 10^{-12}, so pK_w must be between 12 and 13.

B Equation ??? shows that $K_w = [H_3O^+][OH^-]$. Because $[H_3O^+] = [OH^-]$ in a neutral solution, we can let $x = [H_3O^+] = [OH^-]$:

$$\begin{aligned} K_w &= [\mathrm{H_3O^+}][\mathrm{OH^-}] \\ &= (x)(x) \\ &= x^2 \\ x &= \sqrt{K_w} \\ &= \sqrt{4.99 \times 10^{-13}} \\ &= 7.06 \times 10^{-7}\ M \end{aligned}$$

Because x is equal to both $[\mathrm{H_3O^+}]$ and $[\mathrm{OH^-}]$,

$$\begin{aligned} pH = pOH &= -\log(7.06 \times 10^{-7}) \\ &= 6.15 \text{ (to two decimal places)} \end{aligned}$$

We could obtain the same answer more easily (without using logarithms) by using the pK_w. In this case, we know that $pK_w = 12.302$, and from Equation 7.1.3.17, we know that $pK_w = pH + pOH$. Because $pH = pOH$ in a neutral solution, we can use Equation 7.1.3.17 directly, setting $pH = pOH = y$. Solving to two decimal places we obtain the following:

$$pK_w = pH + pOH = y + y = 2y$$

$$y = \frac{pK_w}{2} = \frac{12.302}{2} = 6.15 = pH = pOH$$

? Exercise 7.1.3.3

Humans maintain an internal temperature of about 37°C. At this temperature, $K_w = 3.55 \times 10^{-14}$. Calculate pK_w and the pH and the pOH of a neutral solution at 37°C. Report pH and pOH values to two decimal places.

Answer

$pK_w = 13.45$ and $pH = pOH = 6.73$



Introduction to pH: https://youtu.be/pQOa3bb5YEE

Summary

- For any neutral solution, $pH + pOH = 14.00$ (at 25°C) and $pH = \frac{1}{2}pK_w$.
- Ion-product constant of liquid water:

$$K_w = [H_3O^+][OH^-]$$

- Definition of pH:

$$pH = -\log_{10}[H^+]$$

or

$$[H^+] = 10^{-pH}$$

- Definition of pOH:

$$pOH = -\log_{10}[OH^+]$$

or

$$[OH^-] = 10^{-pOH}$$

- Relationship among pH, pOH, and pK_w:

$$pK_w = pH + pOH$$

Water is amphiprotic: it can act as an acid by donating a proton to a base to form the hydroxide ion, or as a base by accepting a proton from an acid to form the hydronium ion (H_3O^+). The autoionization of liquid water produces OH^- and H_3O^+ ions. The equilibrium constant for this reaction is called the ion-product constant of liquid water (K_w) and is defined as $K_w = [H_3O^+][OH^-]$. At 25°C, K_w is 1.01×10^{-14}; hence $pH + pOH = pK_w = 14.00$. The process is endothermic, and so the extent of ionization and the resulting concentrations of hydronium ion and hydroxide ion **increase with temperature**. For example, at 100 °C, the value for K_w is approximately 5.1×10^{-13}, roughly 100-times larger than the value at 25 °C.

Glossary

acid ionization

reaction involving the transfer of a proton from an acid to water, yielding hydronium ions and the conjugate base of the acid

autoionization

reaction between identical species yielding ionic products; for water, this reaction involves transfer of protons to yield hydronium and hydroxide ions

ion-product constant for water (K_w)

equilibrium constant for the autoionization of water

Contributors and Attributions

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7.1.4: Strong Acids and Strong Bases

Learning Objectives

- Give the names and formulas of some strong acids and bases.
- Explain the pH scale, and convert pH and concentration of hydronium ions.
- Evaluate solution pH and pOH of strong acids or bases.

Acids and bases that are completely ionized when dissolved in water are called **strong acids** and **strong bases** There are only a few strong acids and bases, and everyone should know their names and properties. These acids are often used in industry and everyday life. The concentrations of acids and bases are often expressed in terms of pH, and as an educated person, you should have the skill to convert concentrations into pH and pOH. The pH is an indication of the hydrogen ion concentration, $[H^+]$.

Strong Acids

Strong acids are acids that are completely or nearly 100% ionized in their solutions; Table **7.1.4.1** includes some common strong acids. Hence, the ionization in Equation 7.1.4.1 for a strong acid HA can be represented with a single arrow:

$$HA\,(aq) + H_2O\,(l) \rightarrow H_3O^+\,(aq) + A^-\,(aq) \tag{7.1.4.1}$$

Water is the base that reacts with the acid HA, A^- is the conjugate base of the acid HA, and the hydronium ion is the conjugate acid of water. By definition, a strong acid yields 100% of H_3O^+ and A^- when the acid ionizes in water. Table **7.1.4.1** lists several strong acids.

Table **7.1.4.1**: Some of the common strong acids and bases are listed here.

Strong Acids	Strong Bases
perchloric acid ($HClO_4$)	lithium hydroxide ($LiOH$)
hydrochloric acid (HCl)	sodium hydroxide ($NaOH$)
hydrobromic acid (HBr)	potassium hydroxide (KOH)
hydroiodic acid (HI)	calcium hydroxide ($Ca(OH)_2$)
nitric acid (HNO_3)	strontium hydroxide ($Sr(OH)_2$)
sulfuric acid (H_2SO_4)	barium hydroxide ($Ba(OH)_2$)

For a strong acid, $[H^+] = [A^-]$ = concentration of acid if the concentration is much higher than $1 \times 10^{-7}\,M$. However, for a very dilute strong acid solution with concentration less than $1 \times 10^{-7}\,M$, the pH is dominated by the **autoionization of water**

$$H_2O \rightleftharpoons H^+ + OH^- \tag{7.1.4.2}$$

Example 7.1.4.1

Calculate the pH of a solution with $1.2345 \times 10^{-4}\,M HCl$, a strong acid.

Solution

The solution of a strong acid is completely ionized. That is, this equation goes to completion

$$HCl\,(aq) \longrightarrow H\,(aq) + Cl^-\,(aq)$$

Thus, $[H^+] = 1.2345 \times 10^{-4}$.

$$pH = -\log(1.2345 \times 10^{-4}) = 3.90851$$

? Exercise 7.1.4.1

What is the pH for a solution containing 1.234 M [HCl]?

Answer

pH = -0.0913

✓ Example 7.1.4.2

Calculate the pH of a stock HCl solution that is 32% by mass HCl.

Solution

The density of such a solution is needed before we can calculate the pH. Since the density is not on the label, we need to find it from the Material Safety Data Sheet, which gives the specific gravity of 1.150. Thus, the amount of acid in 1.0 L is 1150 g.

$$\begin{aligned}\text{The amount of HCl} &= 1000 \times 1.150 \times 0.32 \\ &= 368\ \text{g}\ \left(\frac{1\ \text{mol}}{36.5\ \text{g}} \leftarrow \text{molar mass of HCl}\right) \\ &= 10.08\ \text{M} \\ &= [\text{H}^+]\end{aligned}$$

$$\text{pH} = -\log(10.08) = -1.003$$

Discussion

Yes, pH have negative values if $[\text{H}^+] > 1.0$

? Exercise 7.1.4.2

Check out the information on nitric acid, a strong acid, and calculate the pH of a stock nitric acid solution.

✓ Example 7.1.4.3

Calculate the pH of a solution containing $1.00 \times 10^{-7}\ M$ of the strong acid HCl.

Solution

$[\text{H}^+] = 1.0 \times 10^{-7}\ M$ from the strong acid, and if x is the amount from the ionization of water, then we have the equilibrium due to the **autoionization** of water. We can model this with an ICE table.

$$H_2O \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

ICE Table	$H_2O_{(l)}$	$H^+_{(aq)}$	$OH^-_{(aq)}$
Initial	-	1×10^{-7}	0
Change	-	+x	+x
Equilibrium	-	$1 \times 10^{-7} + x$	x

Recall that $K_w = [\text{H}^+]\ [\text{OH}^-\ ] = 1 \times 10^{-14}$, due to the ionization equilibrium of water in the solution:

$$(1.00 \times 10^{-7} + x)x = 1 \times 10^{-14}$$

$$x^2 + 1.00 \times 10^{-7}x - 1.00 \times 10^{-14} = 0$$

Solving this equation for x from the quadratic equation results in

$$x = \frac{-1.00 \times 10^{-7} \pm \sqrt{1.00 \times 10^{-14} + (4)(1)(1.00 \times 10^{-14})}}{2}$$
$$= 0.61 \times 10^{-7}$$

only the additive root is physical (positive concentration); therefore

$$[H^+] = (1.00 + 0.61) \times 10^{-7}\ M$$
$$pH = -\log(1.61 \times 10^{-7})$$
$$= 6.79$$

Discussion

If you require only 1 significant figure, the pH is about 7.

Strong Bases

Strong bases are completely ionized in solution. Table 7.1.4.1 includes some common strong bases. For example, KOH dissolves in water in the reaction

$$KOH \rightarrow K^+ + OH^-$$

Relative to the number of strong acids, there are fewer number of strong bases and most are alkali hydroxides. Calcium hydroxide is considered a strong base, because it is completely, almost completely, ionized. However, the solubility of calcium hydroxide is very low. When $Ca(OH)_2$ dissolves in water, the ionization reaction is as follows:

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2\,OH^-$$

Because of the stoichiometry of calcium hydroxide, upon dissociation, the concentration of OH^- will be twice the concentration of Ca^{2+}:

$$[OH^-] = 2[Ca^{2+}]$$

✔ Example 7.1.4.4

Calculate the pOH of a solution containing $1.2345 \times 10^{-4}\ M\ Ca(OH)_2$.

Solution

Based on complete ionization of

$$Ca(OH)_2 \rightarrow Ca^{+2} + 2\,OH^-$$
$$[OH^-] = 2 \times 1.2345 \times 10^{-4}$$
$$= 2.4690 \times 10^{-4}\ M$$
$$pOH = -\log(2.4690 \times 10^{-4})$$
$$= 3.6074$$

? Exercise 7.1.4.4

The molar solubility of calcium hydroxide is 0.013 M $Ca(OH)_2$. Calculate the pOH.

Answer

pOH = 1.58



Calculating pH in Strong Acid or Strong Base Solutions: https://youtu.be/NNTptn7hV2s

Questions

1. What is the pH of a solution containing 0.01 M $\mathbf{HNO_3}$?
2. What is the pH of a solution containing 0.0220 M $\mathbf{Ba(OH)_2}$? Give 3 significant figures.
3. Exactly 1.00 L solution was made by dissolving 0.80 g of $\mathbf{NaOH}$ in water. What is $[\mathbf{H^+}]$? (Atomic mass: **Na**, 23.0; **O**, 16.0; **H**, 1.0)
4. What is the pH for a solution which is 0.050 M $\mathbf{HCl}$?
5. Which of the following is usually referred to as strong acid in water solution?

$$\mathbf{HF},\ \mathbf{HNO_2},\ \mathbf{H_2CO_3},\ \mathbf{H_2S},\ \mathbf{HSO_4^-},\ \mathbf{Cl^-},\ \mathbf{HNO_3},\ \mathbf{HCN}$$

Solutions

1. ***Answer*** 2

   Hint...

   You do not need a calculator to evaluate $-\log(0.01) = 2$
2. ***Answer*** 12.64

   Hint...

   $\mathbf{Ba(OH)_2} \rightarrow \mathbf{Ba^{2+}} + 2\,\mathbf{OH^-}$
3. ***Answer*** 5.0×10^{-13}

   Hint...

   $[\mathrm{OH^-}] = \dfrac{0.80}{40} = 0.020\ \mathrm{M};\ [H^+] = \dfrac{1.0 \times 10^{-14}}{0.020} = 5 \times 10^{-13} M$. The pH is 12.30.
4. ***Answer*** 1.3

   Hint...

   This solution contains 1.83 g of $\mathbf{HCl}$ per liter. $[\mathbf{H^+}] = 0.050$.
5. ***Answer*** $\mathbf{HNO_3}$

   Consider...

   All others are weak acids

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7.1.5: Weak Acids and Weak Bases

Learning Objectives

- To know the relationship between acid or base strength and the magnitude of K_a, K_b, pK_a, and pK_b.
- To understand the leveling effect.

The magnitude of the equilibrium constant for an ionization reaction can be used to determine the relative strengths of acids and bases. For example, the general equation for the ionization of a weak acid in water, where HA is the parent acid and A− is its conjugate base, is as follows:

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)} \tag{7.1.5.1}$$

The equilibrium constant for this dissociation is as follows:

$$K = \frac{[H_3O^+][A^-]}{[H_2O][HA]} \tag{7.1.5.2}$$

As we noted earlier, the concentration of water is essentially constant for all reactions in aqueous solution, so $[H_2O]$ in Equation 7.1.5.2 can be incorporated into a new quantity, the acid ionization constant (K_a), also called the acid dissociation constant:

$$K_a = K[H_2O] = \frac{[H_3O^+][A^-]}{[HA]} \tag{7.1.5.3}$$

Thus the numerical values of K and K_a differ by the concentration of water (55.3 M). Again, for simplicity, H_3O^+ can be written as H^+ in Equation 7.1.5.3. Keep in mind, though, that free H^+ does not exist in aqueous solutions and that a proton is transferred to H_2O in all acid ionization reactions to form H^3O^+. The larger the K_a, the stronger the acid and the higher the H^+ concentration at equilibrium.Like all equilibrium constants, acid–base ionization constants are actually measured in terms of the activities of H^+ or OH^-, thus making them **unitless**. The values of K_a for a number of common acids are given in Table 7.1.5.1.

Table 7.1.5.1: Values of K_a, pK_a, K_b, and pK_b for Selected Acids (HA and Their Conjugate Bases (A^-)

Acid	HA	K_a	pK_a	A^-	K_b	pK_b
hydroiodic acid	HI	2×10^{9}	−9.3	I^-	5.5×10^{-24}	23.26
sulfuric acid (1)*	H_2SO_4	1×10^{2}	−2.0	HSO_4^-	1×10^{-16}	16.0
nitric acid	HNO_3	2.3×10^{1}	−1.37	NO_3^-	4.3×10^{-16}	15.37
hydronium ion	H_3O^+	1.0	0.00	H_2O	1.0×10^{-14}	14.00
sulfuric acid (2)*	HSO_4^-	1.0×10^{-2}	1.99	SO_4^{2-}	9.8×10^{-13}	12.01
hydrofluoric acid	HF	6.3×10^{-4}	3.20	F^-	1.6×10^{-11}	10.80
nitrous acid	HNO_2	5.6×10^{-4}	3.25	$NO2^-$	1.8×10^{-11}	10.75
formic acid	HCO_2H	1.78×10^{-4}	3.750	HCO_2-	5.6×10^{-11}	10.25
benzoic acid	$C_6H_5CO_2H$	6.3×10^{-5}	4.20	$C_6H_5CO_2^-$	1.6×10^{-10}	9.80
acetic acid	CH_3CO_2H	1.7×10^{-5}	4.76	$CH_3CO_2^-$	5.8×10^{-10}	9.24
pyridinium ion	$C_5H_5NH^+$	5.9×10^{-6}	5.23	C_5H_5N	1.7×10^{-9}	8.77
hypochlorous acid	$HOCl$	4.0×10^{-8}	7.40	OCl^-	2.5×10^{-7}	6.60
hydrocyanic acid	HCN	6.2×10^{-10}	9.21	CN^-	1.6×10^{-5}	4.79
ammonium ion	NH_4^+	5.6×10^{-10}	9.25	NH_3	1.8×10^{-5}	4.75
water	H_2O	1.0×10^{-14}	14.00	OH^-	1.00	0.00
acetylene	C_2H_2	1×10^{-26}	26.0	HC_2^-	1×10^{12}	−12.0
ammonia	NH_3	1×10^{-35}	35.0	NH_2^-	1×10^{21}	−21.0

*The number in parentheses indicates the ionization step referred to for a polyprotic acid.

Weak bases react with water to produce the hydroxide ion, as shown in the following general equation, where B is the parent base and BH+ is its conjugate acid:

$$\mathrm{B\,(aq) + H_2O\,(l) \rightleftharpoons BH^+\,(aq) + OH^-\,(aq)} \tag{7.1.5.4}$$

The equilibrium constant for this reaction is the **base ionization constant** (K_b), also called the base dissociation constant:

$$K_b = K[H_2O] = \frac{[BH^+][OH^-]}{[B]} \tag{7.1.5.5}$$

Once again, the concentration of water is constant, so it does not appear in the equilibrium constant expression; instead, it is included in the K_b. The larger the K_b, the stronger the base and the higher the OH^- concentration at equilibrium. The values of K_b for a number of common weak bases are given in Table 7.1.5.2.

Table 7.1.5.2: Values of K_b, pK_b, K_a, and pK_a for Selected Weak Bases (B) and Their Conjugate Acids (BH+)

Base	B	K_b	pK_b	BH^+	K_a	pK_a
hydroxide ion	OH^-	1.0	0.00*	H_2O	1.0×10^{-14}	14.00
phosphate ion	PO_4^{3-}	2.1×10^{-2}	1.68	HPO_4^{2-}	4.8×10^{-13}	12.32
dimethylamine	$(CH_3)_2NH$	5.4×10^{-4}	3.27	$(CH_3)_2NH_2^+$	1.9×10^{-11}	10.73
methylamine	CH_3NH_2	4.6×10^{-4}	3.34	$CH_3NH_3^+$	2.2×10^{-11}	10.66
trimethylamine	$(CH_3)_3N$	6.3×10^{-5}	4.20	$(CH_3)_3NH^+$	1.6×10^{-10}	9.80
ammonia	NH_3	1.8×10^{-5}	4.75	NH_4^+	5.6×10^{-10}	9.25
pyridine	C_5H_5N	1.7×10^{-9}	8.77	$C_5H_5NH^+$	5.9×10^{-6}	5.23
aniline	$C_6H_5NH_2$	7.4×10^{-10}	9.13	$C_6H_5NH_3^+$	1.3×10^{-5}	4.87
water	H_2O	1.0×10^{-14}	14.00	H_3O^+	1.0*	0.00

*As in Table **7.1.5.1**.

There is a simple relationship between the magnitude of K_a for an acid and K_b for its conjugate base. Consider, for example, the ionization of hydrocyanic acid (HCN) in water to produce an acidic solution, and the reaction of CN^- with water to produce a basic solution:

$$HCN_{(aq)} \rightleftharpoons H^+_{(aq)} + CN^-_{(aq)} \tag{7.1.5.6}$$

$$CN^-_{(aq)} + H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + HCN_{(aq)} \tag{7.1.5.7}$$

The equilibrium constant expression for the ionization of HCN is as follows:

$$K_a = \frac{[H^+][CN^-]}{[HCN]} \tag{7.1.5.8}$$

The corresponding expression for the reaction of cyanide with water is as follows:

$$K_b = \frac{[OH^-][HCN]}{[CN^-]} \tag{7.1.5.9}$$

If we add Equations 7.1.5.6 and 7.1.5.7, we obtain the following (recall that the equilibrium constant for the sum of two reactions is the product of the equilibrium constants for the individual reactions):

$$\cancel{HCN_{(aq)}} \rightleftharpoons H^+_{(aq)} + \cancel{CN^-_{(aq)}} \quad K_a = [H^+]\,\cancel{[CN^-]} / \cancel{[HCN]} \tag{7.1.5.10}$$

$$\cancel{CN^-_{(aq)}} + H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + \cancel{HCN_{(aq)}} \quad K_b = [OH^-]\,\cancel{[HCN]} / \cancel{[CN^-]} \tag{7.1.5.11}$$

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)} \quad K = K_a \times K_b = [H^+][OH^-] \tag{7.1.5.12}$$

In this case, the sum of the reactions described by K_a and K_b is the equation for the autoionization of water, and the product of the two equilibrium constants is K_w:

$$K_aK_b = K_w \tag{7.1.5.13}$$

Thus if we know either K_a for an acid or K_b for its conjugate base, we can calculate the other equilibrium constant for any conjugate acid–base pair.

Just as with pH, pOH, and pK_w, we can use negative logarithms to avoid exponential notation in writing acid and base ionization constants, by defining pK_a as follows:

$$pKa = -\log_{10} K_a \tag{7.1.5.14}$$

$$K_a = 10^{-pK_a} \tag{7.1.5.15}$$

and pK_b as

$$pK_b = -\log_{10} K_b \tag{7.1.5.16}$$

$$K_b = 10^{-pK_b} \tag{7.1.5.17}$$

Similarly, Equation 7.1.5.13, which expresses the relationship between K_a and K_b, can be written in logarithmic form as follows:

$$pK_a + pK_b = pK_w \tag{7.1.5.18}$$

At 25°C, this becomes

$$pK_a + pK_b = 14.00 \tag{7.1.5.19}$$

The values of pK_a and pK_b are given for several common acids and bases in Table 7.1.5.1 and Table 7.1.5.2, respectively, and a more extensive set of data is provided in Tables E1 and E2. Because of the use of negative logarithms, smaller values of pK_a correspond to larger acid ionization constants and hence stronger acids. For example, nitrous acid (HNO_2), with a pK_a of 3.25, is about a 1000 times stronger acid than hydrocyanic acid (HCN), with a pK_a of 9.21. Conversely, smaller values of pK_b correspond to larger base ionization constants and hence stronger bases.

The relative strengths of some common acids and their conjugate bases are shown graphically in Figure 16.5. The conjugate acid–base pairs are listed in order (from top to bottom) of increasing acid strength, which corresponds to decreasing values of pK_a. This order corresponds to decreasing strength of the conjugate base or increasing values of pK_b. At the bottom left of Figure 7.1.5.2 are the common strong acids; at the top right are the most common strong bases. Notice the inverse relationship between the strength of the parent acid and the strength of the conjugate base. Thus the conjugate base of a strong acid is a very weak base, and the conjugate base of a very weak acid is a strong base.

> *The conjugate base of a strong acid is a weak base and vice versa.*

We can use the relative strengths of acids and bases to predict the direction of an acid–base reaction by following a single rule: an acid–base equilibrium always favors the side with the weaker acid and base, as indicated by these arrows:

$$\textbf{stronger acid} + \textbf{stronger base} \rightleftharpoons \textbf{weaker acid} + \textbf{weaker base}$$

In an acid–base reaction, the proton always reacts with the stronger base.

For example, hydrochloric acid is a strong acid that ionizes essentially completely in dilute aqueous solution to produce H_3O^+ and Cl^-; only negligible amounts of HCl molecules remain undissociated. Hence the ionization equilibrium lies virtually all the way to the right, as represented by a single arrow:

$$HCl_{(aq)} + H_2O_{(l)} \rightarrow\rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)} \tag{7.1.5.20}$$

In contrast, acetic acid is a weak acid, and water is a weak base. Consequently, aqueous solutions of acetic acid contain mostly acetic acid molecules in equilibrium with a small concentration of H_3O^+ and acetate ions, and the ionization equilibrium lies far to the left, as represented by these arrows:

$$\mathrm{CH_3CO_2H_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + CH_3CO_{2(aq)}{}^-}$$

Similarly, in the reaction of ammonia with water, the hydroxide ion is a strong base, and ammonia is a weak base, whereas the ammonium ion is a stronger acid than water. Hence this equilibrium also lies to the left:

$$H_2O_{(l)} + NH_{3(aq)} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)}$$

> *All acid–base equilibria favor the side with the weaker acid and base. Thus the proton is bound to the stronger base.*

Example 7.1.5.1: Butyrate and Dimethylammonium Ions

a. Calculate K_b and pK_b of the butyrate ion ($CH_3CH_2CH_2CO_2^-$). The pK_a of butyric acid at 25°C is 4.83. Butyric acid is responsible for the foul smell of rancid butter.

b. Calculate K_a and pK_a of the dimethylammonium ion ($(CH_3)_2NH_2^+$). The base ionization constant K_b of dimethylamine ($(CH_3)_2NH$) is 5.4×10^{-4} at 25°C.

Given: pK_a and K_b

Asked for: corresponding K_b and pK_b, K_a and pK_a

Strategy:

The constants K_a and K_b are related as shown in Equation 7.1.5.13. The pK_a and pK_b for an acid and its conjugate base are related as shown in Equation 7.1.5.18 and Equation 7.1.5.19. Use the relationships $pK = -\log K$ and $K = 10^{-pK}$ (Equations 7.1.5.14 and 7.1.5.16) to convert between K_a and pK_a or K_b and pK_b.

Solution:

We are given the pK_a for butyric acid and asked to calculate the K_b and the pK_b for its conjugate base, the butyrate ion. Because the pK_a value cited is for a temperature of 25°C, we can use Equation 7.1.5.19: $pK_a + pK_b$ = pKw = 14.00. Substituting the pK_a and solving for the pK_b,

$$\begin{aligned} 4.83 + pK_b &= 14.00 \\ pK_b &= 14.00 - 4.83 \\ &= 9.17 \end{aligned}$$

Because $pK_b = -\log K_b$, K_b is $10^{-9.17} = 6.8 \times 10^{-10}$.

In this case, we are given K_b for a base (dimethylamine) and asked to calculate K_a and pK_a for its conjugate acid, the dimethylammonium ion. Because the initial quantity given is K_b rather than pK_b, we can use Equation 7.1.5.13: $K_aK_b = K_w$. Substituting the values of K_b and K_w at 25°C and solving for K_a,

$$\begin{aligned} K_a(5.4 \times 10^{-4}) &= 1.01 \times 10^{-14} \\ K_a &= 1.9 \times 10^{-11} \end{aligned}$$

Because pK_a = −log K_a, we have $pK_a = -\log(1.9 \times 10^{-11}) = 10.72$. We could also have converted K_b to pK_b to obtain the same answer:

$$\begin{aligned} pK_b &= -\log(5.4 \times 10^{-4}) \\ &= 3.27 \end{aligned}$$

$$\begin{aligned} pKa + pK_b &= 14.00 \\ pK_a &= 10.73 \\ K_a &= 10^{-pK_a} \\ &= 10^{-10.73} \\ &= 1.9 \times 10^{-11} \end{aligned}$$

If we are given any one of these four quantities for an acid or a base (K_a, pK_a, K_b, or pK_b), we can calculate the other three.

Exercise 7.1.5.1: Lactic Acid

Lactic acid ($CH_3CH(OH)CO_2H$) is responsible for the pungent taste and smell of sour milk; it is also thought to produce soreness in fatigued muscles. Its pK_a is 3.86 at 25°C. Calculate K_a for lactic acid and pK_b and K_b for the lactate ion.

Answer

$K_a = 1.4 \times 10^{-4}$ for lactic acid; pK_b = 10.14 and $K_b = 7.2 \times 10^{-11}$ for the lactate ion

Solutions of Strong Acids and Bases: The Leveling Effect

You will notice in Table 7.1.5.1 that acids like H_2SO_4 and HNO_3 lie above the hydronium ion, meaning that they have pK_a values less than zero and are stronger acids than the H_3O^+ ion. Recall that the acidic proton in virtually all oxoacids is bonded to one of the oxygen atoms of the oxoanion. Thus nitric acid should properly be written as $HONO_2$. Unfortunately, however, the formulas of oxoacids are almost always written with hydrogen on the left and oxygen on the right, giving HNO_3 instead. In fact, all six of the common strong acids that we first encountered in Chapter 4 have pK_a values less than zero, which means that they have a greater tendency to lose a proton than does the H_3O^+ ion. Conversely, the conjugate bases of these strong acids are weaker bases than water. Consequently, the proton-transfer equilibria for these strong acids lie far to the right, and adding any of the common strong acids to water results in an essentially stoichiometric reaction of the acid with water to form a solution of the H_3O^+ ion and the conjugate base of the acid.

Although K_a for HI is about 108 greater than K_a for HNO_3, the reaction of either HI or HNO_3 with water gives an essentially stoichiometric solution of H_3O^+ and I− or NO_3^-. In fact, a 0.1 M aqueous solution of any strong acid actually contains 0.1 M H_3O^+, regardless of the identity of the strong acid. This phenomenon is called the leveling effect: any species that is a stronger acid than the conjugate acid of water (H_3O^+) is leveled to the strength of H_3O^+ in aqueous solution because H_3O^+ is the strongest acid that can exist in equilibrium with water. Consequently, it is impossible to distinguish between the strengths of acids such as HI and HNO3 in aqueous solution, and an alternative approach must be used to determine their relative acid strengths.

One method is to use a solvent such as anhydrous acetic acid. Because acetic acid is a stronger acid than water, it must also be a weaker base, with a lesser tendency to accept a proton than H_2O. Measurements of the conductivity of 0.1 M solutions of both HI and HNO_3 in acetic acid show that HI is completely dissociated, but HNO_3 is only partially dissociated and behaves like a weak acid in this solvent. This result clearly tells us that HI is a stronger acid than HNO_3. The relative order of acid strengths and approximate K_a and pK_a values for the strong acids at the top of Table 7.1.5.1 were determined using measurements like this and different nonaqueous solvents.

> **Note: Leveling Effect**
>
> In *aqueous solutions*, H_3O^+ is the strongest acid and OH^- is the strongest base that can exist in equilibrium with H_2O.

The leveling effect applies to solutions of strong bases as well: In aqueous solution, any base stronger than OH^- is leveled to the strength of OH^- because OH^- is the strongest base that can exist in equilibrium with water. Salts such as K_2O, $NaOCH_3$ (sodium methoxide), and $NaNH_2$ (sodamide, or sodium amide), whose anions are the conjugate bases of species that would lie below water in Table 7.1.5.2, are all strong bases that react essentially completely (and often violently) with water, accepting a proton to give a solution of OH^- and the corresponding cation:

$$K_2O(s) + H_2O(l) \longrightarrow 2\,OH^-(aq) + 2\,K^+(aq)$$

$$NaOCH_3(s) + H_2O(l) \longrightarrow OH^-(aq) + Na^+(aq) + CH_3OH(aq)$$

$$NaNH_2(s) + H_2O(l) \longrightarrow OH^-(aq) + Na^+(aq) + NH_3(aq)$$

Other examples that you may encounter are potassium hydride (KH) and organometallic compounds such as methyl lithium (CH_3Li).



Calculating the pH of Weak Acids and Weak Bases: https://youtu.be/zr1V1THJ5P0

Summary

Two species that differ by only a proton constitute a conjugate acid–base pair. The magnitude of the equilibrium constant for an ionization reaction can be used to determine the relative strengths of acids and bases. For an aqueous solution of a weak acid, the dissociation constant is called the acid ionization constant (Ka). Similarly, the equilibrium constant for the reaction of a weak base with water is the base ionization constant (Kb). For any conjugate acid–base pair, $K_aK_b = K_w$. Smaller values of pK_a correspond to larger acid ionization constants and hence stronger acids. Conversely, smaller values of pK_b correspond to larger base ionization constants and hence stronger bases. At 25°C, $pK_a + pK_b = 14.00$. Acid–base reactions always proceed in the direction that produces the weaker acid–base pair. No acid stronger than H_3O^+ and no base stronger than OH^- can exist in aqueous solution, leading to the phenomenon known as the leveling effect.

Key Takeaways

- Acid–base reactions always contain two conjugate acid–base pairs.
- Each acid and each base has an associated ionization constant that corresponds to its acid or base strength.

Key Equations

- Acid ionization constant:

$$K_a = K[H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$$

- Base ionization constant:

$$K_b = K[H_2O] = \frac{[BH^+][OH^-]}{[B]}$$

- Relationship between K_a and K_b of a conjugate acid–base pair:

$$K_aK_b = K_w$$

- Definition of pK_a:

$$pKa = -\log_{10} K_a$$

$$K_a = 10^{-pK_a}$$

- Definition of pK_b:

$$pK_b = -\log_{10} K_b$$

$$K_b = 10^{-pK_b}$$

- Relationship between pK_a and pK_b of a conjugate acid–base pair:

$$pK_a + pK_b = pK_w$$

$$pK_a + pK_b = 14.00 \text{ at } 25°C$$

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7.1.6: Polyprotic Acids

Learning Objectives

- Extend previously introduced equilibrium concepts to acids and bases that may donate or accept more than one proton

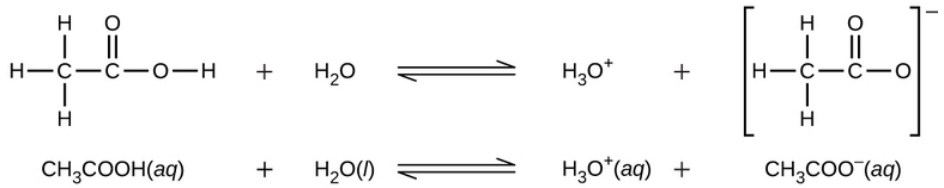
We can classify acids by the number of protons per molecule that they can give up in a reaction. Acids such as $\mathbf{HCl}$, $\mathbf{HNO_3}$, and $\mathbf{HCN}$ that contain one ionizable hydrogen atom in each molecule are called monoprotic acids. Their reactions with water are:

$$\mathbf{HCl}(aq) + \mathbf{H_2O}(l) \longrightarrow \mathbf{H_3O^+}(aq) + \mathbf{Cl^-}(aq)$$

$$\mathbf{HNO_3}(aq) + \mathbf{H_2O}(l) \longrightarrow \mathbf{H_3O^+}(aq) + \mathbf{NO_3^-}(aq)$$

$$\mathbf{HCN}(aq) + \mathbf{H_2O}(l) \longrightarrow \mathbf{H_3O^+}(aq) + \mathbf{CN^-}(aq)$$

Even though it contains four hydrogen atoms, acetic acid, $\mathbf{CH_3CO_2H}$, is also monoprotic because only the hydrogen atom from the carboxyl group ($\mathbf{-COOH}$) reacts with bases:



This image contains two equilibrium reactions. The first shows a C atom bonded to three H atoms and another C atom. The second C atom is double bonded to an O atom and also forms a single bond to another O atom. The second O atom is bonded to an H atom. There is a plus sign and then the molecular formula H subscript 2 O. An equilibrium arrow follows the H subscript 2 O. To the right of the arrow is H subscript 3 O superscript positive sign. There is a plus sign. The final structure shows a C atom bonded the three H atoms and another C atom. This second C atom is double bonded to an O atom and single bonded to another O atom. The entire structure is in brackets and a superscript negative sign appears outside the brackets. The second reaction shows C H subscript 3 C O O H (a q) plus H subscript 2 O (l) equilibrium arrow H subscript 3 O (a q) plus C H subscript 3 C O O superscript negative sign (a q).

Similarly, monoprotic bases are bases that will accept a single proton.

Diprotic Acids

Diprotic acids contain two ionizable hydrogen atoms per molecule; ionization of such acids occurs in two steps. The first ionization always takes place to a greater extent than the second ionization. For example, sulfuric acid, a strong acid, ionizes as follows:

- **The first ionization is**

$$\mathbf{H_2SO_4}(aq) + \mathbf{H_2O}(l) \rightleftharpoons \mathbf{H_3O^+}(aq) + \mathbf{HSO_4^-}(aq)$$

with $K_{a1} > 10^2$; *complete dissociation*.

- **The second ionization is**

$$\mathbf{HSO_4^-}(aq) + \mathbf{H_2O}(l) \rightleftharpoons \mathbf{H_3O^+}(aq) + \mathbf{SO_4^{2-}}(aq)$$

with $K_{a2} = 1.2 \times 10^{-2}$.

This stepwise ionization process occurs for all polyprotic acids. When we make a solution of a weak diprotic acid, we get a solution that contains a mixture of acids. Carbonic acid, $\mathbf{H_2CO_3}$, is an example of a weak diprotic acid. The first ionization of carbonic acid yields hydronium ions and bicarbonate ions in small amounts.

- **First Ionization**

$$\mathbf{H_2CO_3}(aq) + \mathbf{H_2O}(l) \rightleftharpoons \mathbf{H_3O^+}(aq) + \mathbf{HCO_3^-}(aq)$$

with

$$K_{H_2CO_3} = \frac{[H3O+][HCO3-]}{[H2CO3]} = 4.3 \times 10^{-7}$$

The bicarbonate ion can also act as an acid. It ionizes and forms hydronium ions and carbonate ions in even smaller quantities.

- **Second Ionization**

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$$

with

$$K_{HCO_3^-} = \frac{[H3O+][CO3^2-]}{[HCO3-]} = 4.7 \times 10^{-11}$$

$K_{H_2CO_3}$ is larger than $K_{HCO_3^-}$ by a factor of 10^4, so H_2CO_3 is the dominant producer of hydronium ion in the solution. This means that little of the HCO_3^- formed by the ionization of H_2CO_3 ionizes to give hydronium ions (and carbonate ions), and the concentrations of H_3O^+ and HCO_3^- are practically equal in a pure aqueous solution of H_2CO_3.

If the first ionization constant of a weak diprotic acid is larger than the second by a factor of at least 20, it is appropriate to treat the first ionization separately and calculate concentrations resulting from it before calculating concentrations of species resulting from subsequent ionization. This can simplify our work considerably because we can determine the concentration of H_3O^+ and the conjugate base from the first ionization, then determine the concentration of the conjugate base of the second ionization in a solution with concentrations determined by the first ionization.

Example 7.1.6.1: Ionization of a Diprotic Acid

When we buy soda water (carbonated water), we are buying a solution of carbon dioxide in water. The solution is acidic because CO_2 reacts with water to form carbonic acid, H_2CO_3. What are $[H_3O^+]$, $[HCO_3^-]$, and $[CO_3^{2-}]$ in a saturated solution of CO_2 with an initial $[H_2CO_3] = 0.033\ M$?

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq) \quad K_{a1} = 4.3 \times 10^{-7} \qquad \text{(equilibrium step 1)}$$

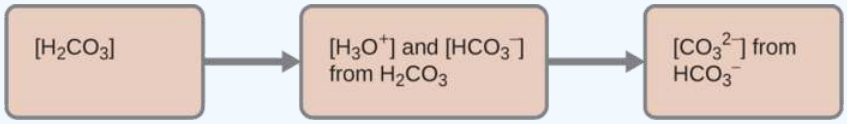
$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq) \quad K_{a2} = 4.7 \times 10^{-11} \qquad \text{(equilibrium step 2)}$$

Solution

As indicated by the ionization constants, H_2CO_3 is a much stronger acid than HCO_3^-, so H_2CO_3 is the dominant producer of hydronium ion in solution. Thus there are two parts in the solution of this problem:

1. Using the customary four steps, we determine the concentration of H_3O^+ and HCO_3^- produced by ionization of H_2CO_3.
2. Then we determine the concentration of CO_3^{2-} in a solution with the concentration of H_3O^+ and HCO_3^- determined in (1).

To summarize:



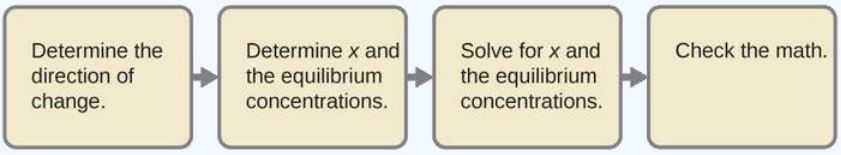
Four tan rectangles are shown that are connected with right pointing arrows. The first is labeled “left bracket H subscript 2 C O subscript 3 right bracket.” The second is labeled “left bracket H subscript 3 O superscript plus right bracket and left bracket H C O subscript 3 superscript negative right bracket from H subscript 2 C O subscript 3.” The third is labeled “left bracket C O subscript 3 superscript 2 negative right bracket from H C O subscript 3 superscript negative.”

1. First Ionization: Determine the concentrations of H_3O^+ *and* HCO_3^-.

Since equilibrium step 1 is has a much bigger $K_{a1} = 4.3 \times 10^{-7}$ than $K_{a2} = 4.7 \times 10^{-11}$ for equilibrium step 2, we can safely ignore the second ionization step and focus only on the first step (but address it in next part of problem).

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq) \quad K_{a1} = 4.3 \times 10^{-7}$$

As for the ionization of any other weak acid:



Four tan rectangles are shown that are connected with right pointing arrows. The first is labeled “Determine the direction of change.” The second is labeled “Determine x and the equilibrium concentrations.” The third is labeled “Solve for x and the equilibrium concentrations.” The fourth is labeled “Check the math.”

An abbreviated table of changes and concentrations shows:

Abbreviated table of changes and concentrations

ICE Table	$H_2CO_3(aq)$	$H_2O(l)$	$H_3O^+(aq)$	$HCO_3^-(aq)$
Initial (M)	$0.033\ M$	-	0	0
Change (M)	$-x$	-	$+x$	$+x$
Equilibrium (M)	$0.033\ M - x$	-	x	x

Substituting the equilibrium concentrations into the equilibrium constant gives us:

$$K_{H_2CO_3} = \frac{[H3O+][HCO3-]}{[H2CO3]} = \frac{(x)(x)}{0.033 - x} = 4.3 \times 10^{-7}$$

Solving the preceding equation making our standard assumptions gives:

$$x = 1.2 \times 10^{-4}$$

Thus:

$$[H_2CO_3] = 0.033\ M$$

$$[H_3O^+] = [HCO_3^-] = 1.2 \times 10^{-4}\ M$$

2. Second Ionization: Determine the concentration of CO_3^{2-} in a solution at equilibrium.

Since the equilibrium step 1 is has a much bigger K_a than equilibrium step 2, we can the equilibrium conditions calculated from first part of example as the initial conditions for an ICER Table for the equilibrium step 2:

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$$

ICER Table for the equilibrium step 2:

ICE Table	$HCO_3^-(aq)$	$H_2O(l)$	$H_3O^+(aq)$	$CO_3^{2-}(aq)$
Initial (M)	$1.2 \times 10^{-4}\ M$	-	$1.2 \times 10^{-4}\ M$	0
Change (M)	$-y$	-	$+y$	$+y$
Equilibrium (M)	$1.2 \times 10^{-4}\ M - y$	-	$1.2 \times 10^{-4}\ M + y$	y

$$K_{HCO_3^-} = \frac{[H3O+][CO3^2-]}{[HCO3-]} = \frac{(1.2 \times 10^{-4}\ M + y)(y)}{(1.2 \times 10^{-4}\ M - y)}$$

To avoid solving a quadratic equation, we can assume $y \ll 1.2 \times 10^{-4}\ M$ so

$$K_{HCO_3^-} = 4.7 \times 10^{-11} \approx \frac{(1.2 \times 10^{-4}\ M)(y)}{(1.2 \times 10^{-4}\ M)}$$

Rearranging to solve for y

$$y \approx \frac{(4.7 \times 10^{-11})(1.2 \times 10^{-4}\ M)}{1.2 \times 10^{-4}\ M}$$

$$[CO_3^{2-}] = y \approx 4.7 \times 10^{-11}$$

To summarize:

In part 1 of this example, we found that the H_2CO_3 in a 0.033-M solution ionizes slightly and at equilibrium $[H_2CO_3] = 0.033\ M$, $[H_3O^+] = 1.2 \times 10^{-4}$, and $[HCO_3^-] = 1.2 \times 10^{-4}\ M$. In part 2, we determined that $[CO_3^{2-}] = 5.6 \times 10^{-11}\ M$.

? Exercise 7.1.6.2: Hydrogen Sulfide

The concentration of H_2S in a saturated aqueous solution at room temperature is approximately 0.1 M. Calculate $[H_3O^+]$, $[HS^-]$, and $[S^{2-}]$ in the solution:

$$H_2S(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HS^-(aq) \quad K_{a1} = 8.9 \times 10^{-8}$$

$$HS^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + S^{2-}(aq) \quad K_{a2} = 1.0 \times 10^{-19}$$

Answer

$[H_2S] = 0.1M$, $[H_3O^+] = [HS^-] = 0.0001\ M$, $[S^{2-}] = 1 \times 10^{-19}\ M$

We note that the concentration of the sulfide ion is the same as K_{a2}. This is due to the fact that each subsequent dissociation occurs to a lesser degree (as acid gets weaker).

Triprotic Acids

A triprotic acid is an acid that has three dissociable protons that undergo stepwise ionization: Phosphoric acid is a typical example:

- **The first ionization is**

$$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2PO_4^-(aq)$$

with $K_{a1} = 7.5 \times 10^{-3}$.

- **The second ionization is**

$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq)$$

with $K_{a2} = 6.2 \times 10^{-8}$.

- **The third ionization is**

$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PO_4^{3-}(aq)$$

with $K_{a3} = 4.2 \times 10^{-13}$.

As with the diprotic acids, the differences in the ionization constants of these reactions tell us that in each successive step the degree of ionization is significantly weaker. This is a general characteristic of polyprotic acids and successive ionization constants often differ by a factor of about 10^5 to 10^6. This set of three dissociation reactions may appear to make calculations of equilibrium concentrations in a solution of H_3PO_4 complicated. However, because the successive ionization constants differ by a factor of 10^5 to 10^6, the calculations can be broken down into a series of parts similar to those for diprotic acids.

Polyprotic bases can accept more than one hydrogen ion in solution. The carbonate ion is an example of a diprotic base, since it can accept up to two protons. Solutions of alkali metal carbonates are quite alkaline, due to the reactions:

$$H_2O(l) + CO_3^{2-}(aq) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$$

and

$$\mathrm{H_2O}(l) + \mathrm{HCO_3^-}(aq) \rightleftharpoons \mathrm{H_2CO_3}(aq) + \mathrm{OH^-}(aq)$$

Summary

An acid that contains more than one ionizable proton is a polyprotic acid. The protons of these acids ionize in steps. The differences in the acid ionization constants for the successive ionizations of the protons in a polyprotic acid usually vary by roughly five orders of magnitude. As long as the difference between the successive values of K_a of the acid is greater than about a factor of 20, it is appropriate to break down the calculations of the concentrations of the ions in solution into a series of steps.

Glossary

diprotic acid

acid containing two ionizable hydrogen atoms per molecule. A diprotic acid ionizes in two steps

diprotic base

base capable of accepting two protons. The protons are accepted in two steps

monoprotic acid

acid containing one ionizable hydrogen atom per molecule

stepwise ionization

process in which an acid is ionized by losing protons sequentially

triprotic acid

acid that contains three ionizable hydrogen atoms per molecule; ionization of triprotic acids occurs in three steps

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7.1.7: Ions as Acids and Bases

Learning Objectives

- Extend previously introduced equilibrium concepts to acids and bases that may donate or accept more than one proton

We can also use the relative strengths of conjugate acid–base pairs to understand the acid–base properties of solutions of salts. A neutralization reaction can be defined as the reaction of an acid and a base to produce a salt and water. That is, another cation, such as Na^+, replaces the proton on the acid. An example is the reaction of CH_3CO_2H, a weak acid, with NaOH, a strong base:

$$\underset{acid}{CH_3CO_2H\,(l)} + \underset{base}{NaOH\,(s)} \xrightarrow{H_2O} \underset{salt}{H_2OCH_3CO_2Na\,(aq)} + \underset{water}{H_2O\,(l)} \tag{7.1.7.1}$$

Depending on the acid–base properties of its component ions, however, a salt can dissolve in water to produce a neutral solution, a basic solution, or an acidic solution.

When a salt such as $NaCl$ dissolves in water, it produces $Na^+_{(aq)}$ and $Cl^-_{(aq)}$ ions. Using a Lewis approach, the Na^+ ion can be viewed as an acid because it is an electron pair acceptor, although its low charge and relatively large radius make it a very weak acid. The Cl^- ion is the conjugate base of the strong acid HCl, so it has essentially no basic character. Consequently, dissolving $NaCl$ in water has no effect on the pH of a solution, and the solution remains neutral.

Now let's compare this behavior to the behavior of aqueous solutions of potassium cyanide and sodium acetate. Again, the cations (K^+ and Na^+) have essentially no acidic character, but the anions (CN^- and $CH_3CO_2^-$) are weak bases that can react with water because they are the conjugate bases of the weak acids HCN and acetic acid, respectively.

$$CN^-\,(aq) + H_2O\,(l) \rightleftharpoons HCN\,(aq) + OH^-\,(aq) \tag{7.1.7.2}$$

$$CH_3CO_2^-\,(aq) + H_2O\,(l) \rightleftharpoons CH_3CO_2H\,(aq) + OH^-\,(aq) \tag{7.1.7.3}$$

Neither reaction proceeds very far to the right as written because the formation of the weaker acid–base pair is favored. Both HCN and acetic acid are stronger acids than water, and hydroxide is a stronger base than either acetate or cyanide, so in both cases, the equilibrium lies to the left. Nonetheless, each of these reactions generates enough hydroxide ions to produce a basic solution. For example, the pH of a 0.1 M solution of sodium acetate or potassium cyanide at 25°C is 8.8 or 11.1, respectively. From Table E1 and E2, we can see that CN^- is a stronger base ($pK_b = 4.79$) than acetate ($pK_b = 9.24$), which is consistent with KCN producing a more basic solution than sodium acetate at the same concentration.

In contrast, the conjugate acid of a weak base should be a weak acid. For example, ammonium chloride and pyridinium chloride are salts produced by reacting ammonia and pyridine, respectively, with HCl. As you already know, the chloride ion is such a weak base that it does not react with water. In contrast, the cations of the two salts are weak acids that react with water as follows:

$$NH_4^+\,(aq) + H_2O\,(l) \rightleftharpoons NH_3\,(aq) + H_3O^+\,(aq) \tag{7.1.7.4}$$

$$C_5H_5NH^+\,(aq) + H_2O\,(l) \rightleftharpoons C_5H_5NH\,(aq) + H_3O^+\,(aq) \tag{7.1.7.5}$$

Figure **7.1.7.2** shows that H_3O^+ is a stronger acid than either NH_4^+ or $C_5H_5NH^+$, and conversely, ammonia and pyridine are both stronger bases than water. The equilibrium will therefore lie far to the left in both cases, favoring the weaker acid–base pair. The H_3O^+ concentration produced by the reactions is great enough, however, to decrease the pH of the solution significantly: the pH of a 0.10 M solution of ammonium chloride or pyridinium chloride at 25°C is 5.13 or 3.12, respectively.

What happens with aqueous solutions of a salt such as ammonium acetate, where both the cation and the anion can react separately with water to produce an acid and a base, respectively? According to Figure 16.10, the ammonium ion will lower the pH, while according to Figure 16.9, the acetate ion will raise the pH. This particular case is unusual, in that the cation is as strong an acid as the anion is a base (pKa ≈ pKb). Consequently, the two effects cancel, and the solution remains neutral. With salts in which the cation is a stronger acid than the anion is a base, the final solution has a pH < 7.00. Conversely, if the cation is a weaker acid than the anion is a base, the final solution has a pH > 7.00.



Ions as Acids and Bases: https://youtu.be/XYAGNonPSow

Acidic Metal Ions

Solutions of simple salts of metal ions can also be acidic, even though a metal ion cannot donate a proton directly to water to produce H_3O^+. Instead, a metal ion can act as a Lewis acid and interact with water, a Lewis base, by coordinating to a lone pair of electrons on the oxygen atom to form a hydrated metal ion (Figure **7.1.7.1***a*). A water molecule coordinated to a metal ion is more acidic than a free water molecule for two reasons. First, repulsive electrostatic interactions between the positively charged metal ion and the partially positively charged hydrogen atoms of the coordinated water molecule make it easier for the coordinated water to lose a proton.

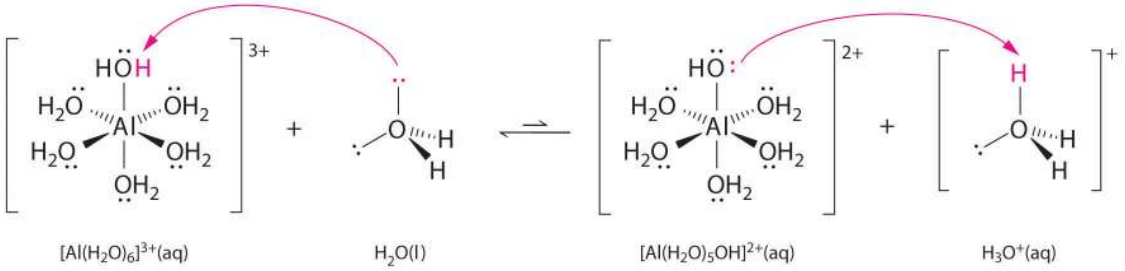
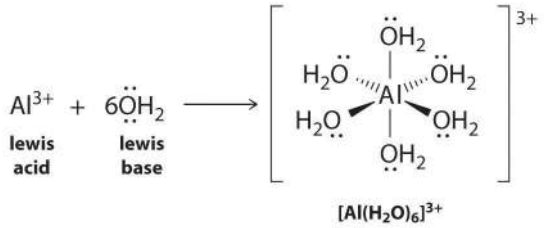
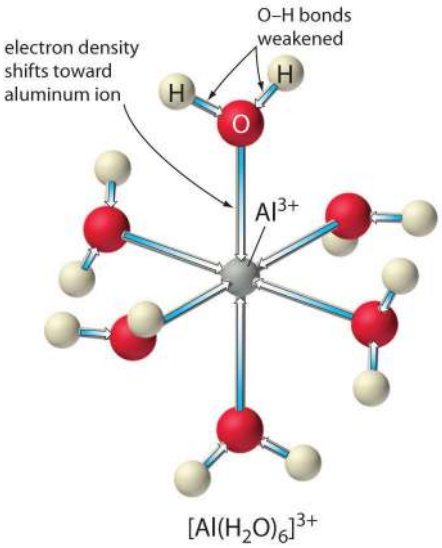


Figure 7.1.7.1

Second, the positive charge on the Al^{3+} ion attracts electron density from the oxygen atoms of the water molecules, which decreases the electron density in the **O–H** bonds, as shown in Figure **7.1.7.1***b*. With less electron density between the *O* atoms and the H atoms, the **O–H** bonds are weaker than in a free H_2O molecule, making it easier to lose a H^+ ion.



(a)



(b)

Figure 7.1.7.2: Effect of a Metal Ion on the Acidity of Water (a) Reaction of the metal ion Al^{3+} with water to form the hydrated metal ion is an example of a Lewis acid–base reaction. (b) The positive charge on the aluminum ion attracts electron density from the oxygen atoms, which shifts electron density away from the O–H bonds. The decrease in electron density weakens the O–H bonds in the water molecules and makes it easier for them to lose a proton.

The magnitude of this effect depends on the following two factors (Figure 7.1.7.3):

1. The charge on the metal ion. A divalent ion (M^{2+}) has approximately twice as strong an effect on the electron density in a coordinated water molecule as a monovalent ion (M^{+}) of the same radius.
2. The radius of the metal ion. For metal ions with the same charge, the smaller the ion, the shorter the internuclear distance to the oxygen atom of the water molecule and the greater the effect of the metal on the electron density distribution in the water molecule.

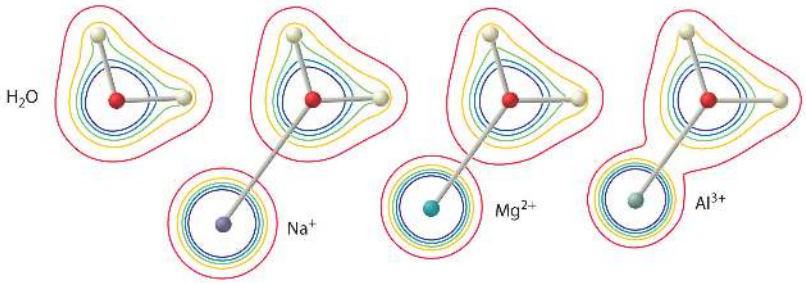


Figure 7.1.7.3: The Effect of the Charge and Radius of a Metal Ion on the Acidity of a Coordinated Water Molecule. The contours show the electron density on the O atoms and the H atoms in both a free water molecule (left) and water molecules coordinated to Na^{+}, Mg^{2+}, and Al^{3+} ions. These contour maps demonstrate that the smallest, most highly charged metal ion (Al^{3+}) causes the greatest decrease in electron density of the O–H bonds of the water molecule. Due to this effect, the acidity of hydrated metal ions increases as the charge on the metal ion increases and its radius decreases.

Thus aqueous solutions of small, highly charged metal ions, such as Al^{3+} and Fe^{3+}, are acidic:

$$[Al(H_2O)_6]^{3+}_{(aq)} \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}_{(aq)} + H^+_{(aq)} \tag{7.1.7.6}$$

The $[Al(H_2O)_6]^{3+}$ ion has a pK_a of 5.0, making it almost as strong an acid as acetic acid. Because of the two factors described previously, the most important parameter for predicting the effect of a metal ion on the acidity of coordinated water molecules is the charge-to-radius ratio of the metal ion. A number of pairs of metal ions that lie on a diagonal line in the periodic table, such as Li^+ and Mg^{2+} or Ca^{2+} and Y^{3+}, have different sizes and charges, but similar charge-to-radius ratios. As a result, these pairs of metal ions have similar effects on the acidity of coordinated water molecules, and they often exhibit other significant similarities in chemistry as well.

Acidic Metal Ions

Solutions of small, highly charged metal ions in water are acidic.

Reactions such as those discussed in this section, in which a salt reacts with water to give an acidic or basic solution, are often called hydrolysis reactions. Using a separate name for this type of reaction is unfortunate because it suggests that they are somehow different. In fact, hydrolysis reactions are just acid–base reactions in which the acid is a cation or the base is an anion; they obey the same principles and rules as all other acid–base reactions.

Hydrolysis

A hydrolysis reaction is an acid–base reaction.

Example 7.1.7.1

Predict whether aqueous solutions of these compounds are acidic, basic, or neutral.

a. KNO_3
b. $CrBr_3 \cdot H_2O$
c. Na_2SO_4

Given: compound

Asked for: acidity or basicity of aqueous solution

Strategy:

A. Assess the acid–base properties of the cation and the anion. If the cation is a weak Lewis acid, it will not affect the pH of the solution. If the cation is the conjugate acid of a weak base or a relatively highly charged metal cation, however, it will react with water to produce an acidic solution.
B. f the anion is the conjugate base of a strong acid, it will not affect the pH of the solution. If, however, the anion is the conjugate base of a weak acid, the solution will be basic.

Solution:

a

A. The K^+ cation has a small positive charge (+1) and a relatively large radius (because it is in the fourth row of the periodic table), so it is a very weak Lewis acid.
B. The NO_3- anion is the conjugate base of a strong acid, so it has essentially no basic character (Table 16.1). Hence neither the cation nor the anion will react with water to produce H^+ or OH^-, and the solution will be neutral.

b.

A. The Cr^{3+} ion is a relatively highly charged metal cation that should behave similarly to the Al^{3+} ion and form the [Cr(H2O)6]3+ complex, which will behave as a weak acid:

$$Cr(H_2O)_6]^{3+}_{(aq)} \rightleftharpoons Cr(H_2O)_5(OH)]^{2+}_{(aq)} + H^+_(aq) \tag{7.1.7.7}$$

B. The Br^- anion is a very weak base (it is the conjugate base of the strong acid HBr), so it does not affect the pH of the solution. Hence the solution will be acidic.

c.

A. The Na^+ ion, like the K^+, is a very weak acid, so it should not affect the acidity of the solution.
B. In contrast, SO_4^{2-} is the conjugate base of HSO_4^-, which is a weak acid. Hence the SO_4^{2-} ion will react with water as shown in Figure 16.6 to give a slightly basic solution.

? Exercise 7.1.7.1

Predict whether aqueous solutions of the following are acidic, basic, or neutral.

a. KI
b. $Mg(ClO_4)_2$
c. $NaHS$

Answer a

neutral

Answer b

acidic

Answer c

basic (due to the reaction of HS^- with water to form H_2S and OH^-)

Summary

A salt can dissolve in water to produce a neutral, a basic, or an acidic solution, depending on whether it contains the conjugate base of a weak acid as the anion (A^-), the conjugate acid of a weak base as the cation (BH^+), or both. Salts that contain small, highly charged metal ions produce acidic solutions in water. The reaction of a salt with water to produce an acidic or a basic solution is called a hydrolysis reaction.

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7.1.8: Molecular Structure and Acid-Base Behavior

Learning Objectives

- To understand how molecular structure affects the strength of an acid or base.

We have seen that the strengths of acids and bases vary over many orders of magnitude. In this section, we explore some of the structural and electronic factors that control the acidity or basicity of a molecule.

Bond Strengths

In general, the stronger the $\mathbf{A–H}$ or $\mathbf{B–H^+}$ bond, the less likely the bond is to break to form H^+ ions and thus the less acidic the substance. This effect can be illustrated using the hydrogen halides:

Relative Acid Strength	HF	HCl	HBr	HI
H–X Bond Energy (kJ/mol)	570	432	366	298
pKa	3.20	−6.1	−8.9	−9.3

The trend in bond energies is due to a steady decrease in overlap between the 1s orbital of hydrogen and the valence orbital of the halogen atom as the size of the halogen increases. The larger the atom to which H is bonded, the weaker the bond. Thus the bond between H and a large atom in a given family, such as I or Te, is weaker than the bond between H and a smaller atom in the same family, such as F or O. As a result, acid strengths of binary hydrides increase as we go down a column of the periodic table. For example, the order of acidity for the binary hydrides of Group 16 elements is as follows, with pK_a values in parentheses:

$$H_2O(14.00 = pK_w) < H_2S(7.05) < H_2Se(3.89) < H_2Te(2.6) \tag{7.1.8.1}$$

Stability of the Conjugate Base

Whether we write an acid–base reaction as $AH \rightleftharpoons A^- + H^+$ or as $BH^+ \rightleftharpoons B + H^+$, the conjugate base ($A^-$ or B) contains one more lone pair of electrons than the parent acid (AH or BH^+). Any factor that stabilizes the lone pair on the conjugate base favors dissociation of H^+ and makes the parent acid a stronger acid. Let's see how this explains the relative acidity of the binary hydrides of the elements in the second row of the periodic table. The observed order of increasing acidity is the following, with pKa values in parentheses:

$$CH_4(\ 50) \ll NH_3(\ 36) < H_2O(14.00) < HF(3.20) \tag{7.1.8.2}$$

Consider, for example, the compounds at both ends of this series: methane and hydrogen fluoride. The conjugate base of CH_4 is CH_3^-, and the conjugate base of HF is F^-. Because fluorine is much more electronegative than carbon, fluorine can better stabilize the negative charge in the F^- ion than carbon can stabilize the negative charge in the CH3− ion. Consequently, $\mathbf{HF}$ has a greater tendency to dissociate to form H^+ and F^- than does methane to form H^+ and CH_3^-, making HF a much stronger acid than CH_4.

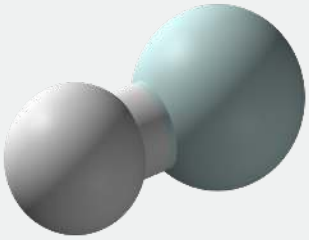
The same trend is predicted by analyzing the properties of the conjugate acids. For a series of compounds of the general formula HE, as the electronegativity of E increases, the E–H bond becomes more polar, favoring dissociation to form E^- and H^+. Due to both the increasing stability of the conjugate base and the increasing polarization of the E–H bond in the conjugate acid, acid strengths of binary hydrides increase as we go from left to right across a row of the periodic table.

Acid strengths of binary hydrides increase as we go down a column or from left to right across a row of the periodic table.

the strongest acid Known: The hydrohelium Cation

The stornger acid, the weaker the covalent bond to a hydrogen atom. So the strongest acid possible is the molecule with the weakest bond. That is the hydrohelium (1+) cation, $\mathbf{HeH^+}$, which is a positively charged ion formed by the reaction of a proton

with a helium atom in the gas phase. It was first produced in the laboratory in 1925 and is isoelectronic with molecular hydrogen (\ce{H2}). It is the strongest known acid, with a proton affinity of 177.8 kJ/mol.



Ball and stick model of the hydrohelium ion. (CC BY-SA 3.0; CCoil).

HeH$^+$ cannot be prepared in a condensed phase, as it would protonate any anion, molecule or atom with which it were associated. However it is possible to estimate a *hypothetical* aqueous acidity using Hess's law:

HHe$^+$(*g*)	→	H$^+$(*g*)	+ He(*g*)	+178 kJ/mol
HHe$^+$(*aq*)	→	HHe$^+$(*g*)		+973 kJ/mol
H$^+$(*g*)	→	H$^+$(*aq*)		−1530 kJ/mol
He(*g*)	→	He(*aq*)		+19 kJ/mol
HHe$^+$(*aq*)	→	H$^+$(*aq*)	+ He(*aq*)	−360 kJ/mol

A free energy change of dissociation of −360 kJ/mol is equivalent to a pK_a of −63.

It has been suggested that **HeH$^+$** should occur naturally in the interstellar medium, but it has not yet been detected.

Inductive Effects

Atoms or groups of atoms in a molecule other than those to which H is bonded can induce a change in the distribution of electrons within the molecule. This is called an inductive effect, and, much like the coordination of water to a metal ion, it can have a major effect on the acidity or basicity of the molecule. For example, the hypohalous acids (general formula HOX, with X representing a halogen) all have a hydrogen atom bonded to an oxygen atom. In aqueous solution, they all produce the following equilibrium:

$$HOX_{(aq)} \rightleftharpoons H^+_{(aq)} + OX^-(aq) \tag{7.1.8.3}$$

The acidities of these acids vary by about three orders of magnitude, however, due to the difference in electronegativity of the halogen atoms:

HOX	Electronegativity of X	pKa
HOCl	3.0	7.40
HOBr	2.8	8.55
HOI	2.5	10.5

As the electronegativity of X increases, the distribution of electron density within the molecule changes: the electrons are drawn more strongly toward the halogen atom and, in turn, away from the H in the O–H bond, thus weakening the O–H bond and allowing dissociation of hydrogen as H^+.

The acidity of oxoacids, with the general formula $HOXO_n$ (with n = 0−3), depends strongly on the number of terminal oxygen atoms attached to the central atom X. As shown in Figure 7.1.8.1, the K_a values of the oxoacids of chlorine increase by a factor of about 10^4 to 10^6 with each oxygen as successive oxygen atoms are added. The increase in acid strength with increasing number of terminal oxygen atoms is due to both an inductive effect and increased stabilization of the conjugate base.

> *Any inductive effect that withdraws electron density from an O–H bond increases the acidity of the compound.*

Because oxygen is the second most electronegative element, adding terminal oxygen atoms causes electrons to be drawn away from the O–H bond, making it weaker and thereby increasing the strength of the acid. The colors in Figure **7.1.8.1** show how the electrostatic potential, a measure of the strength of the interaction of a point charge at any place on the surface of the molecule, changes as the number of terminal oxygen atoms increases. In Figure **7.1.8.1** and Figure **7.1.8.2**, blue corresponds to low electron densities, while red corresponds to high electron densities. The oxygen atom in the O–H unit becomes steadily less red from $HClO$ to $HClO_4$ (also written as $HOClO_3$, while the H atom becomes steadily bluer, indicating that the electron density on the O–H unit decreases as the number of terminal oxygen atoms increases. The decrease in electron density in the O–H bond weakens it, making it easier to lose hydrogen as H^+ ions, thereby increasing the strength of the acid.

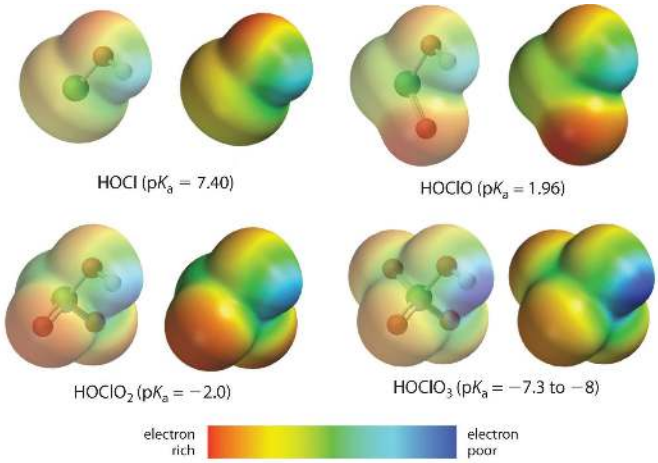
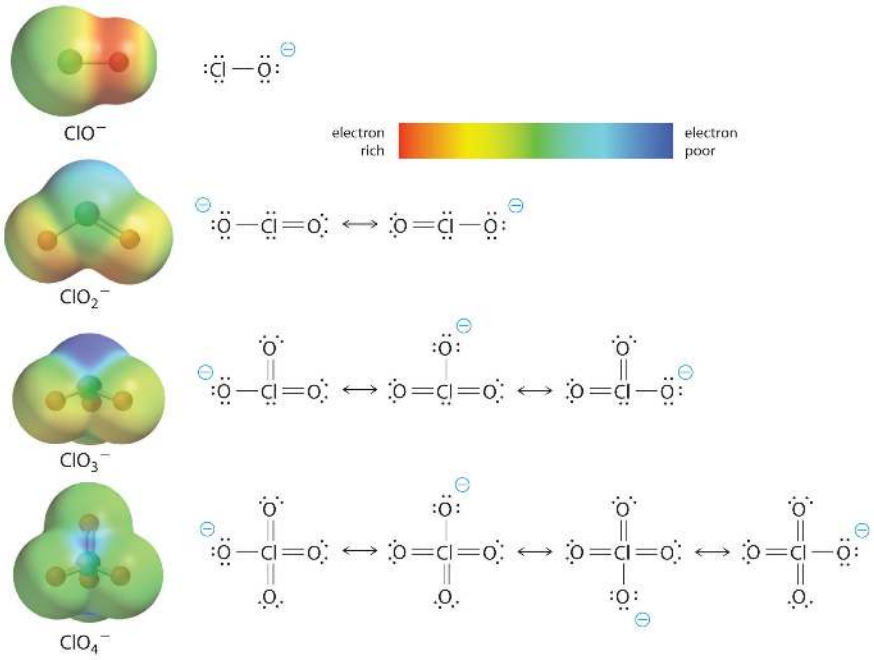


Figure **7.1.8.1**: The Relationship between the Acid Strengths of the Oxoacids of Chlorine and the Electron Density on the O–H Unit. These electrostatic potential maps show how the electron density on the O–H unit decreases as the number of terminal oxygen atoms increases. Blue corresponds to low electron densities, whereas red corresponds to high electron densities. Source: Chlorine oxoacids pKa values from J. R. Bowser, Inorganic Chemistry (Pacific Grove, CA: Brooks-Cole,1993).

At least as important, however, is the effect of delocalization of the negative charge in the conjugate base. As shown in Figure **7.1.8.2**, the number of resonance structures that can be written for the oxoanions of chlorine increases as the number of terminal oxygen atoms increases, allowing the single negative charge to be delocalized over successively more oxygen atoms.

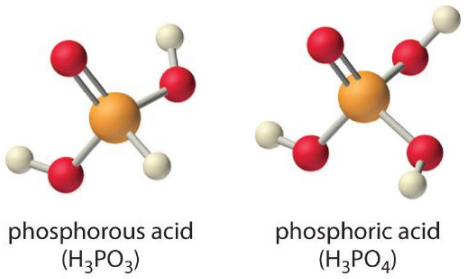
> *Electron delocalization in the conjugate base increases acid strength.*

The electrostatic potential plots in Figure **7.1.8.2** demonstrate that the electron density on the terminal oxygen atoms decreases steadily as their number increases. The oxygen atom in ClO^- is red, indicating that it is electron rich, and the color of oxygen progressively changes to green in ClO_4^+, indicating that the oxygen atoms are becoming steadily less electron rich through the series. For example, in the perchlorate ion (ClO_4^-), the single negative charge is delocalized over all four oxygen atoms, whereas in the hypochlorite ion (OCl^-), the negative charge is largely localized on a single oxygen atom (Figure **7.1.8.2**). As a result, the perchlorate ion has no localized negative charge to which a proton can bind. Consequently, the perchlorate anion has a much lower affinity for a proton than does the hypochlorite ion, and perchloric acid is one of the strongest acids known.



As the number of terminal oxygen atoms increases, the number of resonance structures that can be written for the oxoanions of chlorine also increases, and the single negative charge is delocalized over more oxygen atoms. As these electrostatic potential plots demonstrate, the electron density on the terminal oxygen atoms decreases steadily as their number increases. As the electron density on the oxygen atoms decreases, so does their affinity for a proton, making the anion less basic. As a result, the parent oxoacid is more acidic.

Similar inductive effects are also responsible for the trend in the acidities of oxoacids that have the same number of oxygen atoms as we go across a row of the periodic table from left to right. For example, H_3PO_4 is a weak acid, H_2SO_4 is a strong acid, and $HClO_4$ is one of the strongest acids known. The number of terminal oxygen atoms increases steadily across the row, consistent with the observed increase in acidity. In addition, the electronegativity of the central atom increases steadily from P to S to Cl, which causes electrons to be drawn from oxygen to the central atom, weakening the O–H bond and increasing the strength of the oxoacid.



Careful inspection of the data in Table 7.1.8.1 shows two apparent anomalies: carbonic acid and phosphorous acid. If carbonic acid (H_2CO_3) were a discrete molecule with the structure $(HO)_2C{=}O$, it would have a single terminal oxygen atom and should be comparable in acid strength to phosphoric acid (H_3PO_4), for which pKa1 = 2.16. Instead, the tabulated value of pK_{a1} for carbonic acid is 6.35, making it about 10,000 times weaker than expected. As we shall see, however, H_2CO_3 is only a minor component of the aqueous solutions of CO_2 that are referred to as carbonic acid. Similarly, if phosphorous acid (H_3PO_3) actually had the structure $(HO)_3P$, it would have no terminal oxygen atoms attached to phosphorous. It would therefore be expected to be about as strong an acid as $HOCl$ (pKa = 7.40). In fact, the pK_{a1} for phosphorous acid is 1.30, and the structure of phosphorous acid is $(HO)_2P(=O)H$ with one H atom directly bonded to P and one P=O bond. Thus the pKa1 for phosphorous acid is similar to that of other oxoacids with one terminal oxygen atom, such as H_3PO_4. Fortunately, phosphorous acid is the only common oxoacid in which a hydrogen atom is bonded to the central atom rather than oxygen.

Table 7.1.8.1: Values of pKa for Selected Polyprotic Acids and Bases

Polyprotic Acids	Formula	pK_{a1}	pK_{a2}	pK_{a3}
carbonic acid*	"H_2CO_3"	6.35	10.33	
citric acid	$HO_2CCH_2C(OH)(CO_2H)CH_2CO_2H$	3.13	4.76	6.40
malonic acid	$HO_2CCH_2CO_2H$	2.85	5.70	
oxalic acid	HO_2CCO_2H	1.25	3.81	
phosphoric acid	H_3PO_4	2.16	7.21	12.32
phosphorous acid	H_3PO_3	1.3	6.70	
succinic acid	$HO_2CCH_2CH_2CO_2H$	4.21	5.64	
sulfuric acid	H_2SO_4	−2.0	1.99	
sulfurous acid*	"H_2SO_3"	1.85	7.21	
Polyprotic Bases	**Formula**	pK_{b1}	pK_{b2}	
ethylenediamine	$H_2N(CH_2)_2NH_2$	4.08	7.14	
piperazine	$HN(CH_2CH_2)_2NH$	4.27	8.67	
propylenediamine	$H_2N(CH_2)_3NH_2$	3.45	5.12	

*H_2CO_3 and H_2SO_3 are at best minor components of aqueous solutions of $CO_{2(g)}$ and $SO_{2(g)}$, respectively, but such solutions are commonly referred to as containing carbonic acid and sulfurous acid, respectively.

Inductive effects are also observed in organic molecules that contain electronegative substituents. The magnitude of the electron-withdrawing effect depends on both the nature and the number of halogen substituents, as shown by the pKa values for several acetic acid derivatives:

$$pK_a CH_3CO_2H 4.76 < CH_2ClCO_2H 2.87 < CHCl_2CO_2H 1.35 < CCl_3CO_2H 0.66 < CF_3CO_2H 0.52$$

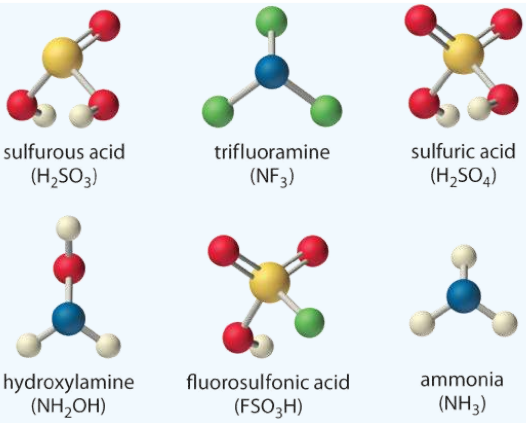
As you might expect, fluorine, which is more electronegative than chlorine, causes a larger effect than chlorine, and the effect of three halogens is greater than the effect of two or one. Notice from these data that inductive effects can be quite large. For instance, replacing the $-CH_3$ group of acetic acid by a $-CF_3$ group results in about a 10,000-fold increase in acidity!

Example 7.1.8.1

Arrange the compounds of each series in order of increasing acid or base strength.

a. sulfuric acid [H_2SO_4, or $(HO)_2SO_2$], fluorosulfonic acid (FSO_3H, or FSO_2OH), and sulfurous acid [H_2SO_3, or $(HO)_2SO$]
b. ammonia (NH_3), trifluoramine (NF_3), and hydroxylamine (NH_2OH)

The structures are shown here.



Given: series of compounds

Asked for: relative acid or base strengths

Strategy:

Use relative bond strengths, the stability of the conjugate base, and inductive effects to arrange the compounds in order of increasing tendency to ionize in aqueous solution.

Solution:

Although both sulfuric acid and sulfurous acid have two –OH groups, the sulfur atom in sulfuric acid is bonded to two terminal oxygen atoms versus one in sulfurous acid. Because oxygen is highly electronegative, sulfuric acid is the stronger acid because the negative charge on the anion is stabilized by the additional oxygen atom. In comparing sulfuric acid and fluorosulfonic acid, we note that fluorine is more electronegative than oxygen. Thus replacing an –OH by –F will remove more electron density from the central S atom, which will, in turn, remove electron density from the S–OH bond and the O–H bond. Because its O–H bond is weaker, FSO_3H is a stronger acid than sulfuric acid. The predicted order of acid strengths given here is confirmed by the measured pKa values for these acids:

$$pKa H_2SO_3 1.85 < H_2SO_4^{-2} < FSO_3H - 10$$

The structures of both trifluoramine and hydroxylamine are similar to that of ammonia. In trifluoramine, all of the hydrogen atoms in NH3 are replaced by fluorine atoms, whereas in hydroxylamine, one hydrogen atom is replaced by OH. Replacing the three hydrogen atoms by fluorine will withdraw electron density from N, making the lone electron pair on N less available to bond to an H^+ ion. Thus NF_3 is predicted to be a much weaker base than NH_3. Similarly, because oxygen is more electronegative than hydrogen, replacing one hydrogen atom in NH_3 by OH will make the amine less basic. Because oxygen is less electronegative than fluorine and only one hydrogen atom is replaced, however, the effect will be smaller. The predicted order of increasing base strength shown here is confirmed by the measured pK_b values:

$$pK_b NF_3 — << NH_2OH 8.06 < NH_3 4.75$$

Trifluoramine is such a weak base that it does not react with aqueous solutions of strong acids. Hence its base ionization constant has never been measured.

? Exercise 7.1.8.1

Arrange the compounds of each series in order of

a. decreasing acid strength: H_3PO_4, $CH_3PO_3H_2$, and $HClO_3$.
b. increasing base strength: CH_3S^-, OH^-, and CF_3S^-.

Answer a

$HClO-3 > CH_3PO_3H_2 > H_3PO_4$

Answer a

$CF_3S^- < CH_3S^- < OH^-$

Summary

Inductive effects and charge delocalization significantly influence the acidity or basicity of a compound. The acid–base strength of a molecule depends strongly on its structure. The weaker the A–H or B–H+ bond, the more likely it is to dissociate to form an H^+ ion. In addition, any factor that stabilizes the lone pair on the conjugate base favors the dissociation of H^+, making the conjugate acid a stronger acid. Atoms or groups of atoms elsewhere in a molecule can also be important in determining acid or base strength through an inductive effect, which can weaken an O–H bond and allow hydrogen to be more easily lost as H^+ ions.

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7.1.9: Lewis Acids and Bases

Learning Objectives

Make sure you thoroughly understand the following essential ideas which have been presented. It is especially important that you know the precise meanings of all the highlighted terms in the context of this topic.

- Write the equation for the proton transfer reaction involving a Brønsted-Lowry acid or base, and show how it can be interpreted as an **electron-pair transfer** reaction, clearly identifying the donor and acceptor.
- Give an example of a **Lewis acid-base reaction** that does not involve protons.
- Write equations illustrating the behavior of a given **non-aqueous acid-base system**.

The Brønsted-Lowry proton donor-acceptor concept has been one of the most successful theories of Chemistry. But as with any such theory, it is fair to ask if this is not just a special case of a more general theory that could encompass an even broader range of chemical science. In 1916, G.N. Lewis of the University of California proposed that the *electron pair* is the dominant actor in acid-base chemistry. The Lewis theory did not become very well known until about 1923 (the same year that Brønsted and Lowry published their work), but since then it has been recognized as a very powerful tool for describing chemical reactions of widely different kinds and is widely used in organic and inorganic chemistry. The Brønsted–Lowry concept of acids and bases defines a base as any species that can accept a proton, and an acid as any substance that can donate a proton. Lewis proposed an alternative definition that focuses on *pairs of electrons* instead. According to Lewis:

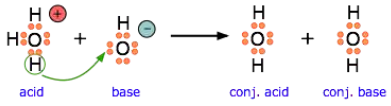
- An *acid* is a substance that **accepts** a pair of electrons, and in doing so, forms a covalent bond with the entity that supplies the electrons.
- A *base* is a substance that **donates** an unshared pair of electrons to a recipient species with which the electrons can be shared.

Note

In modern chemistry, electron donors are often referred to as nucleophiles, while acceptors are electrophiles.

Lewis Acid-Base Neutralization Involving Electron-Pair Transfer

Just as any Arrhenius acid is also a Brønsted acid, any Brønsted acid is also a Lewis acid, so the various acid-base concepts are all "upward compatible". Although we do not really need to think about electron-pair transfers when we deal with ordinary aqueous-solution acid-base reactions, it is important to understand that it is the opportunity for electron-pair sharing that enables proton transfer to take place.

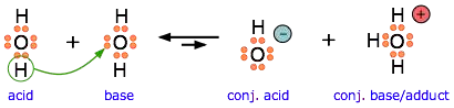


This equation for a simple acid-base neutralization shows how the Brønsted and Lewis definitions are really just different views of the same process. Take special note of the following points:

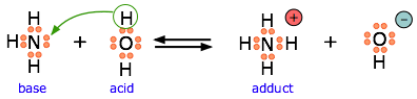
- The arrow shows the movement of a proton from the hydronium ion to the hydroxide ion.
- Note that the electron-pairs themselves do not move; they remain attached to their central atoms. The electron pair on the base is "donated" to the acceptor (the proton) only in the sense that it ends up being *shared* with the acceptor, rather than being the exclusive property of the oxygen atom in the hydroxide ion.
- Although the hydronium ion is the nominal Lewis acid here, it does not itself accept an electron pair, but acts merely as the source of the proton that coordinates with the Lewis base.

The point about the electron-pair remaining on the donor species is especially important to bear in mind. For one thing, it distinguishes a *Lewis acid-base reaction* from an *oxidation-reduction reaction*, in which a physical transfer of one or more electrons from donor to acceptor does occur. The product of a Lewis acid-base reaction is known formally as an "adduct" or "complex", although we do not ordinarily use these terms for simple proton-transfer reactions such as the one in the above

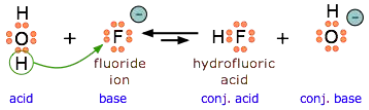
example. Here, the proton combines with the hydroxide ion to form the "adduct" H_2O. The following examples illustrate these points for some other proton-transfer reactions that you should already be familiar with.



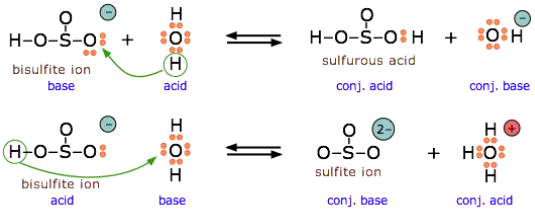
Another example, showing the autoprotolysis of water. Note that the conjugate base is also the adduct.



Ammonia is both a Brønsted and a Lewis base, owing to the unshared electron pair on the nitrogen. The reverse of this reaction represents the *hydrolysis* of the ammonium ion.



Because HF is a weak acid, fluoride salts behave as bases in aqueous solution. As a Lewis base, F^- accepts a proton from water, which is transformed into a hydroxide ion.

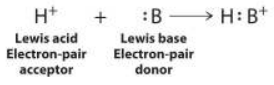


The bisulfite ion is *amphiprotic* and can act as an electron donor or acceptor.

> **Note**
>
> All Brønsted–Lowry bases (proton acceptors), such as OH^-, H_2O, and NH_3, are also electron-pair donors. Thus the Lewis definition of acids and bases does not contradict the Brønsted–Lowry definition. Rather, it expands the definition of acids to include substances other than the H^+ ion.

Lewis Acid-Base Neutralization without Transferring Protons

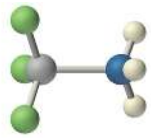
Electron-deficient molecules, such as BCl_3, contain less than an octet of electrons around one atom and have a strong tendency to gain an additional pair of electrons by reacting with substances that possess a lone pair of electrons. Lewis's definition, which is less restrictive than either the Brønsted–Lowry or the Arrhenius definition, grew out of his observation of this tendency. A general Brønsted–Lowry acid–base reaction can be depicted in Lewis electron symbols as follows:



The proton (H^+), which has no valence electrons, is a Lewis acid because it accepts a lone pair of electrons on the base to form a bond. The proton, however, is just one of many electron-deficient species that are known to react with bases. For example, neutral compounds of boron, aluminum, and the other Group 13 elements, which possess only six valence electrons, have a very strong tendency to gain an additional electron pair. Such compounds are therefore potent Lewis acids that react with an electron-pair donor such as ammonia to form an acid–base adduct, a new covalent bond, as shown here for boron trifluoride (BF_3):

$$\underset{\text{Lewis acid}}{BF_3} + \underset{\text{Lewis base}}{:NH_3} \longrightarrow \underset{\text{Acid-base adduct}}{F_3B{:}NH_3}$$

The bond formed between a Lewis acid and a Lewis base is a *coordinate covalent bond* because both electrons are provided by only one of the atoms (N, in the case of $F_3B{:}NH_3$). After it is formed, however, a coordinate covalent bond behaves like any other covalent single bond.



Boron trifluoride-ammonia adduct

Species that are very weak Brønsted–Lowry bases can be relatively strong Lewis bases. For example, many of the group 13 trihalides are highly soluble in ethers (R–O–R′) because the oxygen atom in the ether contains two lone pairs of electrons, just as in H_2O. Hence the predominant species in solutions of electron-deficient trihalides in ether solvents is a Lewis acid–base adduct. A reaction of this type is shown in Figure **7.1.9.1** for boron trichloride and diethyl ether:

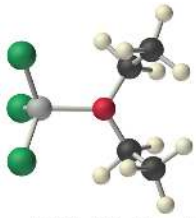
$$\underset{\text{Lewis acid}}{BCl_3} + \underset{\text{Lewis base}}{:\ddot{O}(CH_2CH_3)_2} \longrightarrow \underset{\text{Acid-base adduct}}{Cl_3B{:}\ddot{O}(CH_2CH_3)_2}$$

Figure 7.1.9.1: *Lewis Acid/Base reaction of boron trichloride and diethyl ether reaction*

Note

- Electron-deficient molecules (those with less than an octet of electrons) are Lewis acids.
- The acid-base behavior of many compounds can be explained by their Lewis electron structures.

Many molecules with multiple bonds can act as Lewis acids. In these cases, the Lewis base typically donates a pair of electrons to form a bond to the central atom of the molecule, while a pair of electrons displaced from the multiple bond becomes a lone pair on a terminal atom.



Boron trichloride-diethyl ether adduct

Figure **7.1.9.2**. The highly electronegative oxygen atoms pull electron density away from carbon, so the carbon atom acts as a Lewis acid. Arrows indicate the direction of electron flow.

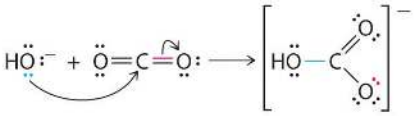


Figure 7.1.9.2: *Lewis Acid/Base reaction of the hydroxide ion with carbon dioxide*

Example 7.1.9.1

Identify the acid and the base in each Lewis acid–base reaction.

a. $BH_3 + (CH_3)_2S \rightarrow H_3B{:}S(CH_3)_2$
b. $CaO + CO_2 \rightarrow CaCO_3$
c. $BeCl_2 + 2\ Cl^- \rightarrow BeCl_4^{2-}$

Given: reactants and products

Asked for: identity of Lewis acid and Lewis base

Strategy:

In each equation, identify the reactant that is electron deficient and the reactant that is an electron-pair donor. The electron-deficient compound is the Lewis acid, whereas the other is the Lewis base.

Solution:

a. In BH_3, boron has only six valence electrons. It is therefore electron deficient and can accept a lone pair. Like oxygen, the sulfur atom in $(CH_3)_2S$ has two lone pairs. Thus $(CH_3)_2S$ donates an electron pair on sulfur to the boron atom of BH_3. The Lewis base is $(CH_3)_2S$, and the Lewis acid is BH_3.
b. As in the reaction shown in Equation 8.21, CO_2 accepts a pair of electrons from the O^{2-} ion in CaO to form the carbonate ion. The oxygen in CaO is an electron-pair donor, so CaO is the Lewis base. Carbon accepts a pair of electrons, so CO_2 is the Lewis acid.
c. The chloride ion contains four lone pairs. In this reaction, each chloride ion donates one lone pair to $BeCl_2$, which has only four electrons around Be. Thus the chloride ions are Lewis bases, and $BeCl_2$ is the Lewis acid.

? Exercise 7.1.9.1

Identify the acid and the base in each Lewis acid–base reaction.

a. $(CH_3)_2O + BF_3 \rightarrow (CH_3)_2O{:}BF_3$
b. $H_2O + SO_3 \rightarrow H_2SO_4$

Answer

a. Lewis base: $(CH_3)_2O$; Lewis acid: BF_3
b. Lewis base: H_2O; Lewis acid: SO_3

? Exercise 7.1.9.2

Here are several more examples of Lewis acid-base reactions that **cannot** be accommodated within the Brønsted or Arrhenius models. Identify the Lewis acid and Lewis base in each reaction.

a. $Al(OH)_3 + OH^- \rightarrow Al(OH)_4^-$
b. $SnS_2 + S^{2-} \rightarrow SnS_3^{2-}$
c. $Cd(CN)_2 + 2CN^- \rightarrow Cd(CN)_4^{2+}$
d. $AgCl + 2NH_3 \rightarrow Ag(NH_3)_2^+ + Cl^-$
e. $Fe^{2+} + NO \rightarrow Fe(NO)^{2+}$
f. $[Ni^{2+} + 6NH_3 \rightarrow Ni(NH_3)_5^{2+}$

Non-Aqueous Acid/Base Systems

We ordinarily think of Brønsted-Lowry acid-base reactions as taking place in aqueous solutions, but this need not always be the case. A more general view encompasses a variety of acid-base *solvent systems*, of which the *water system* is only one (Table **7.1.9.1**). Each of these has as its basis an amphiprotic solvent (one capable of undergoing autoprotolysis), in parallel with the familiar case of water.

The limiting acid in a given solvent is the solvonium ion, such as H_3O^+ (hydronium) ion in water. An acid which has more of a tendency to donate a hydrogen ion than the limiting acid will be a strong acid in the solvent considered, and will exist mostly or entirely in its dissociated form. Likewise, the limiting base in a given solvent is the solvate ion, such as OH^- (hydroxide) ion, in water. A base which has more affinity for protons than the limiting base cannot exist in solution, as it will react with the solvent.

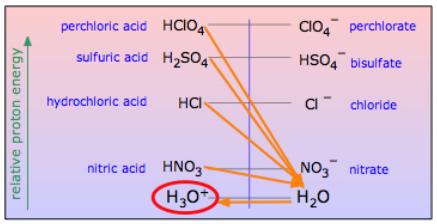


Figure } \PageIndex{3}\): *Use of non-aqueous solvents allows the study of strong acids that are hindered by the "leveling effect" of the solvent.*

The ammonia system is one of the most common non-aqueous system in Chemistry. Liquid ammonia boils at –33° C, and can conveniently be maintained as a liquid by cooling with dry ice (–77° C). It is a good solvent for substances that also dissolve in water, such as ionic salts and organic compounds since it is capable of forming hydrogen bonds. Bases can exist in solution in liquid ammonia which cannot exist in aqueous solution: this is the case for any base which is **stronger** than the hydroxide ion, but **weaker** than the amide ion NH_2^-. The limiting acid in liquid ammonia is the ammonium ion, which has a pK_a value in water of 9.25. The limiting base is the amide ion, NH_2^-. This is a stronger base than the hydroxide ion and so cannot exist in aqueous solution. The pK_a value of ammonia is estimated to be approximately 33. Any acid which is a stronger acid than the ammonium ion will be a strong acid in liquid ammonia. This is the case for acetic acid, which is completely dissociated in liquid ammonia solution. The addition of pure acetic acid and the addition of ammonium acetate have exactly the same effect on a liquid ammonia solution: the increase in its acidity: in practice, the latter is preferred for safety reasons.

Note

As with OH^- and H_3O^+ in water, the strongest acid and base in NH_3 is dictated by the corresponding autoprotolysis reaction of the solvent:

$$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

One use of non-aqueous acid-base systems is to examine the relative strengths of the strong acids and bases, whose strengths are "leveled" by the fact that they are all totally converted into H_3O^+ or OH^- ions in water. By studying them in appropriate non-aqueous solvents which are poorer acceptors or donors of protons, their relative strengths can be determined. Many familiar substances can serve as the basis of protonic solvent systems (Table 7.1.9.1).

Table 7.1.9.1: Popular Solvent systems

solvent	autoprotolysis reaction	pK_a
water	$2H_2O \rightleftharpoons H_3O^+ + OH^-$	14
ammonia	$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$	33
acetic acid	$2CH_3COOH \rightleftharpoons CH_3COOH_2^+ + CH_3COO^-$	13
ethanol	$2C_2H_5OH \rightleftharpoons C_2H_5OH_2^+ + C_2H_5O^-$	19
hydrogen peroxide	$2HO-OH \rightleftharpoons HO-OH_2^+ + HO-O^-$	13
hydrofluoric acid	$2HF \rightleftharpoons H^2F^+ + F^-$	10
sulfuric acid	$2H_2SO_4 \rightleftharpoons H3SO_4^+ + HSO_4^-$	3.5

The extreme case is a **superacid**, a medium in which the hydrogen ion is only very weakly solvated. The classic example is a mixture of antimony pentafluoride and liquid hydrogen fluoride:

$$SbF_5 + HF \rightleftharpoons H^+ + SbF_6^- \qquad (7.1.9.1)$$

The limiting base, the hexfluoroantimonate anion SbF_6^-, is so weakly attracted to the hydrogen ion that virtually any other base will bind more strongly: hence, this mixture can be used to protonate organic molecules which would not be considered bases in other

solvents. It should noted that pH is undefined in aprotic solvents, which assumes presence of hydronium ions. In other solvents, the concentration of the respective solvonium/solvate ions should be used (e.g., $[NH_4^+]$ and $[NH_2^-]$ in $NH_{3(l)}$.

Contributors and Attributions

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SECTION OVERVIEW

7.2: Additional Aspects of Acid-Base Equilibria

Topic hierarchy

7.2.1: Common-Ion Effect in Acid–Base Equilibria

7.2.2: Buffer Solutions

7.2.3: Acid–Base Indicators

7.2.4: Neutralization Reactions and Titration Curves

7.2.5: Solutions of Salts of Polyprotic Acids

7.2.6: Acid–Base Equilibrium Calculations- ASummary

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7.2.1: Common-Ion Effect in Acid–Base Equilibria

Learning Objectives

- Recognize common ions from various salts, acids, and bases.
- Calculate concentrations involving common ions.
- Calculate ion concentrations involving chemical equilibrium.

The common-ion effect is used to describe the effect on an equilibrium involving a substance that adds an ion that is a part of the equilibrium.

Introduction

The solubility products K_{sp}'s are equilibrium constants in heterogeneous equilibria (i.e., between two different phases). If several salts are present in a system, they all ionize in the solution. If the salts contain a common cation or anion, these salts contribute to the concentration of the common ion. Contributions from all salts must be included in the calculation of concentration of the common ion. For example, a solution containing sodium chloride and potassium chloride will have the following relationship:

$$[Na^+] + [K^+] = [Cl^-] \tag{7.2.1.1}$$

Consideration of *charge balance* or *mass balance* or both leads to the same conclusion.

Common Ions

When **NaCl** and **KCl** are dissolved in the same solution, the Cl^- ions are *common* to both salts. In a system containing **NaCl** and **KCl**, the Cl^- ions are common ions.

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

$$KCl \rightleftharpoons K^+ + Cl^-$$

$$CaCl_2 \rightleftharpoons Ca^{2+} + 2Cl^-$$

$$AlCl_3 \rightleftharpoons Al^{3+} + 3Cl^-$$

$$AgCl \rightleftharpoons Ag^+ + Cl^-$$

For example, when **AgCl** is dissolved into a solution already containing **NaCl** (actually Na^+ and Cl^- ions), the Cl^- ions come from the ionization of both **AgCl** and **NaCl**. Thus, $[Cl^-]$ differs from $[Ag^+]$. The following examples show how the concentration of the common ion is calculated.

Example 7.2.1.1

What are $[Na^+]$, $[Cl^-]$, $[Ca^{2+}]$, and $[H^+]$ in a solution containing 0.10 M each of **NaCl**, $CaCl_2$, and **HCl**?

Solution

Due to the conservation of ions, we have

$$[Na^+] = [Ca^{2+}] = [H^+] = 0.10\ M$$

but

$$\begin{aligned}[Cl^-] = &\ 0.10\ (\text{due to NaCl}) \\ &+ 0.20\ (\text{due to } CaCl_2) \\ &+ 0.10\ (\text{due to HCl}) \\ = &\ 0.40\ M\end{aligned}$$

Exercise 7.2.1.1

John poured 10.0 mL of 0.10 M **NaCl**, 10.0 mL of 0.10 M **KOH**, and 5.0 mL of 0.20 M **HCl** solutions together and then he made the total volume to be 100.0 mL. What is $[Cl^-]$ in the final solution?

Solution

$$[Cl^-] = \frac{0.1\ M \times 10\ mL + 0.2\ M \times 5.0\ mL}{100.0\ mL} = 0.020\ M$$

Le Châtelier's Principle states that if an equilibrium becomes unbalanced, the reaction will shift to restore the balance. If a common ion is added to a weak acid or weak base equilibrium, then the equilibrium will shift towards the reactants, in this case the weak acid or base.

Example 7.2.1.2: Solubility of Lead Chloride

Consider the lead(II) ion concentration in this *saturated* solution of $PbCl_2$. The balanced reaction is

$$PbCl_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2Cl^-_{(aq)}$$

Defining s as the concentration of dissolved lead(II) chloride, then:

$$[Pb^{2+}] = s$$

$$[Cl^-] = 2s$$

These values can be substituted into the solubility product expression, which can be solved for s:

$$K_{sp} = [Pb^{2+}][Cl^-]^2 \tag{7.2.1.2}$$

$$= s \times (2s)^2 \tag{7.2.1.3}$$

$$1.7 \times 10^{-5} = 4s^3 \tag{7.2.1.4}$$

$$s^3 = \frac{1.7 \times 10^{-5}}{4} \tag{7.2.1.5}$$

$$= 4.25 \times 10^{-6} \tag{7.2.1.6}$$

$$s = \sqrt[3]{4.25 \times 10^{-6}} \tag{7.2.1.7}$$

$$= 1.62 \times 10^{-2}\ mol\ dm^{-3} \tag{7.2.1.8}$$

The concentration of lead(II) ions in the solution is 1.62 x 10^{-2} M. Consider what happens if sodium chloride is added to this saturated solution. Sodium chloride shares an ion with lead(II) chloride. The chloride ion is **common** to both of them; this is the origin of the term "common ion effect".

Look at the original equilibrium expression again:

$$PbCl_2\,(s) \rightleftharpoons Pb^{2+}\,(aq) + 2Cl^-\,(aq)$$

What happens to that equilibrium if extra chloride ions are added? According to *Le* Châtelier, the position of equilibrium will shift to counter the change, in this case, by removing the chloride ions by making extra solid lead(II) chloride.

Of course, the concentration of lead(II) ions in the solution is so small that only a tiny proportion of the extra chloride ions can be converted into solid lead(II) chloride. The lead(II) chloride becomes even *less soluble*, and the concentration of lead(II) ions in the solution *decreases*. This type of response occurs with any sparingly soluble substance: it is less soluble in a solution which contains any ion which it has in common. This is the common ion effect.

Example 7.2.1.3

If an attempt is made to dissolve some lead(II) chloride in some 0.100 M sodium chloride solution instead of in water, what is the equilibrium concentration of the lead(II) ions this time? As before, define s to be the concentration of the lead(II) ions.

$$[Pb^{2+}] = s \tag{7.2.1.9}$$

The calculations are different from before. This time the concentration of the chloride ions is governed by the concentration of the sodium chloride solution. The number of ions coming from the lead(II) chloride is going to be tiny compared with the 0.100 M coming from the sodium chloride solution.

In calculations like this, it can be assumed that the concentration of the common ion is entirely due to the other solution. This simplifies the calculation.

So we assume:

$$[Cl^-] = 0.100\ M \tag{7.2.1.10}$$

The rest of the mathematics looks like this:

$$\begin{aligned} K_{sp} &= [Pb^{2+}][Cl^-]^2 \\ &= s \times (0.100)^2 \\ 1.7 \times 10^{-5} &= s \times 0.00100 \end{aligned}$$

therefore:

$$\begin{aligned} s &= \frac{1.7 \times 10^{-5}}{0.0100} \\ &= 1.7 \times 10^{-3}\,\text{M} \end{aligned} \tag{7.2.1.11}$$

Finally, compare that value with the simple saturated solution:

Original solution:

$$[Pb^{2+}] = 0.0162\ M \tag{7.2.1.12}$$

Solution in 0.100 M NaCl solution:

$$[Pb^{2+}] = 0.0017\ M \tag{7.2.1.13}$$

The concentration of the lead(II) ions has decreased by a factor of about 10. If more concentrated solutions of sodium chloride are used, the solubility decreases further.



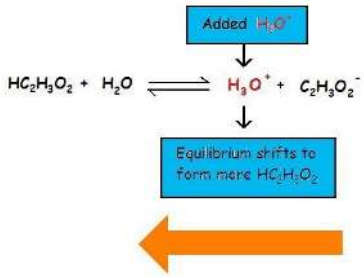
A Video Discussing Finding the Solubility of a Salt: Finding the Solubility of a Salt(opens in new window) [youtu.be]

Common Ion Effect with Weak Acids and Bases

Adding a common ion prevents the weak acid or weak base from ionizing as much as it would without the added common ion. The common ion effect suppresses the ionization of a weak acid by adding more of an ion that is a product of this equilibrium.

> *Adding a common ion to a system at equilibrium affects the equilibrium composition, but not the ionization constant.*

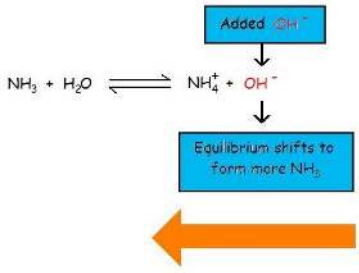
The common ion effect of H_3O^+ on the ionization of acetic acid



HC2H3O2 reactions with H2O to produce H3O plus and C2H3 O2 minus. If more H3O plus is added to the reaction, the equilibrium would shift to form more HC2H3O2.

When a strong acid supplies the common ion $\mathbf{H_3O^+}$ the equilibrium shifts to form more $\mathbf{HC_2H_3O_2}$.

The common ion effect suppresses the ionization of a weak base by adding more of an ion that is a product of this equilibrium. Now consider the common ion effect of $\mathbf{OH^-}$ on the ionization of ammonia



When a strong base supplies the common ion $\mathbf{OH^-}$ the equilibrium shifts to form more $\mathbf{NH_3}$.

NH3 reacts with H2 O to produce NH4 plus and OH minus. If more OH minus is added to the reaction, the equilibrium would shifts to form more NH3.

Adding the common ion of hydroxide shifts the reaction towards the left to decrease the stress (in accordance with Le Chatelier's Principle), forming more reactants. This decreases the reaction quotient, because the reaction is being pushed towards the left to reach equilibrium. The equilibrium constant, $K_b = 1.8 \times 10^{-5}$, does not change. The reaction is put out of balance, or equilibrium.

$$Q_a = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

At first, when more hydroxide is added, the quotient is greater than the equilibrium constant. The reaction then shifts right, causing the denominator to increase, decreasing the reaction quotient and pulling towards equilibrium and causing Q to decrease towards K.

Common Ion Effect on Solubility

When a slightly soluble ionic compound is added to water, some of it dissolves to form a solution, establishing an equilibrium between the pure solid and a solution of its ions. For the dissolution of calcium phosphate, one of the two main components of kidney stones, the equilibrium can be written as follows, with the solid salt on the left:

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3\,Ca^{2+}(aq) + 2\,PO_4^{3-}(aq) \tag{7.2.1.14}$$

As you will discover in more advanced chemistry courses, basic anions, such as S^{2-}, PO_4^{3-}, and CO_3^{2-}, react with water to produce OH^- and the corresponding protonated anion. Consequently, their calculated molarities, assuming no protonation in aqueous solution, are only approximate. The equilibrium constant for the dissolution of a sparingly soluble salt is the **solubility product (K_{sp})** of the salt. Because the concentration of a pure solid such as $Ca_3(PO_4)_2$ is a constant, it does not appear explicitly in the equilibrium constant expression. The equilibrium constant expression for the dissolution of calcium phosphate is therefore

$$K = \frac{[Ca^{2+}]^3[PO_4^{3-}]^2}{[Ca_3(PO_4)_2]} \tag{7.2.1.15}$$

$$[Ca_3(PO_4)_2]K = K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 \tag{7.2.1.16}$$

At 25°C and pH 7.00, K_{sp} for calcium phosphate is 2.07×10^{-33}, indicating that the concentrations of Ca^{2+} and PO_4^{3-} ions in solution that are in equilibrium with solid calcium phosphate are very low. The values of K_{sp} for some common salts vary dramatically for different compounds (Table E3). Although K_{sp} is not a function of pH in Equation 7.2.1.15, changes in pH can affect the solubility of a compound.

The solubility product expression tells us that the equilibrium concentrations of the cation and the anion are inversely related. That is, as the concentration of the anion increases, the maximum concentration of the cation needed for precipitation to occur decreases—and vice versa—so that K_{sp} is constant. **Consequently, the solubility of an ionic compound depends on the concentrations of other salts that contain the same ions.** This dependency is another example of the common ion effect where adding a common cation or anion shifts a solubility equilibrium in the direction predicted by Le Chatelier's principle. As a result, the solubility of any sparingly soluble salt is almost always decreased by the presence of a soluble salt that contains a common ion.

Consider, for example, the effect of adding a soluble salt, such as $CaCl_2$, to a saturated solution of calcium phosphate [$Ca_3(PO_4)_2$]. We have seen that the solubility of $Ca_3(PO_4)_2$ in water at 25°C is 1.14×10^{-7} M ($K_{sp} = 2.07 \times 10^{-33}$). Thus a saturated solution of $Ca_3(PO_4)_2$ in water contains

- $\mathbf{3 \times (1.14 \times 10^{-7}\ M) = 3.42 \times 10^{-7} M\ of\ Ca^{2+}}$
- $\mathbf{2 \times (1.14 \times 10^{-7} M) = 2.28 \times 10^{-7} M\ of\ PO_4^{3-}}$

according to the stoichiometry shown in Equation 7.2.1.15 (neglecting hydrolysis to form HPO_4^{2-}). If $CaCl_2$ is added to a saturated solution of $Ca_3(PO_4)_2$, the Ca^{2+} ion concentration will increase such that $[Ca^{2+}] > 3.42 \times 10^{-7}$ M, making $Q > K_{sp}$. The only way the system can return to equilibrium is for the reaction in Equation 7.2.1.15 to proceed to the left, resulting in precipitation of $Ca_3(PO_4)_2$. This will decrease the concentration of both Ca^{2+} and PO_4^{3-} until $Q = K_{sp}$.

Note

Adding a common ion decreases solubility, as the reaction shifts toward the left to relieve the stress of the excess product. Adding a common ion to a dissociation reaction causes the equilibrium to shift left, toward the reactants, causing precipitation.

Example 7.2.1.5

Consider the reaction:

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$

What happens to the solubility of $PbCl_2$(s) when 0.1 M NaCl is added?

Solution

$$K_{sp} = 1.7 \times 10^{-5}$$

$$Q_{sp} = 1.8 \times 10^{-5}$$

Identify the common ion: Cl^-

Notice: $Q_{sp} > K_{sp}$ The addition of NaCl has caused the reaction to shift out of equilibrium because there are more dissociated ions. Typically, solving for the molarities requires the assumption that the solubility of $PbCl_2$ is equivalent to the concentration of Pb^{2+} produced because they are in a 1:1 ratio.

Because K_{sp} for the reaction is 1.7×10^{-5}, the overall reaction would be $(s)(2s)^2 = 1.7\times10^{-5}$. Solving the equation for s gives $s = 1.62\times10^{-2}$ M. The coefficient on Cl^- is 2, so it is assumed that twice as much Cl^- is produced as Pb^{2+}, hence the '2s.' The solubility equilibrium constant can be used to solve for the molarities of the ions at equilibrium.

The molarity of Cl^- added would be 0.1 M because Na^+ and Cl^- are in a 1:1 ration in the ionic salt, NaCl. Therefore, the overall molarity of Cl^- would be 2s + 0.1, with 2s referring to the contribution of the chloride ion from the dissociation of lead chloride.

$$Q_{sp} = [Pb^{2+}][Cl^-]^2 \quad (7.2.1.17)$$

$$1.8 \times 10^{-5} = (s)(2s + 0.1)^2 \quad (7.2.1.18)$$

$$s = [Pb^{2+}] \quad (7.2.1.19)$$

$$= 1.8 \times 10^{-3} M \quad (7.2.1.20)$$

$$2s = [Cl^-] \quad (7.2.1.21)$$

$$\approx 0.1M \quad (7.2.1.22)$$

Notice that the molarity of Pb^{2+} is lower when NaCl is added. The equilibrium constant remains the same because of the increased concentration of the chloride ion. To simplify the reaction, it can be assumed that $[Cl^-]$ is approximately 0.1M since the formation of the chloride ion from the dissociation of lead chloride is so small. The reaction quotient for $PbCl_2$ is greater than the equilibrium constant because of the added Cl^-. This therefore shift the reaction left towards equilibrium, causing precipitation and lowering the current solubility of the reaction. Overall, the solubility of the reaction decreases with the added sodium chloride.

Exercise 7.2.1.5

Calculate the solubility of silver carbonate in a 0.25 M solution of sodium carbonate. The solubility of silver carbonate in pure water is 8.45×10^{-12} at 25°C.

Answer

2.9×10^{-6} M (versus 1.3×10^{-4} M in pure water)



A Video Discussing the Common Ion Effect in Solubility Products: The Common Ion Effect in Solubility Products (opens in new window) [youtu.be]

References

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7.2.2: Buffer Solutions

Learning Objectives

- To understand how adding a common ion affects the position of an acid–base equilibrium.
- To know how to use the Henderson-Hasselbalch approximation to calculate the pH of a buffer.

Buffers are solutions that maintain a relatively constant pH when an acid or a base is added. They therefore protect, or "buffer," other molecules in solution from the effects of the added acid or base. Buffers contain either a weak acid (HA) and its conjugate base (A^-) or a weak base (B) and its conjugate acid (BH^+), and they are critically important for the proper functioning of biological systems. In fact, every biological fluid is buffered to maintain its physiological pH.

The Common Ion Effect: Weak Acids Combined with Conjugate Bases

To understand how buffers work, let's look first at how the ionization equilibrium of a weak acid is affected by adding either the conjugate base of the acid or a strong acid (a source of H^+). Le Chatelier's principle can be used to predict the effect on the equilibrium position of the solution. A typical buffer used in biochemistry laboratories contains acetic acid and a salt such as sodium acetate. The dissociation reaction of acetic acid is as follows:

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq) \tag{7.2.2.1}$$

and the equilibrium constant expression is as follows:

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3CO_2H]} \tag{7.2.2.2}$$

Sodium acetate (CH_3CO_2Na) is a strong electrolyte that ionizes completely in aqueous solution to produce Na^+ and $CH_3CO_2^-$ ions. If sodium acetate is added to a solution of acetic acid, Le Chatelier's principle predicts that the equilibrium in Equation 7.2.2.1 will shift to the left, consuming some of the added CH_3COO^- and some of the H^+ ions originally present in solution.

Because Na^+ is a **spectator ion**, it has no effect on the position of the equilibrium and can be ignored. The addition of sodium acetate produces a new equilibrium composition, in which $[H^+]$ is less than the initial value. Because $[H^+]$ has decreased, the pH will be higher. Thus adding a salt of the conjugate base to a solution of a weak acid increases the pH. This makes sense because sodium acetate is a base, and adding any base to a solution of a weak acid should increase the pH.

If we instead add a strong acid such as HCl to the system, $[H^+]$ increases. Once again the equilibrium is temporarily disturbed, but the excess H^+ ions react with the conjugate base ($CH_3CO_2^-$), whether from the parent acid or sodium acetate, to drive the equilibrium to the left. The net result is a new equilibrium composition that has a lower $[CH_3CO_2^-]$ than before. In both cases, only the equilibrium composition has changed; the ionization constant K_a for acetic acid remains the same. Adding a strong electrolyte that contains one ion in common with a reaction system that is at equilibrium, in this case $CH_3CO_2^-$, will therefore shift the equilibrium in the direction that reduces the concentration of the common ion. The shift in equilibrium is via the common ion effect.

> *Adding a common ion to a system at equilibrium affects the equilibrium composition, but not the ionization constant.*

Example 7.2.2.1

A 0.150 M solution of formic acid at 25°C (pKa = 3.75) has a pH of 2.28 and is 3.5% ionized.

a. Is there a change to the pH of the solution if enough solid sodium formate is added to make the final formate concentration 0.100 M (assume that the formic acid concentration does not change)?
b. What percentage of the formic acid is ionized if 0.200 M HCl is added to the system?

Given: solution concentration and pH, pK_a, and percent ionization of acid; final concentration of conjugate base or strong acid added

Asked for: pH and percent ionization of formic acid

Strategy:

A. Write a balanced equilibrium equation for the ionization equilibrium of formic acid. Tabulate the initial concentrations, the changes, and the final concentrations.
B. Substitute the expressions for the final concentrations into the expression for Ka. Calculate $[H^+]$ and the pH of the solution.
C. Construct a table of concentrations for the dissociation of formic acid. To determine the percent ionization, determine the anion concentration, divide it by the initial concentration of formic acid, and multiply the result by 100.

Solution:

A Because sodium formate is a strong electrolyte, it ionizes completely in solution to give formate and sodium ions. The Na^+ ions are spectator ions, so they can be ignored in the equilibrium equation. Because water is both a much weaker acid than formic acid and a much weaker base than formate, the acid–base properties of the solution are determined solely by the formic acid ionization equilibrium:

$$HCO_2H(aq) \rightleftharpoons HCO_2^-(aq) + H^+(aq)$$

The initial concentrations, the changes in concentration that occur as equilibrium is reached, and the final concentrations can be tabulated.

Final Concentration

ICE	$[HCO_2H(aq)]$	$[H^+(aq)]$	$[HCO_2^-(aq)]$
Initial	0.150	1.00×10^{-7}	0.100
Change	−x	+x	+x
Equilibrium	(0.150 − x)	x	(0.100 + x)

B We substitute the expressions for the final concentrations into the equilibrium constant expression and make our usual simplifying assumptions, so

$$\begin{aligned} K_a = \frac{[H^+][HCO_2^-]}{[HCO_2H]} &= \frac{(x)(0.100+x)}{0.150-x} \\ &\approx \frac{x(0.100)}{0.150} \\ &\approx 10^{-3.75} \\ &\approx 1.8 \times 10^{-4} \end{aligned}$$

Rearranging and solving for x,

$$\begin{aligned} x &= (1.8 \times 10^{-4}) \times \frac{0.150\ M}{0.100\ M} \\ &= 2.7 \times 10^{-4} \\ &= [H^+] \end{aligned}$$

The value of x is small compared with 0.150 or 0.100 M, so our assumption about the extent of ionization is justified. Moreover,

$$K_aC_{HA} = (1.8 \times 10^{-4})(0.150) = 2.7 \times 10^{-5}$$

which is greater than 1.0×10^{-6}, so again, our assumption is justified. The final pH is:

$$pH = -\log(2.7 \times 10^{-4}) = 3.57$$

compared with the initial value of 2.29. Thus adding a salt containing the conjugate base of the acid has increased the pH of the solution, as we expect based on Le Chatelier's principle; the stress on the system has been relieved by the consumption of H^+ ions, driving the equilibrium to the left.

C Because HCl is a strong acid, it ionizes completely, and chloride is a spectator ion that can be neglected. Thus the only relevant acid–base equilibrium is again the dissociation of formic acid, and initially the concentration of formate is zero. We can construct a table of initial concentrations, changes in concentration, and final concentrations.

$$HCO_2H(aq) \leftrightharpoons H^+(aq) + HCO_2^-(aq)$$

initial concentrations, changes in concentration, and final concentrations

	$[HCO_2H(aq)]$	$[H^+(aq)]$	$[HCO_2^-(aq)]$
initial	0.150	0.200	0
change	−x	+x	+x
final	(0.150 − x)	(0.200 + x)	x

To calculate the percentage of formic acid that is ionized under these conditions, we have to determine the final $[HCO_2^-]$. We substitute final concentrations into the equilibrium constant expression and make the usual simplifying assumptions, so

$$K_a = \frac{[H^+][HCO_2^-]}{[HCO_2H]} = \frac{(0.200 + x)(x)}{0.150 - x} \approx \frac{x(0.200)}{0.150} = 1.80 \times 10^{-4}$$

Rearranging and solving for x,

$$x = (1.80 \times 10^{-4}) \times \frac{0.150\ M}{0.200\ M}$$
$$= 1.35 \times 10^{-4} = [HCO_2^-]$$

Once again, our simplifying assumptions are justified. The percent ionization of formic acid is as follows:

$$\text{percent ionization} = \frac{1.35 \times 10^{-4}\ M}{0.150\ M} \times 100\% = 0.0900\%$$

Adding the strong acid to the solution, as shown in the table, decreased the percent ionization of formic acid by a factor of approximately 38 (3.45%/0.0900%). Again, this is consistent with Le Chatelier's principle: adding H^+ ions drives the dissociation equilibrium to the left.

? Exercise 7.2.2.1

A 0.225 M solution of ethylamine ($CH_3CH_2NH_2$ with $pK_b = 3.19$) has a pH of 12.08 and a percent ionization of 5.4% at 20°C. Calculate the following:

a. the pH of the solution if enough solid ethylamine hydrochloride ($EtNH_3Cl$) is added to make the solution 0.100 M in $EtNH_3^+$
b. the percentage of ethylamine that is ionized if enough solid $NaOH$ is added to the original solution to give a final concentration of 0.050 M $NaOH$

Answer a

11.16

Answer b

1.3%



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The Common Ion Effect: Weak Bases Combined with Conjugate Acids

Now let's suppose we have a buffer solution that contains equimolar concentrations of a weak base (B) and its conjugate acid (BH^+). The general equation for the ionization of a weak base is as follows:

$$B(aq) + H_2O(l) \leftrightharpoons BH^+(aq) + OH^-(aq) \tag{7.2.2.3}$$

If the equilibrium constant for the reaction as written in Equation 7.2.2.3 is small, for example $K_b = 10^{-5}$, then the equilibrium constant for the reverse reaction is very large: $K = \frac{1}{K_b} = 10^5$. Adding a strong base such as OH^- to the solution therefore causes the equilibrium in Equation 7.2.2.3 to shift to the left, consuming the added OH^-. As a result, the OH^- ion concentration in solution remains relatively constant, and the pH of the solution changes very little. Le Chatelier's principle predicts the same outcome: when the system is stressed by an increase in the OH^- ion concentration, the reaction will proceed to the left to counteract the stress.

If the pK_b of the base is 5.0, the pK_a of its conjugate acid is

$$pK_a = pK_w - pK_b = 14.0–5.0 = 9.0.$$

Thus the equilibrium constant for ionization of the conjugate acid is even smaller than that for ionization of the base. The ionization reaction for the conjugate acid of a weak base is written as follows:

$$BH^+(aq) + H_2O(l) \leftrightharpoons B(aq) + H_3O^+(aq) \tag{7.2.2.4}$$

Again, the equilibrium constant for the reverse of this reaction is very large: $K = 1/K_a = 10^9$. If a strong acid is added, it is neutralized by reaction with the base as the reaction in Equation 7.2.2.4 shifts to the left. As a result, the H^+ ion concentration does not increase very much, and the pH changes only slightly. In effect, a buffer solution behaves somewhat like a sponge that can absorb H^+ and OH^- ions, thereby preventing large changes in pH when appreciable amounts of strong acid or base are added to a solution.

Buffers are characterized by the pH range over which they can maintain a more or less constant pH and by their buffer capacity, the amount of strong acid or base that can be absorbed before the pH changes significantly. Although the useful pH range of a buffer depends strongly on the chemical properties of the weak acid and weak base used to prepare the buffer (i.e., on K), its buffer capacity depends solely on the concentrations of the species in the buffered solution. The more concentrated the buffer solution, the greater its buffer capacity. As illustrated in Figure 7.2.2.1, when $NaOH$ is added to solutions that contain different concentrations of an acetic acid/sodium acetate buffer, the observed change in the pH of the buffer is inversely proportional to the concentration of the buffer. If the buffer capacity is 10 times larger, then the buffer solution can absorb 10 times more strong acid or base before undergoing a significant change in pH.

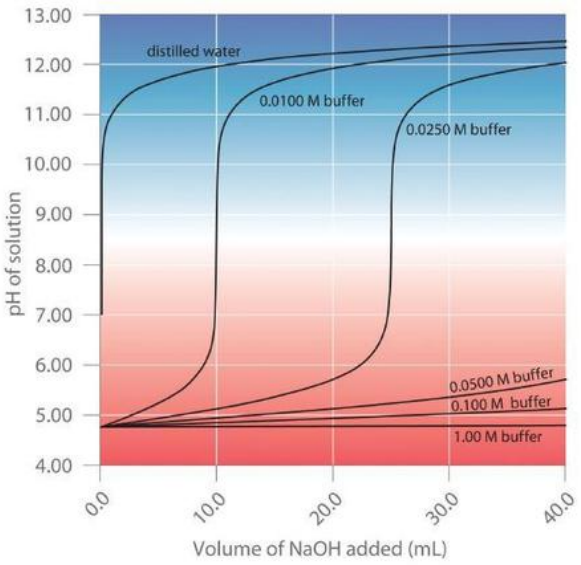


Figure **7.2.2.1**: Effect of Buffer Concentration on the Capacity of a Buffer. (CC BY-SA-NC; Anonymous by request)
Graph of pH of solution against volume of NaOH added. Six different buffer concentrations are plotted.

A buffer maintains a relatively constant pH when acid or base is added to a solution. The addition of even tiny volumes of 0.10 M $NaOH$ to 100.0 mL of distilled water results in a very large change in pH. As the concentration of a 50:50 mixture of sodium acetate/acetic acid buffer in the solution is increased from 0.010 M to 1.00 M, the change in the pH produced by the addition of the same volume of $NaOH$ solution decreases steadily. For buffer concentrations of at least 0.500 M, the addition of even 25 mL of the $NaOH$ solution results in only a relatively small change in pH.

Calculating the pH of a Buffer

The pH of a buffer can be calculated from the concentrations of the weak acid and the weak base used to prepare it, the concentration of the conjugate base and conjugate acid, and the pK_a or pK_b of the weak acid or weak base. The procedure is analogous to that used in Example **7.2.2.1** to calculate the pH of a solution containing known concentrations of formic acid and formate.

An alternative method frequently used to calculate the pH of a buffer solution is based on a rearrangement of the equilibrium equation for the dissociation of a weak acid. The simplified ionization reaction is $HA \leftrightharpoons H^+ + A^-$, for which the equilibrium constant expression is as follows:

$$K_a = \frac{[H^+][A^-]}{[HA]} \tag{7.2.2.5}$$

This equation can be rearranged as follows:

$$[H^+] = K_a \frac{[HA]}{[A^-]} \tag{7.2.2.6}$$

Taking the logarithm of both sides and multiplying both sides by −1,

$$-\log[H^+] = -\log K_a - \log\left(\frac{[HA]}{[A^-]}\right) \tag{7.2.2.7}$$

$$= -\log K_a + \log\left(\frac{[A^-]}{[HA]}\right) \tag{7.2.2.8}$$

Replacing the negative logarithms in Equation 7.2.2.8,

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) \tag{7.2.2.9}$$

or, more generally,

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right) \tag{7.2.2.10}$$

Equation 7.2.2.9 and Equation 7.2.2.10 are both forms of the Henderson-Hasselbalch approximation, named after the two early 20th-century chemists who first noticed that this rearranged version of the equilibrium constant expression provides an easy way to calculate the pH of a buffer solution. In general, the validity of the Henderson-Hasselbalch approximation may be limited to solutions whose concentrations are at least 100 times greater than their K_a values.

There are three special cases where the Henderson-Hasselbalch approximation is easily interpreted without the need for calculations:

- $[base] = [acid]$: Under these conditions,

  $$\frac{[base]}{[acid]} = 1$$

  in Equation 7.2.2.10. Because $\log 1 = 0$,

  $$pH = pK_a$$

  regardless of the actual concentrations of the acid and base. Recall that this corresponds to the midpoint in the titration of a weak acid or a weak base.
- $[base]/[acid] = 10$: In Equation 7.2.2.10, because $\log 10 = 1$,

  $$pH = pK_a + 1.$$
- $[base]/[acid] = 100$: In Equation 7.2.2.10, because $\log 100 = 2$,

  $$pH = pK_a + 2.$$

Each time we increase the [base]/[acid] ratio by 10, the pH of the solution increases by 1 pH unit. Conversely, if the [base]/[acid] ratio is 0.1, then pH = pK_a − 1. Each additional factor-of-10 decrease in the [base]/[acid] ratio causes the pH to decrease by 1 pH unit.

> If [base] = [acid] for a buffer, then pH = pK_a. Changing this ratio by a factor of 10 either way changes the pH by ±1 unit.

Example 7.2.2.2

What is the pH of a solution that contains

a. 0.135 M HCO_2H and 0.215 M HCO_2Na? (The pK_a of formic acid is 3.75.)
b. 0.0135 M HCO_2H and 0.0215 M HCO_2Na?
c. 0.119 M pyridine and 0.234 M pyridine hydrochloride? (The pK_b of pyridine is 8.77.)

Given: concentration of acid, conjugate base, and pK_a; concentration of base, conjugate acid, and pK_b

Asked for: pH

Strategy:

Substitute values into either form of the Henderson-Hasselbalch approximation (Equations 7.2.2.9 or 7.2.2.10) to calculate the pH.

Solution:

According to the Henderson-Hasselbalch approximation (Equation 7.2.2.9), the pH of a solution that contains both a weak acid and its conjugate base is

$$pH = pK_a + \log([A-]/[HA]).$$

A

Inserting the given values into the equation,

$$pH = 3.75 + \log\left(\frac{0.215}{0.135}\right)$$
$$= 3.75 + \log 1.593$$
$$= 3.95$$

This result makes sense because the $[A^-]/[HA]$ ratio is between 1 and 10, so the pH of the buffer must be between the pK_a (3.75) and $pK_a + 1$, or 4.75.

B

This is identical to part (a), except for the concentrations of the acid and the conjugate base, which are 10 times lower. Inserting the concentrations into the Henderson-Hasselbalch approximation,

$$pH = 3.75 + \log\left(\frac{0.0215}{0.0135}\right)$$
$$= 3.75 + \log 1.593$$
$$= 3.95$$

This result is identical to the result in part (a), which emphasizes the point that the pH of a buffer depends only on the ratio of the concentrations of the conjugate base and the acid, not on the magnitude of the concentrations. Because the $[A^-]/[HA]$ ratio is the same as in part (a), the pH of the buffer must also be the same (3.95).

C

In this case, we have a weak base, pyridine (Py), and its conjugate acid, the pyridinium ion (HPy^+). We will therefore use Equation 7.2.2.10, the more general form of the Henderson-Hasselbalch approximation, in which "base" and "acid" refer to the appropriate species of the conjugate acid–base pair. We are given [base] = [Py] = 0.119 M and $[acid] = [HPy^+] = 0.234\,M$. We also are given $pK_b = 8.77$ for pyridine, but we need pK_a for the pyridinium ion. Recall from Equation 16.23 that the pK_b of a weak base and the pK_a of its conjugate acid are related:

$$pK_a + pK_b = pK_w.$$

Thus pK_a for the pyridinium ion is $pK_w - pK_b = 14.00 - 8.77 = 5.23$. Substituting this pK_a value into the Henderson-Hasselbalch approximation,

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right)$$
$$= 5.23 + \log\left(\frac{0.119}{0.234}\right)$$
$$= 5.23 - 0.294$$
$$= 4.94$$

Once again, this result makes sense: the $[B]/[BH^+]$ ratio is about 1/2, which is between 1 and 0.1, so the final pH must be between the pK_a (5.23) and $pK_a - 1$, or 4.23.

? Exercise 7.2.2.2

What is the pH of a solution that contains

a. 0.333 M benzoic acid and 0.252 M sodium benzoate?
b. 0.050 M trimethylamine and 0.066 M trimethylamine hydrochloride?

The pK_a of benzoic acid is 4.20, and the pK_b of trimethylamine is also 4.20.

Answer a

4.08

Answer b

9.68



A Video Discussing Using the Henderson Hasselbalch Equation: Using the Henderson Hasselbalch Equation(opens in new window) [youtu.be] (opens in new window)

The Henderson-Hasselbalch approximation ((Equation 7.2.2.9) can also be used to calculate the pH of a buffer solution after adding a given amount of strong acid or strong base, as demonstrated in Example 7.2.2.3.

Example 7.2.2.3

The buffer solution in Example 7.2.2.2 contained 0.135 M $\mathbf{HCO_2H}$ and 0.215 M $\mathbf{HCO_2Na}$ and had a pH of 3.95.

a. What is the final pH if 5.00 mL of 1.00 M $\boldsymbol{HCl}$ are added to 100 mL of this solution?
b. What is the final pH if 5.00 mL of 1.00 M $\boldsymbol{NaOH}$ are added?

Given: composition and pH of buffer; concentration and volume of added acid or base

Asked for: final pH

Strategy:

A. Calculate the amounts of formic acid and formate present in the buffer solution using the procedure from Example 7.2.2.1. Then calculate the amount of acid or base added.
B. Construct a table showing the amounts of all species after the neutralization reaction. Use the final volume of the solution to calculate the concentrations of all species. Finally, substitute the appropriate values into the Henderson-Hasselbalch approximation (Equation 7.2.2.10) to obtain the pH.

Solution:

The added $\mathbf{HCl}$ (a strong acid) or $\mathbf{NaOH}$ (a strong base) will react completely with formate (a weak base) or formic acid (a weak acid), respectively, to give formic acid or formate and water. We must therefore calculate the amounts of formic acid and formate present after the neutralization reaction.

A We begin by calculating the millimoles of formic acid and formate present in 100 mL of the initial pH 3.95 buffer:

$$100\ \cancel{mL}\left(\frac{0.135\ mmol\ \mathrm{HCO_2H}}{\cancel{mL}}\right) = 13.5\ mmol\ \mathrm{HCO_2H}$$

$$100\ \cancel{mL}\left(\frac{0.215\ mmol\ \mathrm{HCO_2^-}}{\cancel{mL}}\right) = 21.5\ mmol\ \mathrm{HCO_2^-}$$

The millimoles of $\mathbf{H^+}$ in 5.00 mL of 1.00 M $\mathbf{HCl}$ is as follows:

$$5.00\ \cancel{mL}\left(\frac{1.00\ mmol\ \mathrm{H^+}}{\cancel{mL}}\right) = 5\ mmol\ \mathrm{H^+}$$

B Next, we construct a table of initial amounts, changes in amounts, and final amounts:

$$\mathrm{HCO^{2-}(aq) + H^+(aq) \rightleftharpoons HCO_2H(aq)}$$

initial amounts, changes in amounts, and final amounts:

	$HCO^{2-}(aq)$	$H^+(aq)$	$HCO_2H(aq)$
Initial	21.5 mmol	5.00 mmol	13.5 mmol
Change	−5.00 mmol	−5.00 mmol	+5.00 mmol
Final	16.5 mmol	~0 mmol	18.5 mmol

The final amount of H^+ in solution is given as "~0 mmol." For the purposes of the stoichiometry calculation, this is essentially true, but remember that the point of the problem is to calculate the final $[H^+]$ and thus the pH. We now have all the information we need to calculate the pH. We can use either the lengthy procedure of Example 7.2.2.1 or the Henderson–Hasselbach approximation. Because we have performed many equilibrium calculations in this chapter, we'll take the latter approach. The Henderson-Hasselbalch approximation requires the concentrations of HCO_2^- and HCO_2H, which can be calculated using the number of millimoles (n) of each and the total volume (VT). Substituting these values into the Henderson-Hasselbalch approximation (Equation 7.2.2.10):

$$\begin{aligned} pH &= pK_a + \log\left(\frac{[HCO_2^-]}{[HCO_2H]}\right) \\ &= pK_a + \log\left(\frac{n_{HCO_2^-}/V_f}{n_{HCO_2H}/V_f}\right) \\ &= pK_a + \log\left(\frac{n_{HCO_2^-}}{n_{HCO_2H}}\right) \end{aligned}$$

Because the total volume appears in both the numerator and denominator, it cancels. We therefore need to use only the ratio of the number of millimoles of the conjugate base to the number of millimoles of the weak acid. So

$$\begin{aligned} pH &= pK_a + \log\left(\frac{n_{HCO_2^-}}{n_{HCO_2H}}\right) \\ &= 3.75 + \log\left(\frac{16.5\ mmol}{18.5\ mmol}\right) \\ &= 3.75\ -0.050 = 3.70 \end{aligned}$$

Once again, this result makes sense on two levels. First, the addition of HClhas decreased the pH from 3.95, as expected. Second, the ratio of HCO_2^- to HCO_2H is slightly less than 1, so the pH should be between the pK_a and pK_a − 1.

A The procedure for solving this part of the problem is exactly the same as that used in part (a). We have already calculated the numbers of millimoles of formic acid and formate in 100 mL of the initial pH 3.95 buffer: 13.5 mmol of HCO_2H and 21.5 mmol of HCO_2^-. The number of millimoles of OH^- in 5.00 mL of 1.00 M $NaOH$ is as follows:

B With this information, we can construct a table of initial amounts, changes in amounts, and final amounts.

$$\mathrm{HCO_2H(aq) + OH^-(aq) \rightleftharpoons HCO_2^-(aq) + H_2O(l)}$$

initial amounts, changes in amounts, and final amounts

	$HCO_2H(aq)$	OH^-	$HCO_2^-(aq)$
Initial	13.5 mmol	5.00 mmol	21.5 mmol
Change	−5.00 mmol	−5.00 mmol	+5.00 mmol
Final	8.5 mmol	~0 mmol	26.5 mmol

The final amount of OH^- in solution is not actually zero; this is only approximately true based on the stoichiometric calculation. We can calculate the final pH by inserting the numbers of millimoles of both HCO_2^- and HCO_2H into the simplified Henderson-Hasselbalch expression used in part (a) because the volume cancels:

$$\begin{aligned} pH &= pK_a + \log\left(\frac{n_{HCO_2^-}}{n_{HCO_2H}}\right) \\ &= 3.75 + \log\left(\frac{26.5\ mmol}{8.5\ mmol}\right) \\ &= 3.75 + 0.494 = 4.24 \end{aligned}$$

Once again, this result makes chemical sense: the pH has increased, as would be expected after adding a strong base, and the final pH is between the pK_a and pK_a + 1, as expected for a solution with a HCO_2^-/HCO_2H ratio between 1 and 10.

? Exercise 7.2.2.3

The buffer solution from Example **7.2.2.2** contained 0.119 M pyridine and 0.234 M pyridine hydrochloride and had a pH of 4.94.

a. What is the final pH if 12.0 mL of 1.5 M **NaOH** are added to 250 mL of this solution?
b. What is the final pH if 12.0 mL of 1.5 M **HCl** are added?

Answer a

5.30

Answer b

4.42

Only the amounts (in moles or millimoles) of the acidic and basic components of the buffer are needed to use the Henderson-Hasselbalch approximation, not their concentrations.



A Video Discussing the Change in pH with the Addition of a Strong Acid to a Buffer: The Change in pH with the Addition of a Strong Acid to a Buffer(opens in new window) [youtu.be]



The Change in pH with the Addition of a Strong Base to a Buffer:

The Change in pH with the Addition of a Strong Base to a Buffer (opens in new window) [youtu.be]

The results obtained in Example **7.2.2.3** and its corresponding exercise demonstrate how little the pH of a well-chosen buffer solution changes despite the addition of a significant quantity of strong acid or strong base. Suppose we had added the same amount of HCl or $NaOH$ solution to 100 mL of an unbuffered solution at pH 3.95 (corresponding to 1.1×10^{-4} M HCl). In this case, adding 5.00 mL of 1.00 M HCl would lower the final pH to 1.32 instead of 3.70, whereas adding 5.00 mL of 1.00 M $NaOH$ would raise the final pH to 12.68 rather than 4.24. (Try verifying these values by doing the calculations yourself.) Thus the presence of a buffer significantly increases the ability of a solution to maintain an almost constant pH.

> *The most effective buffers contain **equal** concentrations of an acid and its conjugate base.*

A buffer that contains approximately equal amounts of a weak acid and its conjugate base in solution is equally effective at neutralizing either added base or added acid. This is shown in Figure **7.2.2.2** for an acetic acid/sodium acetate buffer. Adding a given amount of strong acid shifts the system along the horizontal axis to the left, whereas adding the same amount of strong base shifts the system the same distance to the right. In either case, the change in the ratio of $CH_3CO_2^-$ to CH_3CO_2H from 1:1 reduces the buffer capacity of the solution.

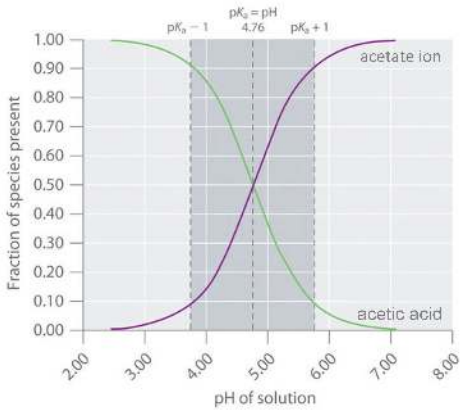


Figure **7.2.2.2**: Distribution Curve Showing the Fraction of Acetic Acid Molecules and Acetate Ions as a Function of pH in a Solution of Acetic Acid. The pH range over which the acetic acid/sodium acetate system is an effective buffer (the darker shaded region) corresponds to the region in which appreciable concentrations of both species are present (pH 3.76–5.76, corresponding to $pH = pK_a \pm 1$). (CC BY-SA-NC; Anonymous by request)

Graph of mole fraction against pH of solution. The green line is acetic acid and the purple line is the acetate ion.



A Video Discussing The Buffer Region: The Buffer Region (opens in new window) [youtu.be]

The Relationship between Titrations and Buffers

There is a strong correlation between the effectiveness of a buffer solution and the titration curves discussed in Section 16.5. Consider the schematic titration curve of a weak acid with a strong base shown in Figure **7.2.2.3**. As indicated by the labels, the region around pK_a corresponds to the midpoint of the titration, when approximately half the weak acid has been neutralized. This portion of the titration curve corresponds to a buffer: it exhibits the smallest change in pH per increment of added strong base, as shown by the nearly horizontal nature of the curve in this region. The nearly flat portion of the curve extends only from approximately a pH value of 1 unit less than the pK_a to approximately a pH value of 1 unit greater than the pK_a, which is why buffer solutions usually have a pH that is within ±1 pH units of the pK_a of the acid component of the buffer.

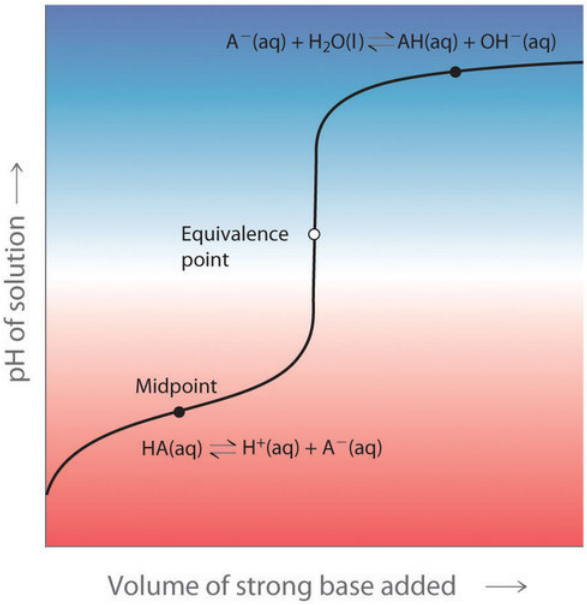


Figure **7.2.2.3**: The Relationship between Titration Curves and Buffers. (CC BY-SA-NC; Anonymous by request)

Titration curves graph pH of solution against volume of strong base added. On the curve we look for the midpoints and equivalence points.

This schematic plot of pH for the titration of a weak acid with a strong base shows the nearly flat region of the titration curve around the midpoint, which corresponds to the formation of a buffer. At the lower left, the pH of the solution is determined by the equilibrium for dissociation of the weak acid; at the upper right, the pH is determined by the equilibrium for reaction of the conjugate base with water.

In the region of the titration curve at the lower left, before the midpoint, the acid–base properties of the solution are dominated by the equilibrium for dissociation of the weak acid, corresponding to K_a. In the region of the titration curve at the upper right, after

the midpoint, the acid–base properties of the solution are dominated by the equilibrium for reaction of the conjugate base of the weak acid with water, corresponding to K_b. However, we can calculate either K_a or K_b from the other because they are related by K_w.

Blood: A Most Important Buffer

Metabolic processes produce large amounts of acids and bases, yet organisms are able to maintain an almost constant internal pH because their fluids contain buffers. This is not to say that the pH is uniform throughout all cells and tissues of a mammal. The internal pH of a red blood cell is about 7.2, but the pH of most other kinds of cells is lower, around 7.0. Even within a single cell, different compartments can have very different pH values. For example, one intracellular compartment in white blood cells has a pH of around 5.0.

Because no single buffer system can effectively maintain a constant pH value over the entire physiological range of approximately pH 5.0 to 7.4, biochemical systems use a set of buffers with overlapping ranges. The most important of these is the CO_2/HCO_3^- system, which dominates the buffering action of blood plasma.

The acid–base equilibrium in the CO_2/HCO_3^- buffer system is usually written as follows:

$$H_2CO_3\,(aq) \rightleftharpoons H^+\,(aq) + HCO_3^-\,(aq) \tag{7.2.2.11}$$

with $K_a = 4.5 \times 10^{-7}$ and $pK_a = 6.35$ at 25°C. In fact, Equation 7.2.2.11 is a grossly oversimplified version of the CO_2/HCO_3^- system because a solution of CO_2 in water contains only rather small amounts of H_2CO_3. Thus Equation 7.2.2.11 does not allow us to understand how blood is actually buffered, particularly at a physiological temperature of 37°C.

As shown in Equation 7.2.2.12, CO_2 is in equilibrium with H_2CO_3, but the equilibrium lies far to the left, with an H_2CO_3/CO_2 ratio less than 0.01 under most conditions:

$$CO_2\,(aq) + H_2O\,(l) \rightleftharpoons H_2CO_3\,(aq) \tag{7.2.2.12}$$

with $K' = 4.0 \times 10^{-3}$ at 37°C. The true pK_a of carbonic acid at 37°C is therefore 3.70, not 6.35, corresponding to a K_a of 2.0×10^{-4}, which makes it a much stronger acid than Equation 7.2.2.11 suggests. Adding Equation 7.2.2.11 and Equation 7.2.2.12 and canceling H_2CO_3 from both sides give the following overall equation for the reaction of CO_2 with water to give a proton and the bicarbonate ion:

$$CO_2\,(aq) + H_2O\,(l) \rightleftharpoons H_2CO_3\,(aq) \tag{7.2.2.13}$$

with $K' = 4.0 \times 10^{-3} (37°C)$

$$H_2CO_3\,(aq) \rightleftharpoons H^+\,(aq) + HCO_3^-\,(aq) \tag{7.2.2.14}$$

with $K_a = 2.0 \times 10^{-4} (37°C)$

$$CO_2\,(aq) + H_2O\,(l) \rightleftharpoons H^+\,(aq) + HCO_3^-\,(aq) \tag{7.2.2.15}$$

with $K = 8.0 \times 10^{-7} (37°C)$

The K value for the reaction in Equation 7.2.2.15 is the product of the true ionization constant for carbonic acid (K_a) and the equilibrium constant (K) for the reaction of $CO_2\,(aq)$ with water to give carbonic acid. The equilibrium equation for the reaction of CO_2 with water to give bicarbonate and a proton is therefore

$$K = \frac{[H^+][HCO_3^-]}{[CO_2]} = 8.0 \times 10^{-7} \tag{7.2.2.16}$$

The presence of a gas in the equilibrium constant expression for a buffer is unusual. According to Henry's law,

$$[CO_2] = kP_{CO_2}$$

where k is the Henry's law constant for CO_2, which is $3.0 \times 10^{-5}\ M/mmHg$ at 37°C. Substituting this expression for $[CO_2]$ in Equation 7.2.2.16,

$$K = \frac{[H^+][HCO_3^-]}{(3.0 \times 10^{-5}\ M/mmHg)(P_{CO_2})}$$

where P_{CO_2} is in mmHg. Taking the negative logarithm of both sides and rearranging,

$$pH = 6.10 + \log\left(\frac{[HCO_3^-]}{(3.0 \times 10^{-5} M/mm\ Hg)\ (P_{CO_2})}\right) \tag{7.2.2.17}$$

Thus the pH of the solution depends on both the CO_2 pressure over the solution and $[HCO_3^-]$. Figure 7.2.2.4 plots the relationship between pH and $[HCO_3^-]$ under physiological conditions for several different values of P_{CO_2}, with normal pH and $[HCO_3^-]$ values indicated by the dashed lines.

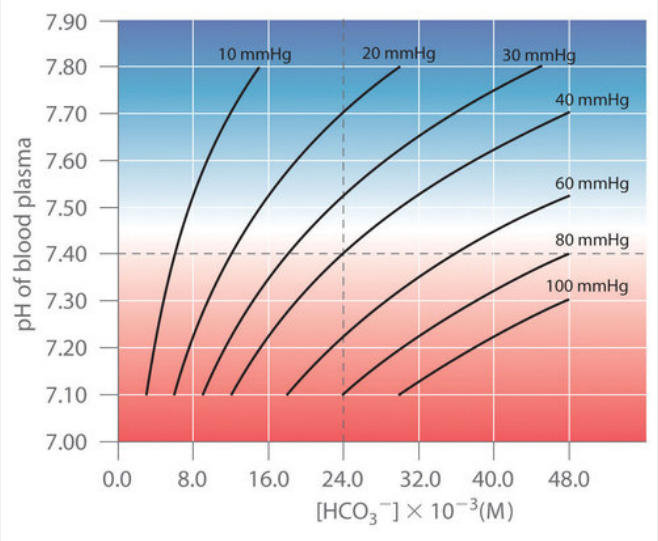


Figure 7.2.2.4: Buffering in Blood: pH versus $[HCO_3^-]$ Curves for Buffers with Different Values of P_{CO_2}. Only those combinations of pH and $[HCO_3^-]$ that lie on a given line are allowed for the particular value of P_{CO_2} indicated. Normal values of blood plasma pH and $[HCO_3^-]$ are indicated by dashed lines. (CC BY-SA-NC; Anonymous by request)

According to Equation 7.2.2.17, adding a strong acid to the CO_2/HCO_3^- system causes $[HCO_3^-]$ to decrease as HCO_3^- is converted to CO_2. Excess CO_2 is released in the lungs and exhaled into the atmosphere, however, so there is essentially no change in P_{CO_2}. Because the change in $[HCO_3^-]/P_{CO_2}$ is small, Equation 7.2.2.17 predicts that the change in pH will also be rather small. Conversely, if a strong base is added, the OH^- reacts with CO_2 to form HCO_3^-, but CO_2 is replenished by the body, again limiting the change in both $[HCO_3^-]/P_{CO_2}$ and pH. The CO_2/HCO_3^- buffer system is an example of an open system, in which the total concentration of the components of the buffer change to keep the pH at a nearly constant value.

If a passenger steps out of an airplane in Denver, Colorado, for example, the lower P_{CO_2} at higher elevations (typically 31 mmHg at an elevation of 2000 m versus 40 mmHg at sea level) causes a shift to a new pH and $[HCO_3^-]$. The increase in pH and decrease in $[HCO_3^-]$ in response to the decrease in P_{CO_2} are responsible for the general malaise that many people experience at high altitudes. If their blood pH does not adjust rapidly, the condition can develop into the life-threatening phenomenon known as altitude sickness.



A Video Summary of the pH Curve for a Strong Acid/Strong Base Titration:

Summary of the pH Curve for a Strong Acid/Strong Base Titration(opens in new window) [youtu.be]

Summary

Buffers are solutions that resist a change in pH after adding an acid or a base. Buffers contain a weak acid (HA) and its conjugate weak base (A^-). Adding a strong electrolyte that contains one ion in common with a reaction system that is at equilibrium shifts the equilibrium in such a way as to reduce the concentration of the common ion. The shift in equilibrium is called the common ion effect. Buffers are characterized by their pH range and buffer capacity. The useful pH range of a buffer depends strongly on the chemical properties of the conjugate weak acid–base pair used to prepare the buffer (the K_a or K_b), whereas its buffer capacity depends solely on the concentrations of the species in the solution. The pH of a buffer can be calculated using the Henderson-Hasselbalch approximation, which is valid for solutions whose concentrations are at least 100 times greater than their K_a values. Because no single buffer system can effectively maintain a constant pH value over the physiological range of approximately 5 to 7.4, biochemical systems use a set of buffers with overlapping ranges. The most important of these is the CO_2/HCO_3^- system, which dominates the buffering action of blood plasma.

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7.2.3: Acid–Base Indicators

Learning Objectives

- Explain the function and color changes of acid-base indicators
- Demonstrate how to select the proper indicator for a titration experiment
- Determine the acidic dissociation constants K_a or K_{ai} of indicators.

Certain organic substances change color in dilute solution when the hydronium ion concentration reaches a particular value. For example, phenolphthalein is a colorless substance in any aqueous solution with a hydronium ion concentration greater than 5.0×10^{-9} *M* (pH < 8.3). In more basic solutions where the hydronium ion concentration is less than 5.0×10^{-9} *M* (pH > 8.3), it is red or pink. Substances such as phenolphthalein, which can be used to determine the pH of a solution, are called acid-base indicators. Acid-base indicators are either weak organic acids or weak organic bases.

The equilibrium in a solution of the acid-base indicator methyl orange, a weak acid, can be represented by an equation in which we use HIn as a simple representation for the complex methyl orange molecule:

$$\underbrace{\mathrm{HIn}_{(aq)}}_{\text{red}} + \mathrm{H_2O}_{(l)} \rightleftharpoons \mathrm{H_3O^+}_{(aq)} + \underbrace{\mathrm{In^-}_{(aq)}}_{\text{yellow}} \tag{7.2.3.1}$$

$$K_a = \frac{[H3O+][In-]}{[HIn]} = 4.0 \times 10^{-4} \tag{7.2.3.2}$$

The anion of methyl orange, In^-, is yellow, and the nonionized form, HIn, is red. When we add acid to a solution of methyl orange, the increased hydronium ion concentration shifts the equilibrium toward the nonionized red form, in accordance with Le Chatelier's principle. If we add base, we shift the equilibrium towards the yellow form. This behavior is completely analogous to the action of buffers.

An indicator's color is the visible result of the ratio of the concentrations of the two species In^- and HIn. If most of the indicator (typically about 60−90% or more) is present as In^-, then we see the color of the In^- ion, which would be yellow for methyl orange. If most is present as HIn, then we see the color of the HIn molecule: red for methyl orange. For methyl orange, we can rearrange the equation for K_a and write:

$$\frac{[\mathrm{In^-}]}{[\mathrm{HIn}]} = \frac{[\text{substance with yellow color}]}{[\text{substance with red color}]} = \frac{K_a}{[\mathrm{H_3O^+}]} \tag{7.2.3.3}$$

This shows us how the ratio of $\frac{[In-]}{[HIn]}$ varies with the concentration of hydronium ion. The above expression describing the indicator equilibrium can be rearranged:

$$\frac{[\mathrm{H_3O^+}]}{K_a} = \frac{[\mathrm{HIn}]}{[\mathrm{In^-}]} \tag{7.2.3.4}$$

$$\log\left(\frac{[\mathrm{H_3O^+}]}{K_a}\right) = \log\left(\frac{[\mathrm{HIn}]}{[\mathrm{In^-}]}\right) \tag{7.2.3.5}$$

$$\log([\mathrm{H_3O^+}]) - \log(K_a) = -\log\left(\frac{[\mathrm{In^-}]}{[\mathrm{HIn}]}\right) \tag{7.2.3.6}$$

$$-\mathrm{pH} + \mathrm{p}K_a = -\log\left(\frac{[\mathrm{In^-}]}{[\mathrm{HIn}]}\right) \tag{7.2.3.7}$$

$$\mathrm{pH} = \mathrm{p}K_a + \log\left(\frac{[\mathrm{In^-}]}{[\mathrm{HIn}]}\right) \text{ or } \mathrm{pH} = \mathrm{p}K_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right) \tag{7.2.3.8}$$

The last formula is the same as the Henderson-Hasselbalch equation, which can be used to describe the equilibrium of indicators.

When $[H_3O^+]$ has the same numerical value as K_a, the ratio of $[In^-]$ to [HIn] is equal to 1, meaning that 50% of the indicator is present in the red form (HIn) and 50% is in the yellow ionic form (In^-), and the solution appears orange in color. When the

hydronium ion concentration increases to 8×10^{-4} *M* (a pH of 3.1), the solution turns red. No change in color is visible for any further increase in the hydronium ion concentration (decrease in pH). At a hydronium ion concentration of 4×10^{-5} *M* (a pH of 4.4), most of the indicator is in the yellow ionic form, and a further decrease in the hydronium ion concentration (increase in pH) does not produce a visible color change. The pH range between 3.1 (red) and 4.4 (yellow) is the color-change interval of methyl orange; the pronounced color change takes place between these pH values.

Many different substances can be used as indicators, depending on the particular reaction to be monitored. For example, red cabbage juice contains a mixture of colored substances that change from deep red at low pH to light blue at intermediate pH to yellow at high pH (Figure **7.2.3.1**). In all cases, though, a good indicator must have the following properties:

- The color change must be easily detected.
- The color change must be rapid.
- The indicator molecule must not react with the substance being titrated.
- To minimize errors, the indicator should have a pKin that is within one pH unit of the expected pH at the equivalence point of the titration.



Figure **7.2.3.1**: Naturally Occurring pH Indicators in Red Cabbage Juice. Image curtesty of Wikipedia.

Red cabbage juice contains a mixture of substances whose color depends on the pH. Each test tube contains a solution of red cabbage juice in water, but the pH of the solutions varies from pH = 2.0 (far left) to pH = 11.0 (far right). At pH = 7.0, the solution is blue.

Synthetic indicators have been developed that meet these criteria and cover virtually the entire pH range. Figure **7.2.3.2** shows the approximate pH range over which some common indicators change color and their change in color. In addition, some indicators (such as thymol blue) are polyprotic acids or bases, which change color twice at widely separated pH values.

Indicator	pK_{in}	Color change
Alizarin yellow R	11.0	yellow to red
Thymolphthalein	9.9	colorless to blue
Phenolphthalein	9.5	colorless to pink
Thymol blue	9.2	yellow to blue
Phenol red	7.4	yellow to red
Bromothymol blue	7.3	yellow to blue
Bromocresol purple	6.4	yellow to purple
Ethyl red	5.4	colorless to red
Resorcin blue	5.3	red to blue
Resazurin	5.1	orange to violet
Methyl red	5.0	red to yellow
Bromophenol blue	4.1	yellow to blue
Thymol blue	1.7	red to yellow
Malachite green	1.3	yellow to turquoise
Methyl violet	0.8	yellow to blue

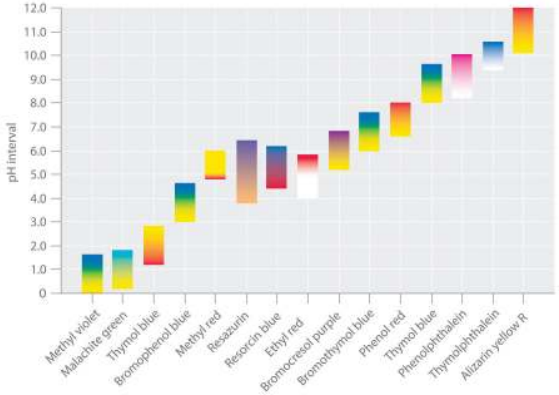


Figure **7.2.3.2**: Some Common Acid–Base Indicators. Approximate colors are shown, along with pKin values and the pH range over which the color changes.

It is important to be aware that an indicator does not change color abruptly at a particular pH value; instead, it actually undergoes a pH titration just like any other acid or base. As the concentration of HIn decreases and the concentration of In^- increases, the color of the solution slowly changes from the characteristic color of HIn to that of In^-. As we will see in Section 16, the $[In^-]/[HIn]$ ratio

changes from 0.1 at a pH one unit below pKin to 10 at a pH one unit above pKin. Thus most indicators change color over a pH range of about two pH units.

We have stated that a good indicator should have a pKin value that is close to the expected pH at the equivalence point. For a strong acid–strong base titration, the choice of the indicator is not especially critical due to the very large change in pH that occurs around the equivalence point. In contrast, using the wrong indicator for a titration of a weak acid or a weak base can result in relatively large errors, as illustrated in Figure **7.2.3.3**. This figure shows plots of pH versus volume of base added for the titration of 50.0 mL of a 0.100 M solution of a strong acid (HCl) and a weak acid (acetic acid) with 0.100 M ***NaOH***. The pH ranges over which two common indicators (methyl red, $pK_{in} = 5.0$, and phenolphthalein, $pK_{in} = 9.5$) change color are also shown. The horizontal bars indicate the pH ranges over which both indicators change color cross the HCl titration curve, where it is almost vertical. Hence both indicators change color when essentially the same volume of ***NaOH*** has been added (about 50 mL), which corresponds to the equivalence point. In contrast, the titration of acetic acid will give very different results depending on whether methyl red or phenolphthalein is used as the indicator. Although the pH range over which phenolphthalein changes color is slightly greater than the pH at the equivalence point of the strong acid titration, the error will be negligible due to the slope of this portion of the titration curve. Just as with the HCl titration, the phenolphthalein indicator will turn pink when about 50 mL of ***NaOH*** has been added to the acetic acid solution. In contrast, methyl red begins to change from red to yellow around pH 5, which is near the midpoint of the acetic acid titration, not the equivalence point. Adding only about 25–30 mL of ***NaOH*** will therefore cause the methyl red indicator to change color, resulting in a huge error.

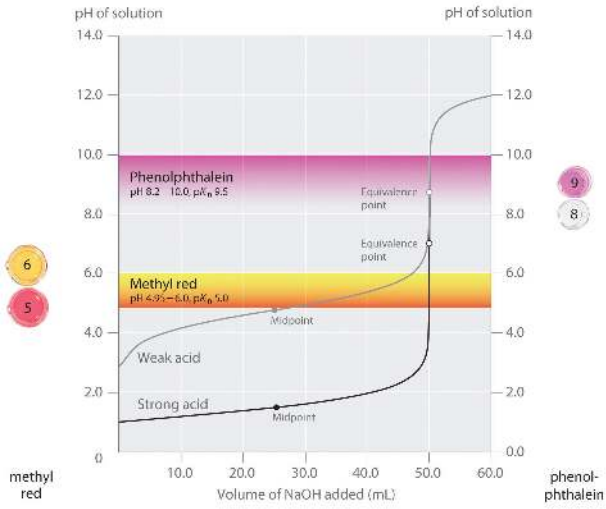


Figure **7.2.3.3**: Choosing the Correct Indicator for an Acid–Base Titration

The graph shows the results obtained using two indicators (methyl red and phenolphthalein) for the titration of 0.100 M solutions of a strong acid (HCl) and a weak acid (acetic acid) with 0.100 M ***NaOH***. Due to the steepness of the titration curve of a strong acid around the equivalence point, either indicator will rapidly change color at the equivalence point for the titration of the strong acid. In contrast, the pKin for methyl red (5.0) is very close to the pKa of acetic acid (4.76); the midpoint of the color change for methyl red occurs near the midpoint of the titration, rather than at the equivalence point.

In general, for titrations of strong acids with strong bases (and vice versa), any indicator with a pK in between about 4.0 and 10.0 will do. For the titration of a weak acid, however, the pH at the equivalence point is greater than 7.0, so an indicator such as phenolphthalein or thymol blue, with pKin > 7.0, should be used. Conversely, for the titration of a weak base, where the pH at the equivalence point is less than 7.0, an indicator such as methyl red or bromocresol blue, with pKin < 7.0, should be used.

✔ Example **7.2.3.1**

In the titration of a weak acid with a strong base, which indicator would be the best choice?

a. Methyl Orange
b. Bromocresol Green
c. Phenolphtalein

Solution

The correct answer is C. In the titration of a weak acid with a strong base, the conjugate base of the weak acid will make the pH at the equivalence point greater than 7. Therefore, you would want an indicator to change in that pH range. Both methyl orange and bromocresol green change color in an acidic pH range, while phenolphtalein changes in a basic pH.

The existence of many different indicators with different colors and pKin values also provides a convenient way to estimate the pH of a solution without using an expensive electronic pH meter and a fragile pH electrode. Paper or plastic strips impregnated with combinations of indicators are used as “pH paper,” which allows you to estimate the pH of a solution by simply dipping a piece of pH paper into it and comparing the resulting color with the standards printed on the container (Figure **7.2.3.4**).



Figure **7.2.3.4**: pH Paper. pH paper contains a set of indicators that change color at different pH values. The approximate pH of a solution can be determined by simply dipping a paper strip into the solution and comparing the color to the standards provided.



pH Indicators: https://youtu.be/1IqzUa5lABs

Summary

Acid–base indicators are compounds that change color at a particular pH. They are typically weak acids or bases whose changes in color correspond to deprotonation or protonation of the indicator itself.

Contributors and Attributions

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7.2.4: Neutralization Reactions and Titration Curves

Learning Objectives

- To calculate the pH at any point in an acid–base titration.

In an acid–base titration, a buret is used to deliver measured volumes of an acid or a base solution of known concentration (the titrant) to a flask that contains a solution of a base or an acid, respectively, of unknown concentration (the unknown). If the concentration of the titrant is known, then the concentration of the unknown can be determined. The following discussion focuses on the pH changes that occur during an acid–base titration. Plotting the pH of the solution in the flask against the amount of acid or base added produces a titration curve. The shape of the curve provides important information about what is occurring in solution during the titration.

Titrations of Strong Acids and Bases

Figure **7.2.4.1***a* shows a plot of the pH as 0.20 M **HCl** is gradually added to 50.00 mL of pure water. The pH of the sample in the flask is initially 7.00 (as expected for pure water), but it drops very rapidly as **HCl** is added. Eventually the pH becomes constant at 0.70—a point well beyond its value of 1.00 with the addition of 50.0 mL of **HCl** (0.70 is the pH of 0.20 M HCl). In contrast, when 0.20 M **NaOH** is added to 50.00 mL of distilled water, the pH (initially 7.00) climbs very rapidly at first but then more gradually, eventually approaching a limit of 13.30 (the pH of 0.20 M NaOH), again well beyond its value of 13.00 with the addition of 50.0 mL of **NaOH** as shown in Figure **7.2.4.1***b*. As you can see from these plots, the titration curve for adding a base is the mirror image of the curve for adding an acid.

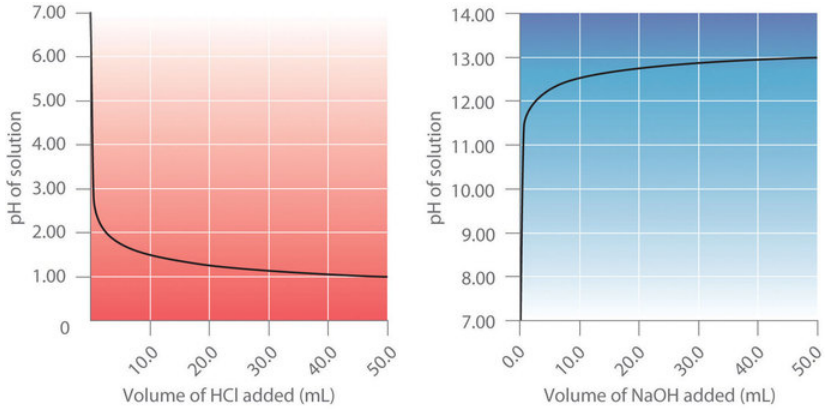


Figure **7.2.4.1**: Solution pH as a Function of the Volume of a Strong Acid or a Strong Base Added to Distilled Water. (a) When 0.20 M **HCl** is added to 50.0 mL of distilled water, the pH rapidly decreases until it reaches a minimum at the pH of 0.20 M **HCl**. (b) Conversely, when 0.20 M **NaOH** is added to 50.0 mL of distilled water, the pH rapidly increases until it reaches a maximum at the pH of 0.20 M ***NaOH***. (CC BY-SA-NC; Anonymous by request)

The graphs of water with strong acid added and water with strong base added are inverses of each other.

Suppose that we now add 0.20 M **NaOH** to 50.0 mL of a 0.10 M solution of **HCl**. Because **HCl** is a strong acid that is completely ionized in water, the initial [H^+] is 0.10 M, and the initial pH is 1.00. Adding **NaOH** decreases the concentration of H+ because of the neutralization reaction (Figure **7.2.4.2***a*):

$$OH^- + H^+ \rightleftharpoons H_2O.$$

Thus the pH of the solution increases gradually. Near the equivalence point, however, the point at which the number of moles of base (or acid) added equals the number of moles of acid (or base) originally present in the solution, the pH increases much more rapidly because most of the H^+ ions originally present have been consumed. For the titration of a monoprotic strong acid (**HCl**) with a monobasic strong base (**NaOH**), we can calculate the volume of base needed to reach the equivalence point from the following relationship:

$$\begin{aligned} moles\ of\ base &= (volume)_b(molarity)_b V_b M_b = moles\ of\ acid \\ &= (volume)_a(molarity)_a = V_a M_a \end{aligned} \tag{7.2.4.1}$$

If 0.20 M **NaOH** is added to 50.0 mL of a 0.10 M solution of **HCl**, we solve for V_b:

$$V_b(0.20 Me) = 0.025 L = 25 mL$$

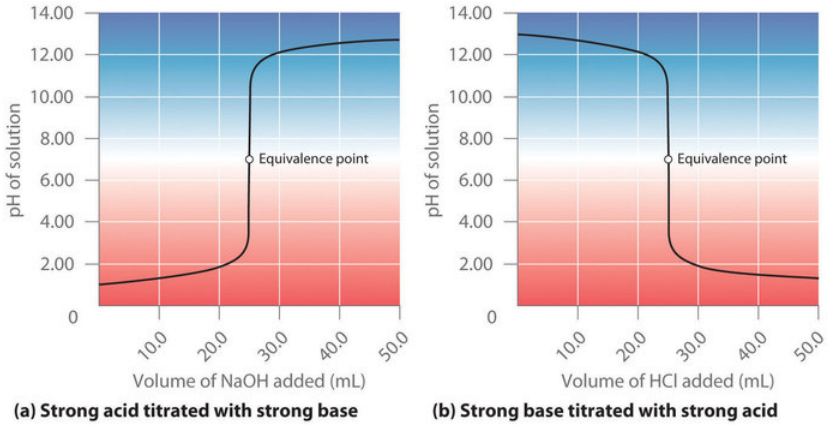


Figure **7.2.4.2**: The Titration of (a) a Strong Acid with a Strong Base and (b) a Strong Base with a Strong Acid(a) As 0.20 M **NaOH** is slowly added to 50.0 mL of 0.10 M HCl, the pH increases slowly at first, then increases very rapidly as the equivalence point is approached, and finally increases slowly once more. (b) Conversely, as 0.20 M **HCl** is slowly added to 50.0 mL of 0.10 M ***NaOH***, the pH decreases slowly at first, then decreases very rapidly as the equivalence point is approached, and finally decreases slowly once more. (CC BY-SA-NC; Anonymous by request)

The titration curves of strong acid titrated with strong base and strong base titrated with strong acid are inverses of each other.

At the equivalence point (when 25.0 mL of **NaOH** solution has been added), the neutralization is complete: only a salt remains in solution (NaCl), and the pH of the solution is 7.00. Adding more **NaOH** produces a rapid increase in pH, but eventually the pH levels off at a value of about 13.30, the pH of 0.20 M ***NaOH***.

As shown in Figure **7.2.4.2*b***, the titration of 50.0 mL of a 0.10 M solution of **NaOH** with 0.20 M **HCl** produces a titration curve that is nearly the mirror image of the titration curve in Figure **7.2.4.2*a***. The pH is initially 13.00, and it slowly decreases as **HCl** is added. As the equivalence point is approached, the pH drops rapidly before leveling off at a value of about 0.70, the pH of 0.20 M **HCl**.

The titration of either a strong acid with a strong base or a strong base with a strong acid produces an S-shaped curve. The curve is somewhat asymmetrical because the steady increase in the volume of the solution during the titration causes the solution to become more dilute. Due to the leveling effect, the shape of the curve for a titration involving a strong acid and a strong base depends on only the concentrations of the acid and base, not their identities.

> The shape of the titration curve involving a strong acid and a strong base depends only on their concentrations, not their identities.

✔ Example 7.2.4.1: Hydrochloric Acid

Calculate the pH of the solution after 24.90 mL of 0.200 M **NaOH** has been added to 50.00 mL of 0.100 M **HCl**.

Given: volumes and concentrations of strong base and acid

Asked for: pH

Strategy:

A. Calculate the number of millimoles of H^+ and OH^- to determine which, if either, is in excess after the neutralization reaction has occurred. If one species is in excess, calculate the amount that remains after the neutralization reaction.
B. Determine the final volume of the solution. Calculate the concentration of the species in excess and convert this value to pH.

Solution

A Because 0.100 mol/L is equivalent to 0.100 mmol/mL, the number of millimoles of $\mathrm{H^+}$ in 50.00 mL of 0.100 M HCl can be calculated as follows:

$$50.00\ \cancel{mL}\left(\frac{0.100\ mmol\ HCl}{\cancel{mL}}\right) = 5.00\ mmol\ HCl = 5.00\ mmol\ H^+$$

The number of millimoles of NaOH added is as follows:

$$24.90\ \cancel{mL}\left(\frac{0.200\ mmol\ NaOH}{\cancel{mL}}\right) = 4.98\ mmol\ NaOH = 4.98\ mmol\ OH^-$$

Thus $\mathrm{H^+}$ is in excess. To completely neutralize the acid requires the addition of 5.00 mmol of $\mathrm{OH^-}$ to the HCl solution. Because only 4.98 mmol of OH^- has been added, the amount of excess $\mathrm{H^+}$ is 5.00 mmol − 4.98 mmol = 0.02 mmol of H^+.

B The final volume of the solution is 50.00 mL + 24.90 mL = 74.90 mL, so the final concentration of $\mathrm{H^+}$ is as follows:

$$[H^+] = \frac{0.02\ mmol\ H^+}{74.90\ mL} = 3 \times 10^{-4}\ M$$

Hence,

$$pH \approx -\log[\mathrm{H^+}] = -\log(3 \times 10^{-4}) = 3.5$$

This is significantly less than the pH of 7.00 for a neutral solution.

Exercise 7.2.4.1

Calculate the pH of a solution prepared by adding $40.00\ mL$ of $0.237\ M\ HCl$ to $75.00\ mL$ of a $0.133M$ solution of $NaOH$.

Answer

11.6



pH after the addition of 10 ml of Strong Base to a Strong Acid:

https://youtu.be/_cM1_-kdJ20 (opens in new window)



pH at the Equivalence Point in a Strong Acid/Strong Base Titration:

https://youtu.be/7POGDA5Ql2M

Titrations of Weak Acids and Bases

In contrast to strong acids and bases, the shape of the titration curve for a weak acid or a weak base depends dramatically on the identity of the acid or the base and the corresponding K_a or K_b. As we shall see, the pH also changes much more gradually around the equivalence point in the titration of a weak acid or a weak base. As you learned previously, [H^+] of a solution of a weak acid (HA) is not equal to the concentration of the acid but depends on both its pK_a and its concentration. Because only a fraction of a weak acid dissociates, [\(H^+] is less than [HA]. Thus the pH of a solution of a weak acid is greater than the pH of a solution of a strong acid of the same concentration.

Figure 7.2.4.3*a* shows the titration curve for 50.0 mL of a 0.100 M solution of acetic acid with 0.200 M NaOH superimposed on the curve for the titration of 0.100 M HCl shown in part (a) in Figure 7.2.4.2. Below the equivalence point, the two curves are very different. Before any base is added, the pH of the acetic acid solution is greater than the pH of the HCl solution, and the pH changes more rapidly during the first part of the titration. Note also that the pH of the acetic acid solution at the equivalence point is greater than 7.00. That is, at the equivalence point, the solution is basic. In addition, the change in pH around the equivalence point is only about half as large as for the HCl titration; the magnitude of the pH change at the equivalence point depends on the pK_a of the acid being titrated. Above the equivalence point, however, the two curves are identical. Once the acid has been neutralized, the pH of the solution is controlled only by the amount of excess NaOH present, regardless of whether the acid is weak or strong.

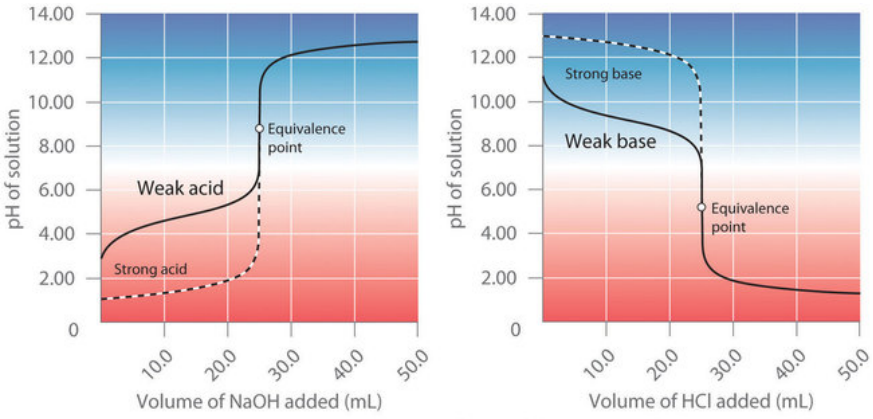


Figure **7.2.4.3**: The Titration of (a) a Weak Acid with a Strong Base and (b) a Weak Base with a Strong Acid. (a) As 0.200 M **NaOH** is slowly added to 50.0 mL of 0.100 M acetic acid, the pH increases slowly at first, then increases rapidly as the equivalence point is approached, and then again increases more slowly. The corresponding curve for the titration of 50.0 mL of 0.100 M **HCl** with 0.200 M **NaOH** is shown as a dashed line. (b) As 0.200 M **HCl** is slowly added to 50.0 mL of 0.100 M NH3, the pH decreases slowly at first, then decreases rapidly as the equivalence point is approached, and then again decreases more slowly. The corresponding curve for the titration of 50.0 mL of 0.100 M **NaOH** with 0.200 M **HCl** is shown as a dashed line. (CC BY-SA-NC; Anonymous by request)

The titration curves of weak acid titrated with strong base and weak base titrated with strong acid are inverse of each other. These curves are shorter than the titration curves with strong acid and strong base.

> The shape of the titration curve of a weak acid or weak base depends heavily on their identities and the K_a or K_b.

The titration curve in Figure **7.2.4.3***a* was created by calculating the starting pH of the acetic acid solution before any **NaOH** is added and then calculating the pH of the solution after adding increasing volumes of $NaOH$. The procedure is illustrated in the following subsection and Example **7.2.4.2** for three points on the titration curve, using the pK_a of acetic acid (4.76 at 25°C; $K_a = 1.7 \times 10^{-5}$.

Calculating the pH of a Solution of a Weak Acid or a Weak Base

As explained discussed, if we know K_a or K_b and the initial concentration of a weak acid or a weak base, we can calculate the pH of a solution of a weak acid or a weak base by setting up a ICE table (i.e, initial concentrations, changes in concentrations, and final concentrations). In this situation, the initial concentration of acetic acid is 0.100 M. If we define x as $[H^+]$ due to the dissociation of the acid, then the table of concentrations for the ionization of 0.100 M acetic acid is as follows:

$$CH_3CO_2H\,(aq) \rightleftharpoons H^+\,(aq) + CH_3CO_2{}^-$$

table of concentrations for the ionization of 0.100 M acetic acid

ICE	$[CH_3CO_2H]$	$[H^+]$	$[CH_3CO_2^-]$
initial	0.100	1.00×10^{-7}	0
change	−x	+x	+x
final	0.100 − x	x	x

In this and all subsequent examples, we will ignore $[H^+]$ and $[OH^-]$ due to the autoionization of water when calculating the final concentration. However, you should use Equation 16.45 and Equation 16.46 to check that this assumption is justified.

Inserting the expressions for the final concentrations into the equilibrium equation (and using approximations),

$$K_a = \frac{[H^+][CH_3CO_2^-]}{[CH_3CO_2H]}$$
$$= \frac{(x)(x)}{0.100 - x}$$
$$\approx \frac{x^2}{0.100}$$
$$\approx 1.74 \times 10^{-5}$$

Solving this equation gives $x = [H^+] = 1.32 \times 10^{-3}\ M$. Thus the pH of a 0.100 M solution of acetic acid is as follows:

$$pH = -\log(1.32 \times 10^{-3}) = 2.879$$



pH at the Start of a Weak Acid/Strong Base Titration: https://youtu.be/AtdBKfrfJNg

Calculating the pH during the Titration of a Weak Acid or a Weak Base

Now consider what happens when we add 5.00 mL of 0.200 M **NaOH** to 50.00 mL of 0.100 M CH_3CO_2H (part (a) in Figure **7.2.4.3**). Because the neutralization reaction proceeds to completion, all of the OH^- ions added will react with the acetic acid to generate acetate ion and water:

$$CH_3CO_2H_{(aq)} + OH^-_{(aq)} \rightarrow CH_3CO^-_{2\ (aq)} + H_2O_{(l)} \qquad (7.2.4.2)$$

All problems of this type must be solved in two steps: a stoichiometric calculation followed by an equilibrium calculation. In the first step, we use the stoichiometry of the neutralization reaction to calculate the amounts of acid and conjugate base present in solution after the neutralization reaction has occurred. In the second step, we use the equilibrium equation to determine $[H^+]$ of the resulting solution.

Step 1

To determine the amount of acid and conjugate base in solution after the neutralization reaction, we calculate the amount of CH_3CO_2H in the original solution and the amount of OH^- in the **NaOH** solution that was added. The acetic acid solution contained

$$50.00\ \cancel{mL}\ (0.100\ mmol(CH_3CO_2H)/\cancel{mL}) = 5.00\ mmol(CH_3CO_2H)$$

The **NaOH** solution contained

5.00 mL=1.00 mmol $NaOH$

Comparing the amounts shows that CH_3CO_2H is in excess. Because OH^- reacts with CH_3CO_2H in a 1:1 stoichiometry, the amount of excess CH_3CO_2H is as follows:

5.00 mmol CH_3CO_2H − 1.00 mmol OH^- = 4.00 mmol CH_3CO_2H

Each 1 mmol of OH^- reacts to produce 1 mmol of acetate ion, so the final amount of $CH_3CO_2^-$ is 1.00 mmol.

The stoichiometry of the reaction is summarized in the following ICE table, which shows the numbers of moles of the various species, not their concentrations.

$$CH_3CO_2H\,(aq) + OH^-\,(aq) \rightleftharpoons CH_3CO_2{}^-\,(aq) + H_2O\,(l)$$

ICE table

ICE	$[CH_3CO_2H]$	$[OH^-]$	$[CH_3CO_2{}^-]$
initial	5.00 mmol	1.00 mmol	0 mmol
change	−1.00 mmol	−1.00 mmol	+1.00 mmol
final	4.00 mmol	0 mmol	1.00 mmol

This ICE table gives the initial amount of acetate and the final amount of OH^- ions as 0. Because an aqueous solution of acetic acid always contains at least a small amount of acetate ion in equilibrium with acetic acid, however, the initial acetate concentration is not actually 0. The value can be ignored in this calculation because the amount of $CH_3CO_2^-$ in equilibrium is insignificant compared to the amount of OH^- added. Moreover, due to the autoionization of water, no aqueous solution can contain 0 mmol of OH^-, but the amount of OH^- due to the autoionization of water is insignificant compared to the amount of OH^- added. We use the initial amounts of the reactants to determine the stoichiometry of the reaction and defer a consideration of the equilibrium until the second half of the problem.

Step 2

To calculate $[H^+]$ at equilibrium following the addition of $NaOH$, we must first calculate $[CH_3CO_2H]$ and $[CH_3CO_2{}^-]$ using the number of millimoles of each and the total volume of the solution at this point in the titration:

$$final\ volume = 50.00\ mL + 5.00\ mL = 55.00\ mL$$

$$[CH_3CO_2H] = \frac{4.00\ mmol\ CH_3CO_2H}{55.00\ mL} = 7.27 \times 10^{-2}\ M$$

$$[CH_3CO_2^-] = \frac{1.00\ mmol\ CH_3CO_2^-}{55.00\ mL} = 1.82 \times 10^{-2}\ M$$

Knowing the concentrations of acetic acid and acetate ion at equilibrium and K_a for acetic acid (1.74×10^{-5}), we can calculate $[H^+]$ at equilibrium:

$$K_a = \frac{[CH_3CO_2^-]\,[H^+]}{[CH_3CO_2H]}$$

$$[H^+] = \frac{K_a\,[CH_3CO_2H]}{[CH_3CO_2^-]} = \frac{(1.72 \times 10^{-5})\,(7.27 \times 10^{-2}\ M)}{(1.82 \times 10^{-2})} = 6.95 \times 10^{-5}\ M$$

Calculating $-\log[H^+]$ gives

$$pH = -\log(6.95 \times 10^{-5}) = 4.158.$$

Comparing the titration curves for HCl and acetic acid in Figure 7.2.4.3*a*, we see that adding the same amount (5.00 mL) of 0.200 M NaOH to 50 mL of a 0.100 M solution of both acids causes a much smaller pH change for HCl (from 1.00 to 1.14) than for acetic acid (2.88 to 4.16). This is consistent with the qualitative description of the shapes of the titration curves at the beginning of this section. In Example 7.2.4.2, we calculate another point for constructing the titration curve of acetic acid.



pH Before the Equivalence Point of a Weak Acid/Strong Base Titration:

https://youtu.be/znpwGCsefXc

Example 7.2.4.2

What is the pH of the solution after 25.00 mL of 0.200 M **NaOH** is added to 50.00 mL of 0.100 M acetic acid?

Given: volume and molarity of base and acid

Asked for: pH

Strategy:

A. Write the balanced chemical equation for the reaction. Then calculate the initial numbers of millimoles of OH^- and CH_3CO_2H. Determine which species, if either, is present in excess.

B. Tabulate the results showing initial numbers, changes, and final numbers of millimoles.

C. If excess acetate is present after the reaction with OH^-, write the equation for the reaction of acetate with water. Use a tabular format to obtain the concentrations of all the species present.

D. Calculate K_b using the relationship $K_w = K_aK_b$. Calculate [OH−] and use this to calculate the pH of the solution.

Solution

A Ignoring the spectator ion (Na^+), the equation for this reaction is as follows:

$$CH_3CO_2H_{(aq)} + OH^-(aq) \rightarrow CH_3CO_2^-(aq) + H_2O(l)$$

The initial numbers of millimoles of OH^- and CH_3CO_2H are as follows:

$$25.00 \text{ mL}(0.200 \text{ mmol OH}-\text{mL}=5.00 \text{ mmol } OH-$$

$$50.00\ mL(0.100 CH_3CO_2HL = 5.00 mmol\ CH_3CO_2H$$

The number of millimoles of OH^- equals the number of millimoles of CH_3CO_2H, so neither species is present in excess.

B Because the number of millimoles of OH^- added corresponds to the number of millimoles of acetic acid in solution, this is the equivalence point. The results of the neutralization reaction can be summarized in tabular form.

$$CH_3CO_2H_{(aq)} + OH^-_{(aq)} \rightleftharpoons CH_3CO_2^-(aq) + H_2O(l)$$

results of the neutralization reaction

ICE	$[CH_3CO_2H]$	$[OH^-]$	$[CH_3CO_2^-]$
initial	5.00 mmol	5.00 mmol	0 mmol
change	−5.00 mmol	−5.00 mmol	+5.00 mmol
final	0 mmol	0 mmol	5.00 mmol

C Because the product of the neutralization reaction is a weak base, we must consider the reaction of the weak base with water to calculate [H+] at equilibrium and thus the final pH of the solution. The initial concentration of acetate is obtained from the neutralization reaction:

$$[CH_3CO_2] = \frac{5.00\ mmol\ CH_3CO_2^-}{(50.00 + 25.00)\ mL} = 6.67 \times 10^{-2}\ M$$

The equilibrium reaction of acetate with water is as follows:

$$CH_3CO_2^-\,(aq) + H_2O\,(l) \rightleftharpoons CH_3CO_2H\,(aq) + OH^-\,(aq)$$

The equilibrium constant for this reaction is

$$K_b = \frac{K_w}{K_a} \tag{7.2.4.3}$$

where K_a is the acid ionization constant of acetic acid. We therefore define x as $[OH^-]$ produced by the reaction of acetate with water. Here is the completed table of concentrations:

$$H_2O_{(l)} + CH_3CO_{2(aq)}^- \rightleftharpoons CH_3CO_2H_{(aq)} + OH_{(aq)}^-$$

completed table of concentrations

	$[CH_3CO_2^-]$	$[CH_3CO_2H]$	$[OH^-]$
initial	0.0667	0	1.00 × 10−7
change	−x	+x	+x
final	(0.0667 − x)	x	x

D We can obtain K_b by substituting the known values into Equation 7.2.4.3:

$$K_b = \frac{K_w}{K_a} = \frac{1.01 \times 10^{-14}}{1.74 \times 10^{-5}} = 5.80 \times 10^{-10} \tag{7.2.4.4}$$

Substituting the expressions for the final values from the ICE table into Equation 7.2.4.4 and solving for x:

$$\frac{x^2}{0.0667} = 5.80 \times 10^{-10}$$

$$x = \sqrt{(5.80 \times 10^{-10})(0.0667)}$$

$$= 6.22 \times 10^{-6}$$

Thus $[OH^-] = 6.22 \times 10^{-6}\ M$ and the pH of the final solution is 8.794 (Figure 7.2.4.3*a*). As expected for the titration of a weak acid, the pH at the equivalence point is greater than 7.00 because the product of the titration is a base, the acetate ion, which then reacts with water to produce OH^-.

? Exercise 7.2.4.2

Calculate the pH of a solution prepared by adding 45.0 mL of a 0.213 M HCl solution to 125.0 mL of a 0.150 M solution of ammonia. The pK_b of ammonia is 4.75 at 25°C.

Answer

9.23

As shown in part (b) in Figure **7.2.4.3**, the titration curve for NH3, a weak base, is the reverse of the titration curve for acetic acid. In particular, the pH at the equivalence point in the titration of a weak base is less than 7.00 because the titration produces an acid.

The identity of the weak acid or weak base being titrated strongly affects the shape of the titration curve. Figure **7.2.4.4** illustrates the shape of titration curves as a function of the pK_a or the pK_b. As the acid or the base being titrated becomes weaker (its pK_a or pK_b becomes larger), the pH change around the equivalence point decreases significantly. With very dilute solutions, the curve becomes so shallow that it can no longer be used to determine the equivalence point.

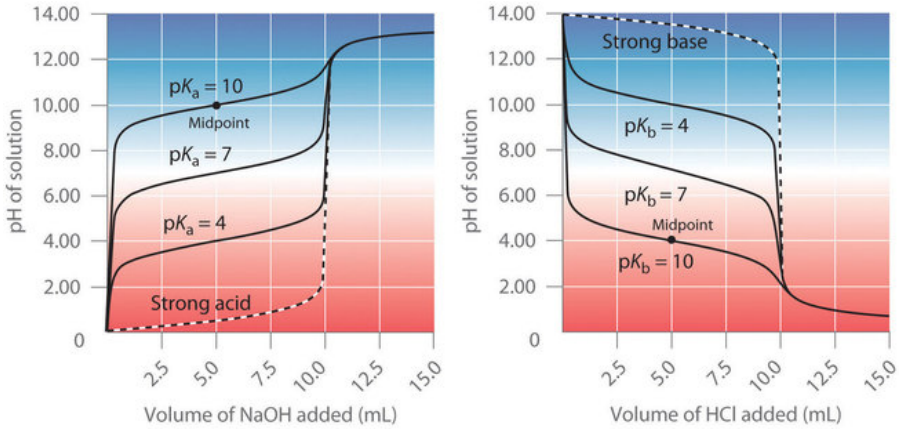


Figure **7.2.4.4**: Effect of Acid or Base Strength on the Shape of Titration Curves. Unlike strong acids or bases, the shape of the titration curve for a weak acid or base depends on the pK_a or pK_b of the weak acid or base being titrated. (a) Solution pH as a function of the volume of 1.00 M **NaOH** added to 10.00 mL of 1.00 M solutions of weak acids with the indicated pK_a values. (b) Solution pH as a function of the volume of 1.00 M **HCl** added to 10.00 mL of 1.00 M solutions of weak bases with the indicated pK_b values. The shapes of the two sets of curves are essentially identical, but one is flipped vertically in relation to the other. Midpoints are indicated for the titration curves corresponding to $pK_a = 10$ and $pK_b = 10$. (CC BY-SA-NC; Anonymous by request)

The titration curves of weak acids with strong base and weak bases titrated with strong acid are inverses of each other. Three weak acids and three weak bases with pKa and pKb of 4, 7, and 10 are used.

One point in the titration of a weak acid or a weak base is particularly important: the midpoint of a titration is defined as the point at which exactly enough acid (or base) has been added to neutralize one-half of the acid (or the base) originally present and occurs halfway to the equivalence point. The midpoint is indicated in Figures **7.2.4.4*a*** and **7.2.4.4*b*** for the two shallowest curves. By definition, at the midpoint of the titration of an acid, [HA] = [A−]. Recall that the ionization constant for a weak acid is as follows:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

If $[HA] = [A^-]$, this reduces to $K_a = [H_3O^+]$. Taking the negative logarithm of both sides,

$$-\log K_a = -\log[H_3O+]$$

From the definitions of pK_a and pH, we see that this is identical to

$$pK_a = pH \tag{7.2.4.5}$$

Thus the pH at the midpoint of the titration of a weak acid is equal to the pK_a of the weak acid, as indicated in part (a) in Figure **7.2.4.4** for the weakest acid where we see that the midpoint for $pK_a = 10$ occurs at pH = 10. Titration methods can therefore be used to determine both the concentration and the pK_a (or the pK_b) of a weak acid (or a weak base).

The pH at the midpoint of the titration of a weak acid is equal to the pK_a of the weak acid.

Titrations of Polyprotic Acids or Bases

When a strong base is added to a solution of a polyprotic acid, the neutralization reaction occurs in stages. The most acidic group is titrated first, followed by the next most acidic, and so forth. If the pK_a values are separated by at least three pK_a units, then the

overall titration curve shows well-resolved “steps” corresponding to the titration of each proton. A titration of the triprotic acid H_3PO_4 with NaOH is illustrated in Figure 7.2.4.5 and shows two well-defined steps: the first midpoint corresponds to pK_a1, and the second midpoint corresponds to pK_a2. Because HPO_4^{2-} is such a weak acid, pK_a3 has such a high value that the third step cannot be resolved using 0.100 M NaOH as the titrant.

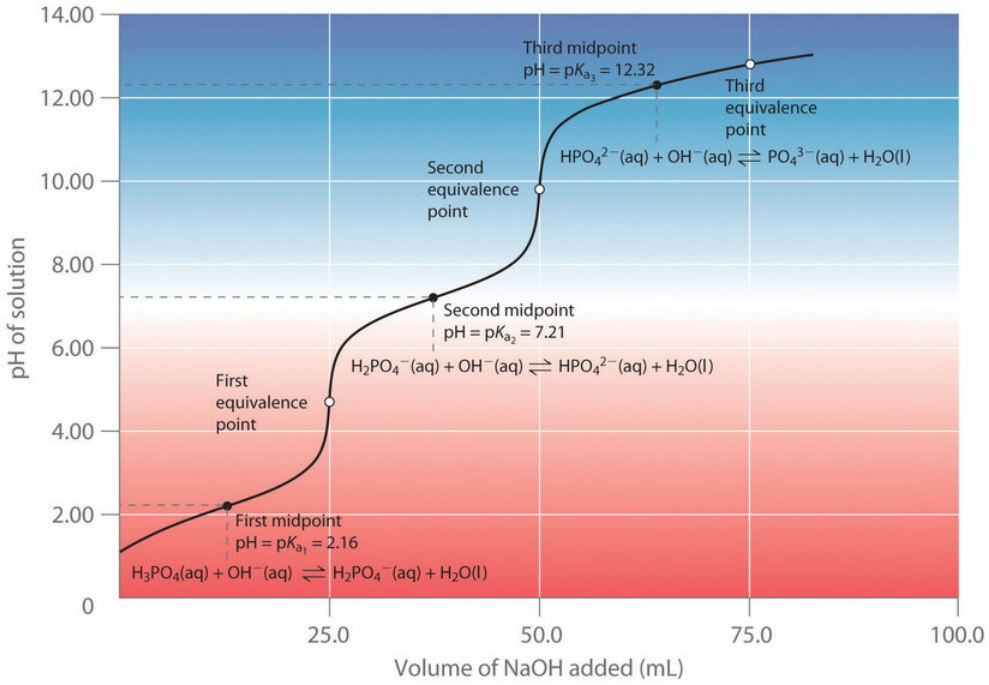
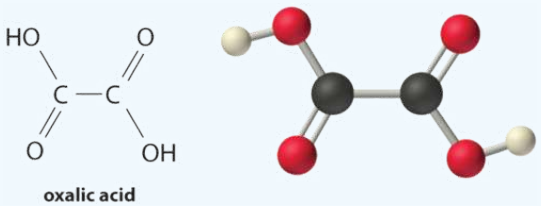


Figure 7.2.4.5: Titration Curve for Phosphoric Acid (H_3PO_4, a Typical Polyprotic Acid. The curve for the titration of 25.0 mL of a 0.100 M H_3PO_4 solution with 0.100 M NaOH along with the species in solution at each Ka is shown. Note the two distinct equivalence points corresponding to deprotonation of H_3PO_4 at pH ≈ 4.6 and $H_2PO_4^{2-}$ at pH ≈ 9.8. Because HPO_4^{2-} is a very weak acid, the third equivalence point, at pH ≈ 13, is not well defined. (CC BY-SA-NC; Anonymous by request)

The titration curve for the reaction of a polyprotic base with a strong acid is the mirror image of the curve shown in Figure 7.2.4.5. The initial pH is high, but as acid is added, the pH decreases in steps if the successive pK_b values are well separated. Table E1 lists the ionization constants and pK_a values for some common polyprotic acids and bases.

Example 7.2.4.3

Calculate the pH of a solution prepared by adding 55.0 mL of a 0.120 M NaOH solution to 100.0 mL of a 0.0510 M solution of oxalic acid (HO_2CCO_2H), a diprotic acid (abbreviated as H_2ox). Oxalic acid, the simplest dicarboxylic acid, is found in rhubarb and many other plants. Rhubarb leaves are toxic because they contain the calcium salt of the fully deprotonated form of oxalic acid, the oxalate ion ($O_2CCO_2^{2-}$, abbreviated ox^{2-}).Oxalate salts are toxic for two reasons. First, oxalate salts of divalent cations such as Ca^{2+} are insoluble at neutral pH but soluble at low pH. As a result, calcium oxalate dissolves in the dilute acid of the stomach, allowing oxalate to be absorbed and transported into cells, where it can react with calcium to form tiny calcium oxalate crystals that damage tissues. Second, oxalate forms stable complexes with metal ions, which can alter the distribution of metal ions in biological fluids.



oxalic acid

Given: volume and concentration of acid and base

Asked for: pH

Strategy:

A. Calculate the initial millimoles of the acid and the base. Use a tabular format to determine the amounts of all the species in solution.
B. Calculate the concentrations of all the species in the final solution. Determine [H+] and convert this value to pH.

Solution:

A Table E5 gives the pK_a values of oxalic acid as 1.25 and 3.81. Again we proceed by determining the millimoles of acid and base initially present:

$$100.00\,\cancel{mL}\left(\frac{0.510\ mmol\ H_2ox}{\cancel{mL}}\right) = 5.10\ mmol\ H_2ox$$

$$55.00\,\cancel{mL}\left(\frac{0.120\ mmol\ NaOH}{\cancel{mL}}\right) = 6.60\ mmol\ NaOH$$

The strongest acid (H_2ox) reacts with the base first. This leaves (6.60 − 5.10) = 1.50 mmol of OH^- to react with Hox−, forming ox^{2-} and H_2O. The reactions can be written as follows:

$$\underset{5.10\ mmol}{H_2ox} + \underset{6.60\ mmol}{OH^-} \rightarrow \underset{5.10\ mmol}{Hox^-} + \underset{5.10\ mmol}{H_2O}$$

$$\underset{5.10\ mmol}{Hox^-} + \underset{1.50\ mmol}{OH^-} \rightarrow \underset{1.50\ mmol}{ox^{2-}} + \underset{1.50\ mmol}{H_2O}$$

In tabular form,

Solutions to Example 17.3.3

	H_2ox	OH^-	Hox^-	ox^{2-}
initial	5.10 mmol	6.60 mmol	0 mmol	0 mmol
change (step 1)	−5.10 mmol	−5.10 mmol	+5.10 mmol	0 mmol
final (step 1)	0 mmol	1.50 mmol	5.10 mmol	0 mmol
change (step 2)	—	−1.50 mmol	−1.50 mmol	+1.50 mmol
final	0 mmol	0 mmol	3.60 mmol	1.50 mmol

B The equilibrium between the weak acid (Hox^-) and its conjugate base (ox^{2-}) in the final solution is determined by the magnitude of the second ionization constant, $K_{a2} = 10^{-3.81} = 1.6 \times 10^{-4}$. To calculate the pH of the solution, we need to know $[H^+]$, which is determined using exactly the same method as in the acetic acid titration in Example 7.2.4.2:

$$\text{final volume of solution} = 100.0\,mL + 55.0\,mL = 155.0\,mL$$

Thus the concentrations of Hox^- and ox^{2-} are as follows:

$$[Hox^-] = \frac{3.60\ mmol\ Hox^-}{155.0\ mL} = 2.32 \times 10^{-2}\ M$$

$$[ox^{2-}] = \frac{1.50\ mmol\ ox^{2-}}{155.0\ mL} = 9.68 \times 10^{-3}\ M$$

We can now calculate [H+] at equilibrium using the following equation:

$$K_{a2} = \frac{[ox^{2-}]\,[H^+]}{[Hox^-]}$$

Rearranging this equation and substituting the values for the concentrations of Hox^- and ox^{2-},

$$[H^+] = \frac{K_{a2}[Hox^-]}{[ox^{2-}]} = \frac{(1.6 \times 10^{-4})(2.32 \times 10^{-2})}{(9.68 \times 10^{-3})} = 3.7 \times 10^{-4}\ M$$

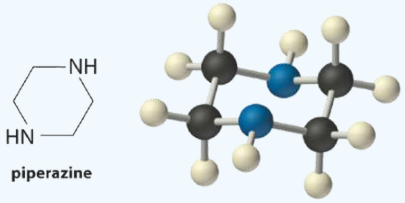
So

$$pH = -\log[H^+] = -\log(3.7 \times 10^{-4}) = 3.43$$

This answer makes chemical sense because the pH is between the first and second pK_a values of oxalic acid, as it must be. We added enough hydroxide ion to completely titrate the first, more acidic proton (which should give us a pH greater than pK_{a1}), but we added only enough to titrate less than half of the second, less acidic proton, with pK_{a2}. If we had added exactly enough hydroxide to completely titrate the first proton plus half of the second, we would be at the midpoint of the second step in the titration, and the pH would be 3.81, equal to pK_{a2}.

? Exercise 7.2.4.3: Piperazine

Piperazine is a diprotic base used to control intestinal parasites ("worms") in pets and humans. A dog is given 500 mg (5.80 mmol) of piperazine (pK_{b1} = 4.27, pK_{b2} = 8.67). If the dog's stomach initially contains 100 mL of 0.10 M HCl (pH = 1.00), calculate the pH of the stomach contents after ingestion of the piperazine.



Answer

pH=4.9

Indicators

In practice, most acid–base titrations are not monitored by recording the pH as a function of the amount of the strong acid or base solution used as the titrant. Instead, an acid–base indicator is often used that, if carefully selected, undergoes a dramatic color change at the pH corresponding to the equivalence point of the titration. Indicators are weak acids or bases that exhibit intense colors that vary with pH. The conjugate acid and conjugate base of a good indicator have very different colors so that they can be distinguished easily. Some indicators are colorless in the conjugate acid form but intensely colored when deprotonated (phenolphthalein, for example), which makes them particularly useful.

We can describe the chemistry of indicators by the following general equation:

$$\mathrm{HIn\,(aq) \rightleftharpoons H^+\,(aq) + In^-\,(aq)}$$

where the protonated form is designated by HIn and the conjugate base by In^-. The ionization constant for the deprotonation of indicator HIn is as follows:

$$K_{In} = \frac{[H^+][In^-]}{[HIn]} \tag{7.2.4.6}$$

The pK_{in} (its pK_a) determines the pH at which the indicator changes color.

Many different substances can be used as indicators, depending on the particular reaction to be monitored. For example, red cabbage juice contains a mixture of colored substances that change from deep red at low pH to light blue at intermediate pH to yellow at high pH. Similarly, *Hydrangea macrophylla* flowers can be blue, red, pink, light purple, or dark purple depending on the soil pH (Figure 7.2.4.6). Acidic soils will produce blue flowers, whereas alkaline soils will produce pinkish flowers.

Irrespective of the origins, a good indicator must have the following properties:

- The color change must be easily detected.

- The color change must be rapid.
- The indicator molecule must not react with the substance being titrated.
- To minimize errors, the indicator should have a pK_{in} that is within one pH unit of the expected pH at the equivalence point of the titration.



Figure 7.2.4.6: Naturally occurring pH indicators can be found in red cabbage and Hydrangea macrophylla flowers. Red Cabbage image (CC BY-SA 3.0; KENPEI via Wikipedia) and Hydrangea macrophylla flowers (pixabay).

Synthetic indicators have been developed that meet these criteria and cover virtually the entire pH range. Figure 7.2.4.7 shows the approximate pH range over which some common indicators change color and their change in color. In addition, some indicators (such as thymol blue) are polyprotic acids or bases, which change color twice at widely separated pH values.

Indicator	pK_{in}	Color change
Alizarin yellow R	11.0	yellow to red
Thymolphthalein	9.9	colorless to blue
Phenolphthalein	9.5	colorless to pink
Thymol blue	9.2	yellow to blue
Phenol red	7.4	yellow to red
Bromothymol blue	7.3	yellow to blue
Bromocresol purple	6.4	yellow to purple
Ethyl red	5.4	colorless to red
Resorcin blue	5.3	red to blue
Resazurin	5.1	orange to violet
Methyl red	5.0	red to yellow
Bromophenol blue	4.1	yellow to blue
Thymol blue	1.7	red to yellow
Malachite green	1.3	yellow to turquoise
Methyl violet	0.8	yellow to blue

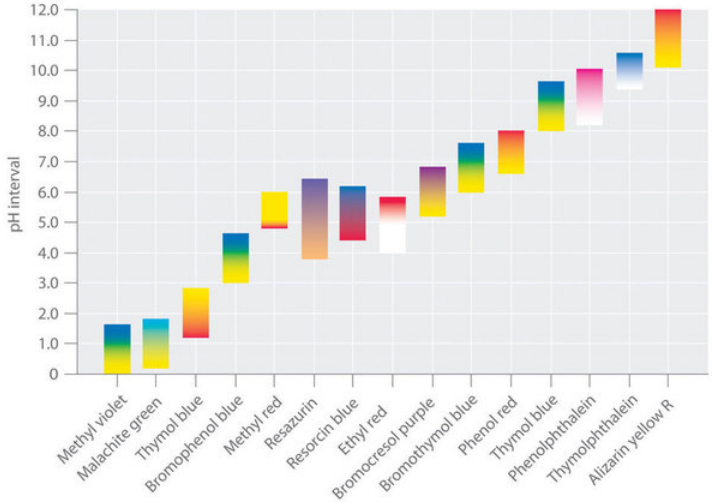


Figure 7.2.4.7: Some Common Acid–Base Indicators. Approximate colors are shown, along with pK_{in} values and the pH range over which the color changes. (CC BY-SA-NC; Anonymous by request)

It is important to be aware that an indicator does not change color abruptly at a particular pH value; instead, it actually undergoes a pH titration just like any other acid or base. As the concentration of HIn decreases and the concentration of In− increases, the color of the solution slowly changes from the characteristic color of HIn to that of In−. As we will see later, the [In−]/[HIn] ratio changes from 0.1 at a pH one unit below pKin to 10 at a pH one unit above pKin. Thus most indicators change color over a pH range of about two pH units.

We have stated that a good indicator should have a pKin value that is close to the expected pH at the equivalence point. For a strong acid–strong base titration, the choice of the indicator is not especially critical due to the very large change in pH that occurs around the equivalence point. In contrast, using the wrong indicator for a titration of a weak acid or a weak base can result in relatively large errors, as illustrated in Figure 7.2.4.8. This figure shows plots of pH versus volume of base added for the titration of 50.0 mL of a 0.100 M solution of a strong acid (HCl) and a weak acid (acetic acid) with 0.100 M $NaOH$. The pH ranges over which two common indicators (methyl red, $pK_{in} = 5.0$, and phenolphthalein, $pK_{in} = 9.5$) change color are also shown. The horizontal bars indicate the pH ranges over which both indicators change color cross the HCl titration curve, where it is almost vertical. Hence both indicators change color when essentially the same volume of NaOH has been added (about 50 mL), which corresponds to the equivalence point. In contrast, the titration of acetic acid will give very different results depending on whether

methyl red or phenolphthalein is used as the indicator. Although the pH range over which phenolphthalein changes color is slightly greater than the pH at the equivalence point of the strong acid titration, the error will be negligible due to the slope of this portion of the titration curve. Just as with the **HCl** titration, the phenolphthalein indicator will turn pink when about 50 mL of **NaOH** has been added to the acetic acid solution. In contrast, methyl red begins to change from red to yellow around pH 5, which is near the midpoint of the acetic acid titration, not the equivalence point. Adding only about 25–30 mL of **NaOH** will therefore cause the methyl red indicator to change color, resulting in a huge error.

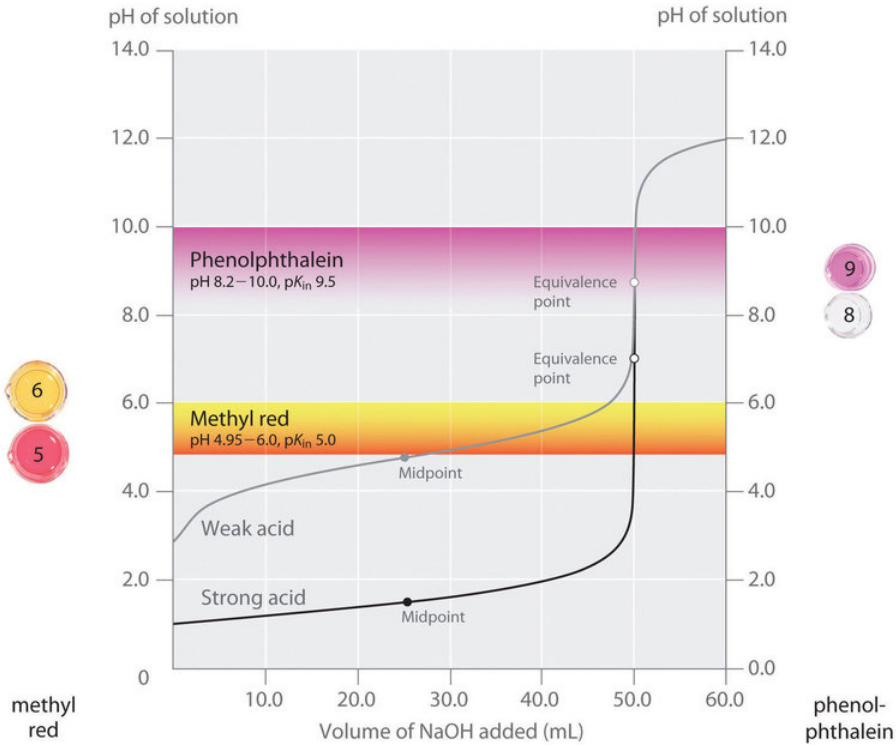


Figure **7.2.4.8**: Choosing the Correct Indicator for an Acid–Base Titration. (CC BY-SA-NC; Anonymous by request)

If the pH of the solution is between 4.95 and 6 then methyl red should be used. If the pH is between 8,2 and 10 then phenolphthalein should be used.

The graph shows the results obtained using two indicators (methyl red and phenolphthalein) for the titration of 0.100 M solutions of a strong acid (HCl) and a weak acid (acetic acid) with 0.100 M ***NaOH***. Due to the steepness of the titration curve of a strong acid around the equivalence point, either indicator will rapidly change color at the equivalence point for the titration of the strong acid. In contrast, the pKin for methyl red (5.0) is very close to the pK_a of acetic acid (4.76); the midpoint of the color change for methyl red occurs near the midpoint of the titration, rather than at the equivalence point.

In general, for titrations of strong acids with strong bases (and vice versa), any indicator with a pKin between about 4.0 and 10.0 will do. For the titration of a weak acid, however, the pH at the equivalence point is greater than 7.0, so an indicator such as phenolphthalein or thymol blue, with pKin > 7.0, should be used. Conversely, for the titration of a weak base, where the pH at the equivalence point is less than 7.0, an indicator such as methyl red or bromocresol blue, with pKin < 7.0, should be used.

The existence of many different indicators with different colors and pKin values also provides a convenient way to estimate the pH of a solution without using an expensive electronic pH meter and a fragile pH electrode. Paper or plastic strips impregnated with combinations of indicators are used as “pH paper,” which allows you to estimate the pH of a solution by simply dipping a piece of pH paper into it and comparing the resulting color with the standards printed on the container (Figure **7.2.4.9**).

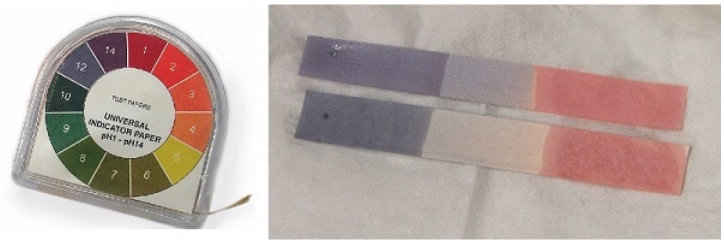


Figure **7.2.4.9**: pH Paper. pH paper contains a set of indicators that change color at different pH values. The approximate pH of a solution can be determined by simply dipping a paper strip into the solution and comparing the color to the standards provided. (CC BY-SA-NC; Anonymous by request)



pH Indicators: pH Indicators(opens in new window) [youtu.be]

Summary and Takeaway

Plots of acid–base titrations generate titration curves that can be used to calculate the pH, the pOH, the pK_a, and the pK_b of the system. The shape of a titration curve, a plot of pH versus the amount of acid or base added, provides important information about what is occurring in solution during a titration. The shapes of titration curves for weak acids and bases depend dramatically on the identity of the compound. The equivalence point of an acid–base titration is the point at which exactly enough acid or base has been added to react completely with the other component. The equivalence point in the titration of a strong acid or a strong base occurs at pH 7.0. In titrations of weak acids or weak bases, however, the pH at the equivalence point is greater or less than 7.0, respectively. The pH tends to change more slowly before the equivalence point is reached in titrations of weak acids and weak bases than in titrations of strong acids and strong bases. The pH at the midpoint, the point halfway on the titration curve to the equivalence point, is equal to the pK_a of the weak acid or the pK_b of the weak base. Thus titration methods can be used to determine both the concentration and the pK_a (or the pK_b) of a weak acid (or a weak base). Acid–base indicators are compounds that change color at a particular pH. They are typically weak acids or bases whose changes in color correspond to deprotonation or protonation of the indicator itself.

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7.2.5: Solutions of Salts of Polyprotic Acids

Learning Objectives

- Predict and calculate the pH of a solution of salts of polyprotic acids

Salts can be thought of as being derived from the neutralization of an acid and a base. A salt formed from a strong acid and a strong base will not hydrolyze (e.g., extract a proton from water). When placed in water, these salts dissociate completely, and their ions remain uncombined in solution (e.g., the NaCl salt is formed from a strong acid (HCl) and a strong base (NaOH).

In discussing the titration of acids and bases, the acid or basic properties of the corresponding salts after a neutralization reaction must be addressed to calculate the final pH of a solution. To calculate the pH of a salt solution one needs to know the concentration of the salt solution, whether the salt is an acidic, basic, or neutral salt, the equation for the interaction of the ion with the water, the equilibrium expression for this interaction and the K_a or K_b value.

Note: The Hydrolysis of Salts

As a quick review, the general rules for the hydrolysis of monoprotic salts are:

1. If neither the cation/anion can affect the pH, the solution is neutral
2. If **only** the cation of the salt is acidic, the solution is acidic
3. If **only** the anion of the salt is basic, the solution will be basic
4. If a salt has a cation that is acidic and an anion that is basic, the pH of the solution is determined by the relative strengths of the acid and base
    - if $K_a = K_b$, then no net effect on pH
    - if $K_a > K_b$, then the solution is slightly acidic
    - if $K_b > K_b$, then the solution is slightly basic

Salts of Polyprotic Acids

Do not be intimidated by the salts of polyprotic acids. Yes they're bigger and "badder" then most other salts, but they can be handled the exact same way as other salts, just with a bit more math.

- All of the rules from above still apply, e.g., the pH of a salt of polyprotic acid will always be greater than 7.
- The same way that polyprotic acids lose H^+ stepwise, salts of polyprotic acids gain H^+ in the same manner, but in reverse order of the polyprotic acid.

Take for example dissociation of carbonic acid (H_2CO_3):

$$H_2CO_{3(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HCO^-_{3(aq)} \tag{7.2.5.1}$$

with $K_{a1} = 2.5 \times 10^{-4}$

$$HCO^-_{3(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CO^{2-}_{3(aq)} \tag{7.2.5.2}$$

with $K_{a2} = 5.61 \times 10^{-11}$. This means that when calculating the values for K_b of CO_3^{2-}, The K_b of the first hydrolysis reaction will be $K_{b1} = \frac{K_w}{K_{a2}}$ since it will go in the reverse order.

Example 7.2.5.1: $NaHSO_4$

What is the pH of a 0.100 M $\mathbf{NaHSO_4}$ solution? Sulfuric acid is a strong acid, and the $\mathbf{pK_{a_2}}$ of $\mathbf{HSO_4^-}$ is 1.92.

Solution

First review the ions generates immediate upon dissociation of the salt.

- Na^+ is a non-acidic "spectator ion" that does not affect the acidity or basicity of a solution and can be ignored.

- The HSO_4^- anion will affect the pH

HSO_4^- is part of the dissociation chain of diprotic sulfuric acid (H_2SO_4) with the following steps

$$H_2SO_4 + H_2O \rightarrow H_3O^+ + HSO_4^- \tag{7.2.5.3}$$

Because H_2SO_4 is a strong acid, this step goes to completion and no H_2SO_4 exists in the solution. The HSO_4^- ion is a weak acid and dissociates to a small extent:

$$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-} \tag{7.2.5.4}$$

with $K_{a2} = 1.0 \times 10^{-2}$ from Table E1. The equilibrium favors the reactants.

The $NaHSO4$ salt is completely ionized in its solution.

$$\mathrm{NaHSO_{4\,(s)} \rightarrow Na^+_{(sq)} + HSO_4{}^-_{(sq)}} \tag{7.2.5.5}$$

The anion then further ionizes (Equation 7.2.5.4). We can construct an ICE table to solve for the final value of this ionization and hence $[H_3O^+]$

ICE Table	HSO_4^-	H_2O	H_3O^+	SO_4^{2-}
Initial	0.1 M	-	0	0
Change	-x	-	+x	+x
Equilibrium	0.1 M -x	-	x	x

$$K_{a2} = \frac{x^2}{0.100 - x} = 0.0100$$

$$\begin{aligned}[\mathrm{H_3O^+}] &= x \\ &= \frac{-0.120 + \sqrt{0.012^2 + 4 \times 0.00120}}{2} \\ &= 0.0292 \text{ M}\end{aligned}$$

Thus,

$$\mathrm{pH} = -\log\ 0.0292 = 1.54$$

Note that while the dissociation is weak, the quadratic equation cannot be avoided since 0.0292 cannot be ignore when compared to 0.1 M.

? Exercise 7.2.5.1

Which of the following solutions are acidic, basic, or neutral?

a. $\mathrm{Na_2SO_4}$
b. $\mathrm{NaH_2PO_4}$
c. $\mathrm{Na_2HPO_4}$
d. $\mathrm{Na_3PO_4}$
e. $\mathrm{NaNO_3}$

✓ Example 7.2.5.2: Qualitatively Estimating the pH of a Polyprotic Salt Solution

Predict whether the Na_2HPO_4 salt will form an acidic or basic solution when dissolved in water. You will need values from Table E1 to address this.

Solution

First review the ions generates immediate upon dissociation of the salt.

- Na^+ is a non-acidic "spectator ion" that does not affect the acidity or basicity of a solution and can be ignored.
- The HPO_4^{2-} anion will affect the pH and does so via competing hydrolysis steps as discussed below.

From Table E1, the three equilibria values for the three acid/base reactions of the phosphate ion are:

$$H_3PO_{4(sq)} \rightleftharpoons H^+_{(aq)} + H_2PO^{2-}_{4(aq)} \tag{7.2.5.6}$$

with $K_{a1} = 6.9 \times 10^{-3}$

$$H_2PO^-_{4(sq)} \rightleftharpoons H^+_{(aq)} + HPO^{2-}_{4(aq)} \tag{7.2.5.7}$$

with $K_{a2} = 6.2 \times 10^{-8}$

$$HPO^{2-}_{4(sq)} \rightleftharpoons H^+_{(aq)} + PO^{3-}_{4(aq)} \tag{7.2.5.8}$$

with $K_{a3} = 4.8 \times 10^{-11}$

The low K_a value for the deprotonation of $HPO^{2-}_{4(sq)}$ means that it is a poor acid and better functions as a (Brønsted-Lowry) base:

$$HPO^{2-}_{4(aq)} + H_2O_{(l)} \rightleftharpoons H_2PO^-_{4(aq)} + OH^-_{(aq)} \tag{7.2.5.9}$$

The two possible reactions that $HPO^{2-}_{4(aq)}$ undergoes are the acid reaction in Equation 7.2.5.7 and the basic reaction in Equation 7.2.5.9. Whether this ion will cause the solution to be acidic or basic depends on whether the K_a for Equation 7.2.5.7 is bigger than the K_b for Equation 7.2.5.9.

The K_b of this reaction is related to the K_{a2} by

$$K_b = \frac{K_w}{K_a}$$

$$K_b = \frac{1 \times 10^{-14}}{6.2 \times 10^{-8}} = 1.6 \times 10^{-7} \text{ for } HPO_4^{2-}$$

Since $K_b > K_a$, the solution will be **basic**. To determine just how basic requires the use of an ICE table as discussed in Example 7.2.5.3.

Solving the final pH for a Na_2HPO_4 salt solution is more complex than for the $NaHSO_4$, since the latter involves a single equilibrium. Two equilibria must be simultaneously solved for Na_2HPO_4. However, often time (but not always), they can be easily approximated given the relative pk_a describing the reversible reaction.

Example 7.2.5.3: Quantitatively Estimating the pH of a Polyprotic Salt Solution

Calculate the pH of the solution containing 3.875 g of Na_2HPO_4 that has been dissolved in a 250 mL of water.

Solution

First it is best to identify the molarity of Na_2HPO_4 that was initially generated (i.e., before any hydrolysis reactions happens).

$$c = \frac{3.875\ g/\text{molecular mass}}{\text{volume}} = \frac{3.875\ g/141.98\ g/mol}{250\ mL} = 0.11\ M$$

As discussed in Example 7.2.5.1, the low K_a value for the deprotonation of $HPO^{2-}_{4(sq)}$ means that it is a poor acid and instead functions as a base instead. From comparing the ionization constant in Example 7.2.5.1, the Na_2HPO_4 is a far better base than acid. If we ignore the acid properties of the ion and focus on the basic we get the following reaction

$$HPO^{2-}_{4(aq)} + H_2O_{(l)} \rightleftharpoons H_2PO^-_{4(aq)} + OH^-_{(aq)} \tag{7.2.5.10}$$

with a K_b of 1.6×10^{-7}. Now do an ICE table to get the final $[H^+]$ concentration.

ICE Table	$HPO_{4(aq)}^{2-}$	$H_2O_{(l)}$	$H_2PO_{4(aq)}^{-}$	$OH_{(aq)}^{-}$
Initial	0.11 M	-	-	0
Change	-x	-	+x	+x
Equilibrium	0.11 M - x	-	x	x

$$K_b = \frac{[H_2PO_{4(aq)}^{-}][OH_{(aq)}^{-}]}{[HPO_{4(aq)}^{2-}]} = 1.6 \times 10^{-7} \tag{7.2.5.11}$$

$$\frac{x^2}{0.11\ M - x} = 1.6 \times 10^{-7} \tag{7.2.5.12}$$

if $x << 0.11\ M$ then $0.11\ M - x \approx 0.11\ M$ then

$$x = 1.3 \times 10^{-4} = [OH^-] \tag{7.2.5.13}$$

$$pOH = -\log_{10}[OH^-] = 3.8 \tag{7.2.5.14}$$

\[pH = pK_w - pOH]

Assuming that the reaction is at 25°, then $pK_w = 14$ and

$$pH = 14 - 3.8 = 10.2 \tag{7.2.5.15}$$

As expected, the solution is basic.

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7.2.6: Acid–Base Equilibrium Calculations- ASummary

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7.3: Hard and Soft Acids and Bases

Origin of the Hard-Soft Acid-Base Principle

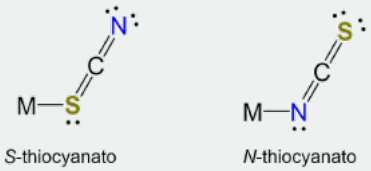
One of the strengths of the Lewis acid-base concept is the readiness with which it illuminates the role that covalent and electrostatic interactions in acid base behavior, specifically through its ability to explain chemical interactions in terms of frontier orbitals and the interactions between charged groups as electrons are donated from a base to an acid. However, simply acknowledging the presence of such interactions does little to illuminate the degree to which each mode of explanation best explains the bonding in a given system? To what extent is a given adduct better described as held together by covalent bonds as opposed to ionic ones - *e.g.* better described as a molecule rather than an ion pair? Moreover, does it even matter, given that the orbitals of quantum mechanics result from the combination of electrons' wavelike behavior with their electrostatic attraction to nuclei in either case?[1] These questions and more are addressed by one of the most important conceptual tools in contemporary inorganic chemistry, the Hard-Soft acid-base principle.

The **Hard-Soft acid-base principle (HSAB principle)** stems from the recognition that some Lewis acids and bases seem to have a natural affinity for one another.* Consider the following:

- Some metals are commonly found in nature as salts of chloride or as oxide ores while others are found in combination with sulfur. Geochemists even use the Goldschmidtt classification scheme to classify the halide and oxide formers as lithophiles and the sulfide formers as chalcophiles.
- In living systems small highly charged metals ions like Fe^{3+} are usually found bound to N and O atoms while larger metals with lower charges such as Zn^{2+} are often found attached to at least one S atom. Similarly, metals prefer to bind to one coordination site over the other when forming complexes with ambidentate ligands. The most well-known instances involve complexes of cyanate and thiocyanate, which can coordinate metals through either the N or chalcogen atom. For instance, Cu^{2+} and Zn^{2+} form *N*-thiocyanato complexes in species like $[Cu(NCS)_2(py)_2]$ and $[Zn(NCS)_4]^{2-}$ while their larger cogeners Au^{3+} and Hg^{2+} preferentially forms *S*-thiocyanato complexes, giving speciles like $[Hg(SCN)_4]^{2-}$.

Ambidentate ligands

Ambidentate ligands possess multiple coordination sites through which a metal may bind. For instance, thiocyanate may coordinate metals (M) at either the S or N to give *S*-thiocyanato or *N*-thiocyanato complexes.



S-thiocyanato *N*-thiocyanato

- The solubility trends for the alklai metal halides and silver halides are opposite, even though both involve salts of formula M^+X^- (salts can be thought of as involving Lewis acid-base adduct formation between the anions and cations). Specifically, although the silver halides are all relatively insoluble in water, the very modest solubility they possess follows the order:

$$X = F >> Cl > Br > I \text{ (for the solubility of AgX)}$$

In contrast, the much more ample solubility of the alkali metal halides** follows the opposite order. For example, the order for the lithium halides is

$$X = F << Cl < Br << I \text{ (for the solubility of LiX)}$$

Notes

1. Albeit suitably fudged through such niceties as the Aufbau principle and other approximations.

* Despite the fruitfulness of this observation, in general it is important to reduce the potential for observer bias by checking observations like these against compounds reported in the chemical literature and databases like the Inorganic Crystal Structure and Cambridge Crystallographic Databases.

** These are very soluble in water, to the point where some solutions are perhaps better described as solutions of water in the halide.

† This can be predicted based on the relative hardness of BF_3, BR_3, and BH_3 in the list of hard and soft acids. However, for those of you who may be confused as to why H is considered a better electron donor for the purposes of softening a Lewis acid center while alkyl groups are better electron donors for the purposes of stabilizing carbocations in organic chemistry, the dominant effect is the lower electronegativity of H relative to carbon (in CH_3). The effect of electron donation due to hyperconjugation isn't as great for thermodynamically stable bases like BX_3/BR_3.

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7.3.1: Theory of Hard and Soft Acids and Bases

Pearson Absolute Hardness is a useful metric of hardness based on orbital energies

The recognition that hard acids and bases possess a large HOMO-LUMO gap suggests that the gap size itself might serve as a useful index of hardness. The basis for this idea may be found by considering Pearson's definition of absolute hardness, η.[1] **Pearson's absolute hardness, η**, is half the second derivative of a species' energy with respect to changes in total number of electrons, N_{e^-}.

$$\text{Pearson's absolute hardness} = \eta = \frac{1}{2}\frac{d^2E}{dN_{e^-}^2}$$

$$(in \;\; eV)$$

and, since acids' and bases' hardness and softness are inversely related, Pearson's absolute softness, σ, is just the inverse of hardness.

$$\text{Pearson's softness} = \frac{1}{\eta}$$

Of these, Pearson's absolute hardness is related to the **Mulliken definition of electronegativity** as the first derivative of a species' energy with respect to changes in total number of electrons.

$$\text{Mulliken electronegativity} = \chi = \frac{dE}{dN_{e^-}}$$

$$(in \;\; eV)$$

Operationally, both the Pearson hardness and Mulliken electronegativity are approximated in terms of the energies associated with unit changes in the number of electrons – *i.e.*, in terms of ionization energies and electronegativities. Specifically,

$$\text{Pearson's absolute hardness} = \eta \approx \frac{IE - EA}{2}$$

$$\text{Mulliken electronegativity} = \chi \approx \frac{IE + EA}{2}$$

where IE and EA are in eV.

The connection between Pearson's absolute hardness/softness and the HOMO-LUMO gap then follows from Koopman's theorem, in which the ionization energy (IE) is just the opposite of the HOMO energy.

$$IE = -E_{HOMO}$$

Similarly, the electron affinity (EA), defined as the opposite of the energy released on absorption of an electron, may be taken as an approximation of the LUMO energy.

$$E_{LUMO} \approx -EA$$

So Pearson's absolute hardness is just half the HOMO-LUMO gap (band gap) size in electron volts:

$$\text{Pearson's absolute hardness} = \eta \approx \frac{E_{LUMO} - E_{HOMO}}{2}$$

where all values are given in eV,

and the Mulliken electronegativity is just the average of the HOMO and LUMO energies (~Fermi energy):

$$Mulliken\ electronegativity, \chi \approx -\frac{E_{LUMO} + E_{HOMO}}{2}$$

$$where\ all\ values\ are\ given\ in\ eV$$

The relationships between the Pearson absolute hardness, Mulliken electronegativity, and HOMO and LUMO energies are depicted schematically for the group 1A monocations in Figure **7.3.1.1**.

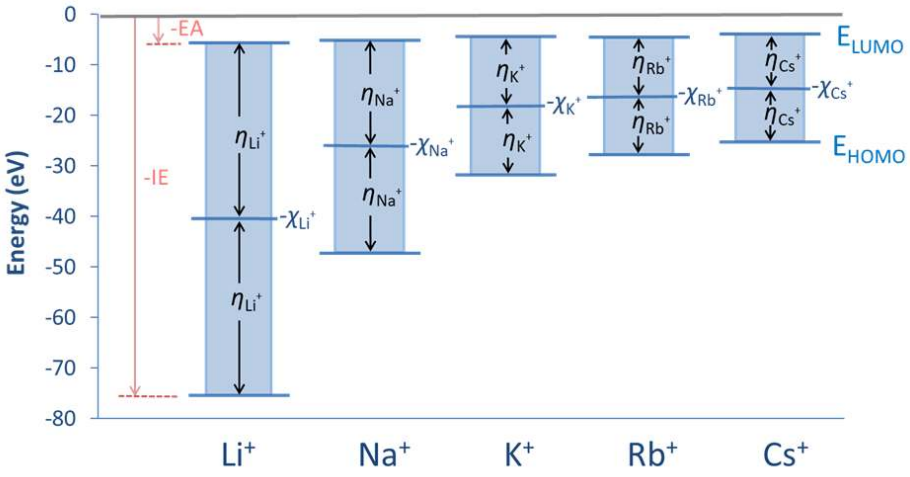


Figure **7.3.1.1**. Relationships between Pearson absolute hardness, Mulliken electronegativity, and HOMO and LUMO energies for the group 1A monocations.

Values of the Pearson hardness and Mulliken electronegativity for several acids and bases are given in Table **7.3.1.1**. The values in the table confirm the expected trends, showing an increase in hardness with size (down a group), with increasing charge, and as substituent electronegativity increases for a series of isolobal ions.

Table **7.3.1.1**: Pearson Absolute Hardness and Related Parameters for Selected Acids and Bases.[2] Taken from Pearson, R. G., Absolute electronegativity and hardness: application to inorganic chemistry. Inorganic Chemistry 1988, 27 (4), 734-740.

Species	Ionization Energy, IE or I (eV)	Electron Affinity, EA or A (eV)	Mulliken Electronegativity, χ (eV)	Pearson Absolute Hardness, η (eV)
Selected Acids				
Group 1A monocations				
Li^+	75.64	5.39	40.52	35.12
Na^+	47.29	5.14	26.21	21.08
K^+	31.63	4.34	17.99	13.64
Rb^+	27.28	4.18	15.77	11.55
Cs^+	25.1	3.89	14.5	10.6
Group 11 monocations				
Cu^+	20.29	7.73	14.01	6.28
Ag^+	21.49	7.58	14.53	6.96
Au^+	20.5	9.23	14.9	5.6
Isoelectronic Row 3 Metal Cations				
Na^+	47.29	5.14	26.21	21.08
Mg^{2+}	80.14	15.04	47.59	32.55
Al^{3+}	119.99	28.45	74.22	45.77
Changes with Transition Metal Ion Charge				
Fe^{2+}	30.65	16.18	23.42	7.24
Fe^{3+}	54.8	30.65	42.73	12.08
Co^{2+}	33.50	17.06	25.28	8.22
Co^{3+}	51.3	22.5	42.4	8.9
Boron trihalides				
BF_3	15.81	-3.5	6.2	9.7
BCl_3	11.60	0.33	5.97	5.64
BBr_3	10.51	0.82	5.67	4.85
CO_2	13.8	-3.8	5.0	8.8
CS_2	10.08	0.62	5.35	5.56
Selected Bases				
Group 17 monoanions (taken to be identical to the free atom values; for arguments as to why this is reasonable see Pearson, R. G., Inorg. Chem. 1988, 27 (4), 734-740.)				
F^-	17.42	3.40	10.41	7.01
Cl^-	13.01	3.62	8.31	4.70
Br^-	11.84	3.36	7.60	4.24
I^-	10.45	3.06	6.76	3.70

Species	Ionization Energy, IE or I (eV)	Electron Affinity, EA or A (eV)	Mulliken Electronegativity, χ (eV)	Pearson Absolute Hardness, η (eV)
Group 15 hydrides				
NH_3	10.7	-5.6	2.6	8.2
PH_3	10.0	-1.9	4.1	6.0
Trimethylpnictides				
NMe_3	7.8	-4.8	1.5	6.3
PMe_3	8.6	-3.1	2.8	5.9
$AsMe_3$	8.7	-2.7	3.0	5.7
Group 16 hydrides				
H_2O	12.6	-6.4	3.1	9.5
H_2S	10.5	-2.1	4.2	6.2
Phosphorous trihalides				
PF_3	12.3	-1.0	5.7	6.7
$PC1_3$	10.2	0.8	5.5	4.7
PBr_3	9.9	1.6	5.6	4.2

Drago-Wayland Acid-Base Parameters allow for estimation of the electrostatic and covalent contributions to the enthalpy of formation of a Lewis acid-base adduct.

Although Pearson hardness values are a useful metric of acids' and bases' hardness, they cannot easily be used to estimate the Lewis acid-base interaction energy. This is not the case for the EC model developed by Drago and Wayland.[3] In the **Drago and Wayland's EC Model,** the enthalpy of formation of an acid-base adduct, AB,

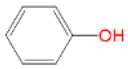
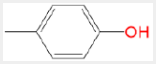
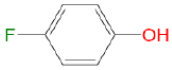
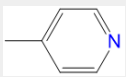
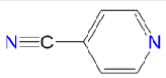
$$A + B \rightleftharpoons AB \qquad \Delta H_{AB\ adduct}$$

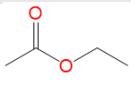
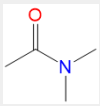
from the acid (A) and base (B) can be calculated as the sum of products of electrostatic (E) and covalent (C) factors that reflect the propensity of the acid and base to engage in strong electrostatic and covalent interactions with one another:

$$-\Delta H_{AB\ adduct} = E_A E_B + C_A C_B$$

where E_A and C_A are the electrostatic and covalent parameters for the acid and E_B and C_B the electrostatic and covalent parameters for the base given in units of $kcal^{½}\ mol^{-½}$. E and C parameters for selected acids and bases are given in Table **7.3.1.2** .

Table **7.3.1.2**: E and C Parameters for selected Lewis acids and bases according to the ECW model.[4,5] Taken from Vogel, G. C.; Drago, R. S., The ECW Model. *Journal of Chemical Education* 1996, 73 (8), 701 and Drago, R. S. A modern approach to acid-base chemistry. *Journal of Chemical Education* 1974, 51 (5), 300 (for BF_3).

Species	E (kcal^{½} mol$^{-½}$)	C (kcal^{½} mol$^{-½}$)	W (kcal mol^{-1})	C/E
Acids				
I_2	0.5†	2†	0	4
ICl	2.92	1.66	0	0.57
H_2O	1.31	0.78	0	0.59
SO_2	0.51	1.56	0	3.1
$HCCl_3$ (chloroform)	1.56	0.44	0	0.28
$(CH_3)_3COH$	1.07	0.69	0	0.65
$(CF_3)_3COH$	3.06	1.88	-0.87	0.61
	2.27	1.07	0	0.47
	2.23	1.03	0	0.46
	2.30	1.11	0	0.48
	1.38	0.68	0	0.49
BF_3	1.62	9.88		6.10
$B(CH_3)_3$	2.90	3.60	0	1.2
$Al(CH_3)_3$	8.66	3.68	0	0.43
$Ga(C_2H_5)_3$	6.95	1.48	0	0.21
$In(CH_3)_3$	6.60	2.15	0	0.33
$Zn[N(Si(CH_3)_3)]_2$	2.75	2.32	0	0.84
$Cd[N(Si(CH_3)_3)]_2$	2.50	1.83	0	0.73
Bases				
NH_3	2.31	2.04		0.88
CH_3NH_2	2.16	3.13		1.4
$(CH_3)_2NH$	1.80	4.21		2.3
$(CH_3)_3N$	1.21	5.61		4.6
	1.78	3.54		2.0
	1.81	3.73		2.0
	1.53	2.94		1.9

Species	E ($kcal^{½}\ mol^{-½}$)	C ($kcal^{½}\ mol^{-½}$)	W ($kcal\ mol^{-1}$)	C/E
CH_3CN	1.64	0.71		0.43
$ClCH_2CN$	1.67	0.33		0.20
$CH_3C(O)CH_3$	1.74	1.26		0.72
$(C_2H_5)_2O$	1.80	1.63		0.91
	1.64	2.18		1.3
 (EtOAc)	1.63	0.95		0.58
	2.35†	1.31		0.56
$(CH_3)_2S$	0.25	3.75		15
$(CH_3CH_2)_2S$	0.24	3.92†		15
	0.26	4.07		16
$(CH_3)_2Se$	0.05	4.24		83
$(CH_3)_2SO$	2.4	1.47		0.61
$(CH_3)_3P$	0.25	5.81		24
$(CH_3O)_3P$	0.13	4.83		37
$(C_6H_5)_3PO$	2.59	1.67		0.64
$(C_6H_5)_3PS$	0.35	3.65		10
C_6H_6	0.70	0.45		0.64

† These values were fixed to parameterize the rest of the E and C parameters.

Trends in the relative values of C and E for the acids and bases in Table **7.3.1.2** are very roughly consistent with the trends in hardness and softness outlined earlier. However, the parameters suggest that some trends in hardness reflect changes in species' ability to engage in ionic interactions while others reflect changes in species' ability to engage in strong covalent interactions. For example, C_B for the dimethylchalcogenides increases steadily from 1.5 to 4.25 $kcal^{½}\ mol^{-½}$ on going from Me_2O to Me_2Se while E_B decreases from 1.68 to 0.05 $kcal^{½}\ mol^{-½}$, suggesting that electrostatic and covalent factors are both involved in a decrease in base hardness down group 16. However, in the case of phosphines and amines it appears that electrostatic factors are primarily responsible for the decrease in hardness down group 15. On going from Me_3N to Me_3P, C_B only increases slightly from 5.61 to 5.81 $kcal^{½}\ mol^{-½}$ while E_B decreases from 1.21 to 0.25 $kcal^{½}\ mol^{-½}$ - *i.e.*, to 20% of the Me_3N value.

However, some species tend to have very high values for both E and C, reflecting their ability to engage in strong electrostatic and covalent interactions, while others have small values for both, reflecting their relative stability as free species in solution.

As can be seen by comparing the acids and bases listed in the absolute hardness table (Table **7.3.1.1**) and the EC parameters table (Table **7.3.1.2**). The EC model has primarily been applied to organic and main group organometallic acids and bases. However, a variety of extensions have been proposed that enable its wider applicability.

The simple EC model only includes electrostatic and covalent considerations and thus ignores steric, lattice energy, and other contributions to the interaction energy. Thus it is only useful for analyzing the interaction energies of sterically unhindered adducts in which solvation energy and other contributions to the overall interaction energy are insignificant. However, additional refinements of the model attempt to extend its usefulness by accomodating various factors, such as

- *Steric strain.* Specifically, Hancock and Martell[6] introduced a D parameter to account for any additional steric strain introduced upon adduct formation,* giving

$$-\Delta H_{AB\ adduct} = E_A E_B + C_A C_B - D_A D_B$$

- *Charge transfer upon adduct formation.* As discussed in section 6.4.2, the formation of a Lewis acid-base complex results in a net transfer of electron density from the electron donor (base) to the acceptor (acid). Drago and Wong[7] extended the EC model to include that charge transfer by adding what they called receptance factors that account for the acid's ability to receive electron density (R_A) and transference factors that account for the base's ability to donate electron density (T_B), giving

$$-\Delta H_{AB\ adduct} = E_A E_B + C_A C_B + R_A T_B$$

  This extension of the EC model is called the **electrostatic-covalent-transfer or ECT model**. Notably, it has been applied successfully to adducts involving ions, for which the $R_A T_B$ term can account for as much as 31% of the interaction energy.

- *Any constant energy term, such as the energy needed to cleave a dimer in order to make the Lewis acid (e.g., $Al_2Cl_6 \rightarrow 2AlCl_3$).* Drago and Vogel[4] extended the EC model to accommodate these constant energy terms, which they designated W. The resulting model is called the **ECW model,** for which

$$-\Delta H_{AB\ adduct} = E_A E_B + C_A C_B + W$$

where

$$W = W_A + W_B$$

A simple application of EC and extended EC models is that they allow the enthalpy of adduct formation to be calculated. These enthalpy calculations based on the EC model are consistent with the superior interaction energy of hard-hard and soft-soft interactions compared to hard-soft ones. Consider, for example, the transfer of I_2 between BF_3 and $InMe_3$, H_3N-BF_3, and H_3N-$InMe_3$.

$$H_3N - BF_3 + InMe_3 \rightleftharpoons BF_3 + H_3N - InMe_3$$

Since H_3N is a hard base and BF_3 and $InMe_3$ are harder and softer acids, respectively, the equilibrium is expected to favor the reactant, H_3N-BF_3. Assuming the equilbrium is enthalpically driven, this qualitative analysis is consistent with the expected endothermic enthalpy of the reaction, as may be seen from the calculated enthalpies of adduct formation for both H_3N-BF_3 and H_3N-$InMe_3$.

For H_3N-BF_3:

$$-\Delta H_{H_3N-BF_3} = E_{BF_3} E_{NH_3} + C_{BF_3} C_{NH_3}$$

$$-\Delta H_{H_3N-BF_3} = (1.62)(2.31) + (9.88)(2.04)$$

$$-\Delta H_{H_3N-BF_3} = 3.74\ kcal/mol + 20.1\ kcal/mol = 23.8\ kcal/mol$$

$$\Delta H_{H_3N-BF_3} = -23.8\ kcal/mol$$

For H_3N-$InMe_3$:

$$-\Delta H_{H_3N-InMe_3} = E_{InMe_3} E_{NH_3} + C_{InMe_3} C_{NH_3}$$

$$-\Delta H_{H_3N-InMe_3} = (6.6)(2.31) + (2.15)(2.04)$$

$$-\Delta H_{H_3N-InMe_3} = 15.25\ kcal/mol + 4.39\ kcal/mol = 19.63\ kcal/mol$$

$$\Delta H_{H_3N-InMe_3} = -19.63\ kcal/mol$$

So H_3N-BF_3 is enthalpically favored by -4.2 kcal/mol [=-23.8 kcal/mol - (-19.63 kcal/mol) according to Hess' Law].

In addition to their utility for estimating enthalpies of Lewis acid-base complex formation, EC and related models serve as a useful tool for estimating the relative importance of ionic, covalent, and steric factors in complex formation. Specifically,

- The relative contributions of ionic and covalent factors can be calculated directly, as from the E and C terms. This can provide insight into why some complexes are more stable than others. Such calculations reveal that the hard-hard adduct H_3N-BF_3 is favored over the hard-soft adduct H_3N-$InMe_3$ because of the strong covalent interaction holding together H_3N-BF_3. The covalent term accounts for 84% of the energy of the H_3N-BF_3 interaction and is largely lost upon formation of H_3N-$InMe_3$, for which it contributes only 22% of the interaction energy. When the electrostatic term is accounted for, it can be seen that the formation of H_3N-$InMe_3$ from H_3N-BF_3 is disfavored, since it would result in a loss of 15.7 kcal/mol of covalent stabilization that would be incompletely compensated for by a gain of 11.5 kcal/mol of electrostatic stabilization.
- The role of other contributions to the bonding in a Lewis acid-base complex may be estimated from the discrepancy between the experimental and EC model calculated stabilization energies. This is because the EC parameters assume sigma bonding and so any deviation between the calculated and experimental enthalpies of complex formation can be attributed to non-sigma contributions.
    - This is done explicitly in extensions of the EC model. For instance, in the case of the Hancock and Martell, ECT, and ECW extensions of the EC model, the contributions of the steric, charge transfer, and constant energy factors (like dimer dissociation) are directly computed in the model.
    - Comparisons of the difference between the energies calculated using ordinary EC parameters and the observed enthalpies has also been used as an estimate of the
        - steric strain energy in strained adducts, which exhibit a less exothermic heat of adduct formation than expected
        - π-backbonding energy in adducts which are capable of such interactions and exhibit a more exothermic heat of formation than expected.[8-10]
    - For examples see (a) Drago, R. S., The interpretation of reactivity in chemical and biological systems with the E and C model. Coordination Chemistry Reviews 1980, 33 (3), 251-277; (b) Drago, R. S.; Bilgrien, C. J., Inductive transfer and coordination of ligands in metal—metal bonded systems. Polyhedron 1988, 7 (16), 1453-1468; (c) Drago, R. S., The question of a synergistic metal-metal interaction leading to .pi.-back-bond stabilization in dirhodium tetrabutyrate adducts. Inorganic Chemistry 1982, 21 (4), 1697-1698.
- The role of electrostatic, covalent, and other contributions to the spectroscopic behavior of Lewis acid-base complexes can be assessed similarly using specialized versions of the ECW or ECT model that allow for calculation of changes in spectroscopic parameters upon adduct formation - *e.g.*, OH stretching frequencies. Details are beyond the scope of this text but may be found in the original literature,[11] for example, Drago, R. S.; Vogel, G. C. *JACS* 1992, 114 (24), 9527-9532; Vogel, G. C.; Drago, R. S., *J. Chem. Educ.* 1996, 73 (8), 701; Drago, R. S.; Wong, N. M., *J. Chem. Educ.* 1996, 73 (2), 123.).

Pearson Softness Parameters have been proposed as a means of calculating the equilibrium constant for formation of a Lewis acid-base adduct, although they are more commonly used to estimate metal toxicity

Pearson also proposed a softness parameter that can be used to estimate the thermodynamics of Lewis acid-base complex formation, this time in the form of the equilibrium constant for

$$A + B \overset{K}{\rightleftharpoons} AB$$

for which Pearson proposed

$$logK = S_A S_B + \sigma_A \sigma_B$$

where S_A and S_B are acid and base parameters related to the strength of the acid-base interaction and σ_A and σ_B are acid and base parameters related to softness. This approach hasn't found as wide an acceptance in studies of chemical reactivity as the Drago-Wayland and absolute hardness parameters. However, because the toxicity of metal ions sometimes depends on their propensity to bind soft Lewis bases in living systems, the softness parameters which Pearson and Mawby subsequently proposed based on the relative energies of metal fluorine and metal iodine bonds[12] have been widely used as a tool for predicting metal ion toxicity.[13]

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Notes

* More precisely, the D parameters account for the difference in steric strain in the adduct relative to a water adduct of the Lewis acid.

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- **6.6.1: Quantitative Measures of Hardness, Softness, and Acid-Base Interactions from a Hard Soft Acid-Base Principle Perspective Involve Orbital Energies and/or Apportioning Acid-Base Bonding in Terms of Electrostatic and Covalent Factors** by Stephen M. Contakes is licensed CC BY 4.0.

7.3.2: HSAB Quantitative Measures

The Hard Soft Acid Base Principle is a Conceptual Tool for Thinking About Patterns of Lewis Acid-Base Reactivity

The explanation of the trends in metal distribution, halide salt solubility, and preferred metal coordination patterns is rooted in Arland, Chatt, and Davies' observation that *Lewis acids and bases could be classified into two groups based on their propensity to form stable compounds with one another* (*e.g.* acids in a class tend to form more stable adducts with bases in the same class than they did with bases in the other).[1] Arland, Chatt, and Davies somewhat boringly termed these groups class a and class b but today they are known by Ralph Pearson's name for them. Pearson called the class a acids and bases hard and class b acids and bases soft. These terms reflect how "soft" these substance's electron clouds are towards distortion or, in other words, their polarizability (Figure **7.3.2.1**). Pearson terms acids and bases which are relatively polarizable **soft** and those which are difficult to polarize **hard.**

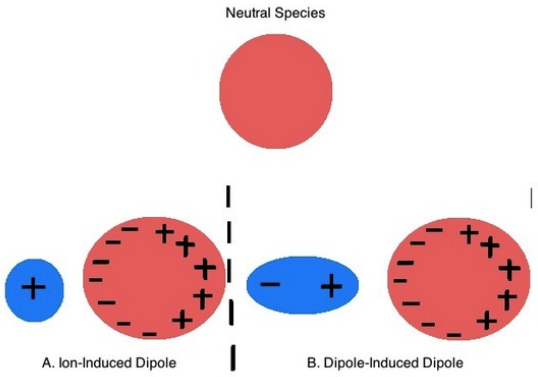


Figure **7.3.2.1**: Polarizability refers to the ease with which a substance's electron cloud may be distorted under the action of an electric field. A fragment's polarizability determines the degree to which its electron cloud is distorted by A.) an Ion and B.) a polar molecule to induce a dipole moment. The figure is taken from (and the caption expanded from) Cox, Kelly and Dana Reusser "Polarizability"

Recognizing Hard and Soft Acids and Bases

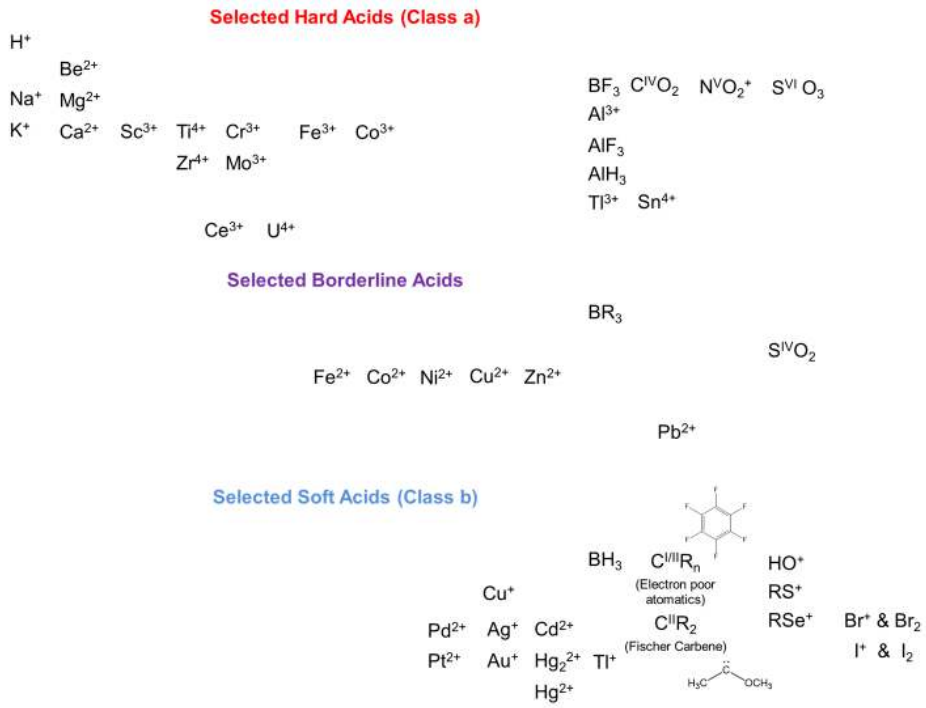
Hard acids and bases come in two varieties:

1. hard acid and base sites that possess few valence electrons and for which polarization therefore involves distorting core electrons, which are difficult to distort because they are close to the nucleus and experience a high nuclear charge. The most common examples of such substances are Lewis acid hard acids towards the left of the periodic table.
2. hard acid and base sites with a high charge density (highly charged relative to size) and/or which are electron deficient. In these cases polarization involves distorting electrons that already experience strong unshielded electrostatic interactions.

Soft acids and bases also come in two varieties

1. soft acids and bases which posses many valence electrons and so are more readily polarized. In consequence, all other things being equal, soft acids and bases are more likely to be found towards the middle or right of the periodic table.
2. soft acids and bases with little charge density and/or which are relatively electron rich.

Note that the hard-soft classification should not be thought of as if all hard acids and bases are equally hard and all soft acids and bases equally soft. There is a graduation in hardness and softness and a number of intermediate acids and bases which do not fit neatly in either category. With this caveat in mind, representative **hard, soft, and borderline acids** are given below. Notice how they illustrate the trends just outlined.



As expected, hard acids tend to be found towards the left side of the periodic table and involve higher oxidation states and/or electron donating substituents while soft acids are more common to the right of the periodic table and involve lower oxidation states and/or electron donating substituents.

Illustrative hard, soft, and borderline bases are given below. Again, notice how these substances illustrate the general trends.

Selected Hard Bases (Class a)

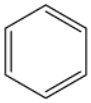
Nitrogen bases	Oxygen bases		small halides
NH_2^-	OH^-	CO_3^{2-}	F^-
NH_3	H_2O	RCO_2^-	Cl^-
RNH_2	ROH	NO_3^-	
NH_2NH_2	ROR	PO_4^{3-}	
		SO_4^{2-}	

Selected Borderline Bases

electron-poor Nitrogen bases		low oxidation state element oxyanions	intermediate halides
N_3^-		NO_2^-	
NO_2^-			Br^-
SCN^-		SO_3^{2-}	
N_2			

Selected Soft Bases (Class b)

Carbon bases	P and As bases	Sulfur bases	large halides & pseudohalides
R^-	PR_3	RS^-	H^-
CO	$P(OR)_3$	RSH	I^-
CN^-	AsR_3	RSR	
RNC		SCN^-	
$R_2C{=}CR_2$ (alkenes)			



(electron-rich aromatics)

Qualitative Estimation of the Relative Hardness and Softness of Lewis Acids and Bases

As can be seen from the examples above, **hard acids are relatively electron-poor and hard bases electron-rich** since they have comparatively

- small frontier orbitals, reflective of their relatively small atom/ion/fragment sizes
- high (for acids) or low (for bases) oxidation states on the base atom, reflected in a large positive formal charge (for acids) or negative formal charge (for bases)
- low polarizability, due to loss or gain of substantial numbers of electrons, or the localization of
  - positive charge on an electropositive element or an atom bearing electron-withdrawing substituents
  - negative charge on an electronegative element or an atom bearing electron-donating substituents

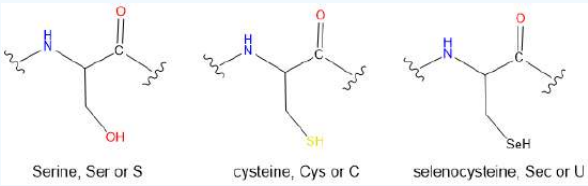
In contrast to hard acids and bases, **soft acids are relatively electron-rich and soft bases larger and more electron poor** since they have comparatively

- large frontier orbitals, reflective of their relatively large atom/ion/fragment sizes
- low oxidation states, often resulting in small or nonexistent atomic charges
- high polarizability, as might be expected of species in which electron-electron repulsions are lower and electrons are spread over a large volume. Sometimes this is indicated by
  - positive charge on an electronegative element or an atom bearing electron-donating substituents
  - negative charge on an electropositive element or an atom bearing electron-withdrawing substituents

Exercise 7.3.2.1

Rank the acids or bases in each set in increasing order of expected hardness.

a. Cr^{2+} and Cr^{3+}
b. H^+, Cs^+, and Tl^+
c. SCN^- (acting as a base at N) and SCN^- (acting as a base at S)
d. AlF_3, AlH_3, $AlMe_3$
e. The side chains of the following proteinogenic amino acids

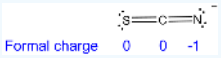


Answer

(a) $Cr^{2+} < Cr^{3+}$ All other things being equal, hardness increases with oxidation state.

(b) $Tl^+ < Cs^+ < H^+$ The order reflects Cs^+ and Tl^+'s larger size relative to H^+ (which doesn't possess any electrons that can be polarized anyway) and that Tl^+ still possesses two valence electrons while Cs^+ possesses none.

(c) SCN^- (acting as a base at S) < SCN^- (acting as a base at N). The order reflects the greater electronegativity of N than S and N's possession of a more negative formal charge of -1.



(d) $AlH_3 < AlMe_3 < AlF_3$. The hardness increases as the substituents on the Lewis acid Al center become less electron donating and more electron withdrawing (and, incidentally, harder bases) as their electronegativity increases in the order H^- < CH_3^- < F^-. Note that the order of electron donating ability for H^- and CH_3^- is the opposite observed for carbocations, for which hyperconjugation plays a larger role.

(e) Sec < Cys < Ser. The hardness increases as the electronegativity of the Lewis base chalcogen increases on going from a selenol to a thiol to an alcohol.

The Hard-Soft Acid-Base Principle (HSAB Principle)

The **Hard-Soft acid-base principle (HSAB Principle) explains patterns in Lewis acid-base reactivity in terms of a *like reacts with like preference***. Both thermodynamically and kinetically, hard acids prefer hard bases and soft acids soft bases. Specifically,

- Thermodynamically, hard acids form stronger acid-base complexes with hard bases while soft acids form stronger complexes with soft bases.
- Kinetically, hard acids/electrophiles react more quickly with hard bases/nucleophiles while soft acids/electrophiles react more quickly with soft bases/neucleophiles.

Applications of the HSAB principle include

1. Predicting the equilibrium or speed of *Lewis acid-base metathesis and displacement reactions.* In a Lewis acid-base **metathesis reaction** the acids and bases swap partners

$$\mathbf{A_1 : B_1 + A_2 : B_2 \overset{k_1,\, K_{eq_1}}{\rightleftharpoons} A_1 : B_2 + A_2 : B_1}$$

For example, the equilibrium position of the metathesis reaction between $\mathbf{TlF}$ and $\mathbf{K_2S}$ favors the products:

$$\mathbf{2\,TlF + H_2S \rightleftharpoons Tl_2S + 2\,KF}$$

consistent with the HSAB's hard-hard and soft-soft preference.



The HSAB principle also allows for prediction of the position of displacement reactions, in which a Lewis acid or base forms an adduct using a base or acid from an existing Lewis acid-base complex. In these reactions, the displacement of acid or base from the reactant complex may be thought of as a sort of metathesis reaction, one in which in the unbound acid or base switches places with one in the complex. For example, the reaction between **HI** and methylmercury cation

$$\mathbf{HI + HgSCH_3^+ \rightleftharpoons CH_3SHgI + H^+}$$

involves displacement of an iodide from **HI** to give $\mathbf{CH_3HgI}$. The position of the equilibrium favors $\mathbf{CH_3HgI}$ since both $\mathbf{CH_3Hg^+}$ and $\mathbf{I^-}$ are soft, while $\mathbf{H^+}$ is a hard acid.



? Exercise 7.3.2.2

Predict the position of equilibrium for the following reaction.

$$\mathbf{Fe_2O_3 + 3\,Ag_2S \rightleftharpoons Fe_2S_3 + 3\,Ag_2O}$$

Answer

The equilibrium will favor the reactants (K<1) since the hard-hard and soft-soft interactions in the reactants are more stable than the hard-soft interactions in the products.



? Exercise 7.3.2.3

Predict whether K for the following equilibria will be <<1, ~1, or >>1.

a. $\mathbf{2\,HF + (CH_3Hg)_2S \rightleftharpoons 2\,CH_3HgF + H_2S}$
b. $\mathbf{Ag(NH_3)_2^+ + 2\,PH_3 \rightleftharpoons Ag(PH_3)_2^+ + 2\,NH_3}$
c. $\mathbf{Ag(PH_3)_2^+ + 2\,H_3B{-}SH_2 \rightleftharpoons 2\,H_3B{-}PH_3 + Ag(SH_2)_2^+}$
d. $\mathbf{H_3B{-}NH_3 + F_3B{-}SH_2 \rightleftharpoons H_3B{-}SH_2 + F_3B{-}NH_3}$

Answer

a. K< < 1 since the reactant adducts are hard-hard and soft-soft while the products involve hard-soft interactions.

b. K>>1 since the reactant complex, diamine silver(I), is a complex of a hard base, NH_3, with the soft acid, Ag^+, while the product is a complex of the same soft acid with the soft base phosphine.

c. K~1 since all the adducts amongst the reactants and products involve soft acids and bases.

d. K>>1 since BH_3 is a softer acid than BF_3, so it will form a stronger complex with the softer base H_2S while the harder BF_3 forms a stronger complex with the harder base NH_3.

2. Predicting the relative strengths of a given set of *Lewis acids or bases towards a particular substrate*. Consider, for example, the relative strengths of a BH_3, BMe_3, and BF_3 towards group 15 hydrides like NH_3, PH_3, and AsH_3. Of the

boranes listed, the hardest acid BF_3 is the strongest acid towards the hard base NH_3 while BH_3 is the strongest towards AsH_3.[†]

? Exercise 7.3.2.4

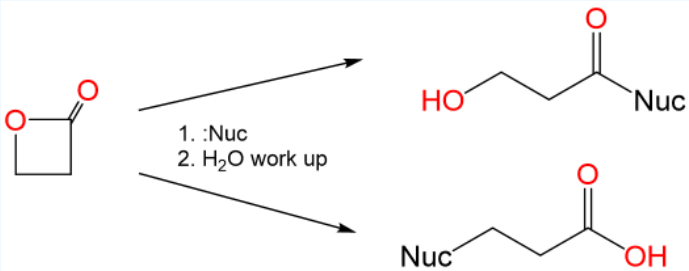
Which acid will form the most stable complex with **CO**: $\mathbf{BH_3}$, $\mathbf{BF_3}$, or $\mathbf{BMe_3}$?

Answer

$\mathbf{BH_3}$. Since **CO** forms complexes primarily through its carbon lone pair, it is a soft base and so will form the strongest complex with the softest Lewis acid.

? Exercise 7.3.2.5

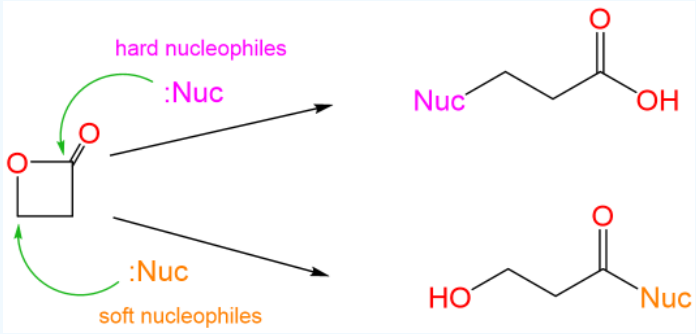
When lactones react with nucleophiles, they can undergo ring opening reactions to give either an alcohol or a carboxylic acid, as shown for propiolactone below:



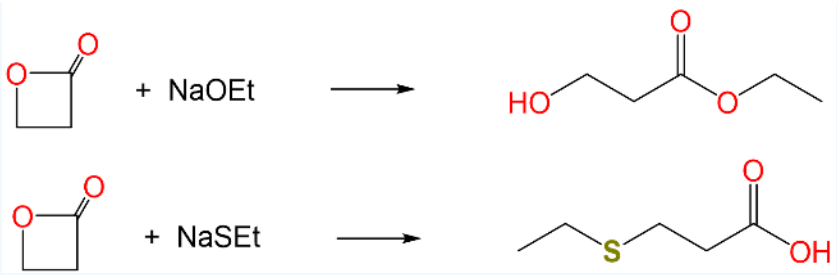
In the reaction above, sterically unhindered alkoxides give one product and sterically unhindered thioalkoxides the other. Explain why this is the case and predict the products of the reaction between propiolactone and the sodium salts of ethoxide and thioethoxide.

Answer

The two reaction products correspond to nucleophilic attack at the lactones' two electrophilic carbon centers. Specifically, the acid is produced by attack at the softer C^{I} center of the CH_2 directly attached to the ester oxygen and the alcohol by nucleophilic attack at the harder C^{III} center of the ester carbonyl.



Consequently, it is reasonable to expect that the harder base ethoxide will nucleophilically attack the harder carbonyl carbon while the softer thioethoxide will attack the softer methylene carbon.



The theoretical interpretation of the hard-soft acid-base principle is that hard-hard preferences reflect superior electrostatic stabilization while soft-soft preferences reflect superior covalent stabilization.

The hard-hard and soft-soft preferences in Lewis acid-base interactions reflect that

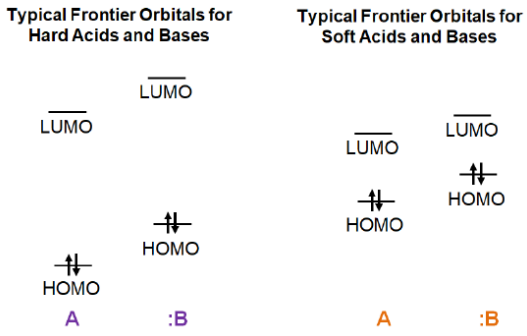
- The lone pair of a hard base is strongly stabilized electrostatically by a hard acid.
- The lone pair of a soft base is strongly stabilized by forming a covalent bond with a soft acid.
- The lone pair of a hard or soft base is comparatively weakly stabilized by an acid opposite to it in hardness or softness since the overall electrostatic and covalent stabilization of the adduct is comparatively weak.

To see why this is the case it is helpful to divide the contributions to the interaction energy between an acid and a base as follows:

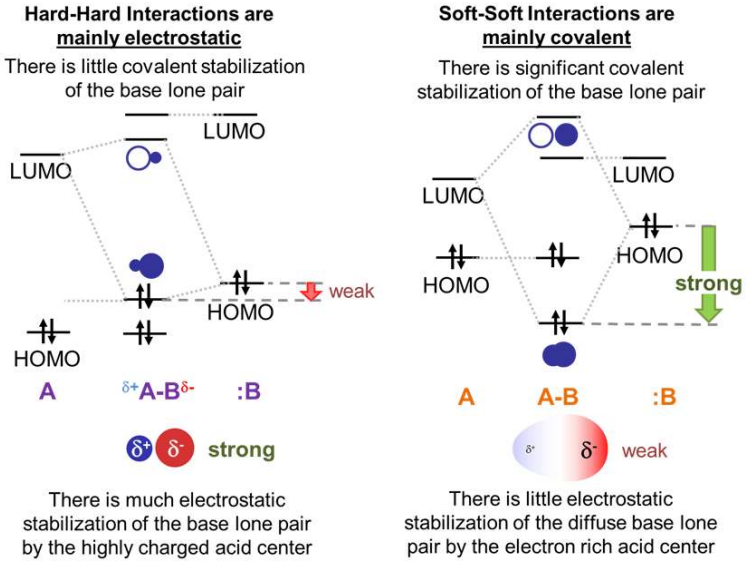
$$\text{Interaction Energy} = \underbrace{\text{Electrostatic attractions and repulsions of partial atomic charges}}_{\text{Ionic term}} + \underbrace{\text{Interactions between filled orbitals on one fragment and unfilled orbitals on the other}}_{\text{Covalent term}} + \underbrace{\text{Electrostatic repulsions between filled orbitals on the two fragments}}_{\text{Steric term}}$$

Of the three contributions to the interaction energy, only the ionic and covalent terms directly relate to the hardness of the interacting acid and base. One approach to thinking about how hardness influences the ionic and covalent contributions is to consider the frontier orbitals involved in the acid-base interaction. This is sometimes done through the use of the Salem-Klopman equation,[1,*] although in the treatment which follows a more qualitative approach will be employed.

Both hard acids and bases will have comparatively low energy HOMO levels and high energy LUMO levels, with a correspondingly high HOMO-LUMO gap. In contrast, soft acids and bases will have comparatively high-energy HOMO levels and low-energy LUMO levels, giving a comparatively smaller HOMO-LUMO gap.



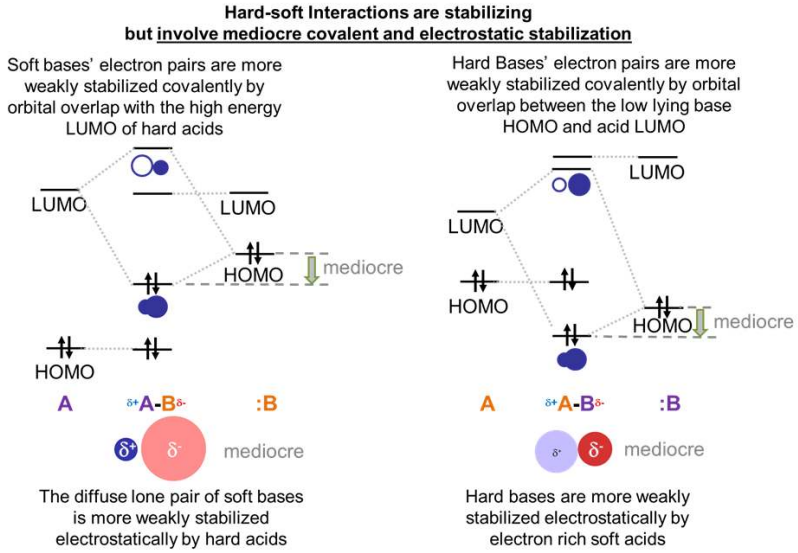
Given this, consider the frontier orbital interactions involved in the formation of an acid-base complex for the possible cases, as illustrated schematically below.



The large gap in energy between hard bases' highly stabilized HOMO lone pairs and the high energy LUMO of hard acids ensures that in **hard acid-hard base adducts the dominant stabilizing interaction will involve electrostatic attraction between the base lone pair and the electropositive Lewis acid center**. Fortunately, since the electron clouds in hard bases are relatively dense and electron rich while hard Lewis acids are highly charged and small, these electrostatic interactions are strong.

In contrast, in **soft acid-soft base adducts, the dominant stabilizing interaction will be covalent.** This is because the small gap in energy between a soft base HOMO and soft acid LUMO enables the formation of a well-stabilized bonding orbital with significant electron density between the acid and base.

The orbitals' interactions between hard acids and soft bases and soft acids and hard bases are intermediate between the hard acid-hard base and soft acid-soft base cases.



This means that the adducts are stable relative to free acid and base – just not as well stabilized as in the hard acid and hard base case. In the case of hard acids and soft bases the hard acids are less able to stabilize the soft bases' relatively diffuse electron pair electrostatically and there isn't as much covalent stabilization as in adducts of soft acids and bases due to the hard acid's high energy.

References

1. Ahrland, S.; Chatt, J.; Davies, N. R., The relative affinities of ligand atoms for acceptor molecules and ions. Quarterly Reviews, Chemical Society 1958, 12 (3), 265-276.

2. Pearson, R. G., Hard and Soft Acids and Bases. Journal of the American Chemical Society 1963, 85 (22), 3533-3539.

3. Fleming, I., Molecular orbitals and organic chemical reactions. Reference ed.; Wiley: Hoboken, N.J., 2010.

Notes

* Despite the fruitfulness of this observation, in general it is important to reduce the potential for observer bias by checking observations like these against compounds reported in the chemical literature and databases like the Inorganic Crystal Structure and Cambridge Crystallographic Databases.

** These are very soluble in water, to the point where some solutions are perhaps better described as solutions of water in the halide.

† This can be predicted based on the relative hardness of BF_3, BR_3, and BH_3 in the list of hard and soft acids. However, for those of you who may be confused as to why H is considered a better electron donor for the purposes of softening a Lewis acid center while alkyl groups are better electron donors for the purposes of stabilizing carbocations in organic chemistry, the dominant effect is the lower electronegativity of H relative to carbon (in CH_3). The effect of electron donation due to hyperconjugation isn't as great for thermodynamically stable bases like BX_3/BR_3.

†† For more on the Salem-Klopman equation see Fleming, I., Molecular orbitals and organic chemical reactions. Reference ed.; Wiley: Hoboken, N.J., 2010; pp. 138-143.

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- **6.6.2: Hard-Hard and Soft-Soft preferences may be explained and quantified in terms of electrostatic and covalent and electronic stabilization on the stability of Lewis acid-base adducts** by Stephen M. Contakes is licensed CC BY 4.0.

CHAPTER OVERVIEW

8: Electrochemistry

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.

8.1: Oxidation-Reduction Reactions
8.2: Balancing Redox Reactions
8.3: Galvanic Cells
8.4: Standard Electrode Potentials
8.5: Strengths of Oxidants and Reductants
8.6: E, ΔG, and K (The Big Triangle of Chemistry)
8.7: Cell Potential as a Function of Concentrations
8.8: Batteries- Producing Electricity Through Chemical Reactions
8.9: Corrosion- Unwanted Voltaic Cells
8.10: Electrolysis- Causing Nonspontaneous Reactions to Occur

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8.1: Oxidation-Reduction Reactions

An oxidation-reduction (redox) reaction is a type of chemical reaction that involves a transfer of electrons between two species. An oxidation-reduction reaction is any chemical reaction in which the oxidation number of a molecule, atom, or ion changes by gaining or losing an electron. Redox reactions are common and vital to some of the basic functions of life, including photosynthesis, respiration, combustion, and corrosion or rusting.

Rules for Assigning Oxidation States

The oxidation state (OS) of an element corresponds to the number of electrons, e^-, that an atom loses, gains, or appears to use when joining with other atoms in compounds. In determining the oxidation state of an atom, there are seven guidelines to follow:

1. The oxidation state of an individual atom is 0.
2. The total oxidation state of all atoms in: a *neutral species* is 0 and in an *ion* is equal to the ion charge.
3. Group 1 metals have an oxidation state of +1 and Group 2 an oxidation state of +2
4. The oxidation state of fluorine is -1 in compounds
5. Hydrogen generally has an oxidation state of +1 in compounds
6. Oxygen generally has an oxidation state of -2 in compounds
7. In binary metal compounds, Group 17 elements have an oxidation state of -1, Group 16 elements of -2, and Group 15 elements of -3.

> *The **sum** of the oxidation states is equal to zero for neutral compounds and equal to the **charge** for polyatomic ion species.*

Example 8.1.1: Assigning Oxidation States

Determine the Oxidation States of each element in the following reactions:

a. $\mathbf{Fe}(s) + \mathbf{O_2}(g) \longrightarrow \mathbf{Fe_2O_3}(g)$
b. $\mathbf{Fe^{2+}}(aq)$
c. $\mathbf{Ag}(s) + \mathbf{H_2S} \longrightarrow \mathbf{Ag_2S}(g) + \mathbf{H_2}(g)$

Solutions

A. **Fe** and $\mathbf{O_2}$ are free elements; therefore, they each have an oxidation state of 0 according to Rule #1. The product has a total oxidation state equal to 0, and following Rule #6, **O** has an oxidation state of -2, which means **Fe** has an oxidation state of +3.
B. The oxidation state of **Fe** ions just corresponds to its charge since it is a single element species; therefore, the oxidation state is +2.
C. **Ag** has an oxidation state of 0, **H** has an oxidation state of +1 according to Rule #5, $\mathbf{H_2}$ has an oxidation state of 0, **S** has an oxidation state of -2 according to Rule #7, and hence **Ag** in $\mathbf{Ag_2S}$ has an oxidation state of +1.

Example 8.1.2: Assigning Oxidation States

Determine the oxidation states of the phosphorus atom bold element in each of the following species:

a. $\mathbf{Na_3PO_3}$
b. $\mathbf{H_2PO_4^-}$

Solutions

a. The oxidation numbers of **Na** and **O** are +1 and -2. Because sodium phosphite is neutral species, the sum of the oxidation numbers must be zero. Letting *x* be the oxidation number of phosphorus, 0= 3(+1) + *x* + 3(-2). *x*=oxidation number of P= +3.

b. Hydrogen and oxygen have oxidation numbers of +1 and -2. The ion has a charge of -1, so the sum of the oxidation numbers must be -1. Letting *y* be the oxidation number of phosphorus, -1= *y* + 2(+1) +4(-2), *y*= oxidation number of P= +5.

Example 8.1.3: Identifying Reduced and Oxidized Elements

Determine which element is oxidized and which element is reduced in the following reactions (be sure to include the oxidation state of each):

a. $\mathrm{Zn + 2\,H^+ \longrightarrow Zn^{2+} + H_2}$
b. $\mathrm{2\,Al + 3\,Cu^{2+} \longrightarrow 2\,Al^{3+} + 3\,Cu}$
c. $\mathrm{CO_3^{2-} + 2\,H^+ \longrightarrow CO_2 + H_2O}$

Solutions

a. Zn is oxidized (Oxidation number: 0 → +2); H^+ is reduced (Oxidation number: +1 → 0)
b. Al is oxidized (Oxidation number: 0 → +3); Cu^{2+} is reduced (+2 → 0)
c. This is not a redox reaction because each element has the same oxidation number in both reactants and products: O= -2, H= +1, C= +4.

An atom is oxidized if its oxidation number increases, the reducing agent, and an atom is reduced if its oxidation number decreases, the oxidizing agent. The atom that is oxidized is the reducing agent, and the atom that is reduced is the oxidizing agent. (Note: the oxidizing and reducing agents can be the same element or compound).

Oxidation-Reduction Reactions

Redox reactions are comprised of two parts, a reduced half and an oxidized half, that *always* occur together. The reduced half gains electrons and the oxidation number decreases, while the oxidized half loses electrons and the oxidation number increases. Simple ways to remember this include the mnemonic devices **OIL RIG,** meaning "*oxidation is loss*" and "*reduction is gain.*" There is no net change in the number of electrons in a redox reaction. Those given off in the oxidation half reaction are taken up by another species in the reduction half reaction.

The two species that exchange electrons in a redox reaction are given special names:

1. The ion or molecule that accepts electrons is called the **oxidizing agent** - by accepting electrons it oxidizes other species.
2. The ion or molecule that donates electrons is called the **reducing agent** - by giving electrons it reduces the other species.

Hence, what is oxidized is the reducing agent and what is reduced is the oxidizing agent. (Note: the oxidizing and reducing agents can be the same element or compound, as in disproportionation reactions discussed below).

A good example of a redox reaction is the thermite reaction, in which iron atoms in ferric oxide lose (or give up) **O** atoms to **Al** atoms, producing $\mathrm{Al_2O_3}$.

$$\mathrm{Fe_2O_3\,(s) + 2\,Al\,(s) \ \rightarrow Al_2O_3\,(s) + 2\,Fe\,(l)}$$

Example 8.1.4: Identifying Oxidizing and Reducing Agents

Determine what is the oxidizing and reducing agents in the following reaction.

$$\mathrm{Zn + 2\,H^+ \longrightarrow Zn^{2+} + H_2}$$

Solution

The oxidation state of **H** changes from +1 to 0, and the oxidation state of **Zn** changes from 0 to +2. Hence, **Zn** is oxidized and acts as the *reducing agent*. $\mathrm{H^+}$ ion is reduced and acts as the *oxidizing agent*.

Combination Reactions

Combination reactions are among the simplest redox reactions and, as the name suggests, involves "combining" elements to form a chemical compound. As usual, oxidation and reduction occur together. The general equation for a combination reaction is given

below:

$$\mathbf{A + B \longrightarrow AB}$$

Example 8.1.5: Combination Reaction

Consider the combination reaction of hydrogen and oxygen

$$\mathbf{H_2 + O_2 \longrightarrow H_2O}$$

Solution

$$0 + 0 \rightarrow \mathbf{(2)(+1) + (-2) = 0}$$

In this reaction both H_2 and O_2 are free elements; following Rule #1, their oxidation states are 0. The product is H_2O, which has a total oxidation state of 0. According to Rule #6, the oxidation state of oxygen is usually -2. Therefore, the oxidation state of H in H_2O must be +1.

Decomposition Reactions

A **decomposition** reaction is the reverse of a combination reaction, the breakdown of a chemical compound into individual elements:

$$\mathbf{AB \longrightarrow A + B}$$

Example 8.1.6: Decomposition Reaction

Consider the following reaction:

$$\mathbf{H_2O \longrightarrow H_2 + O_2}$$

This follows the definition of the decomposition reaction, where water is "decomposed" into hydrogen and oxygen.

$$(2)(+1) + (-2) = 0 \rightarrow 0 + 0$$

As in the previous example the $\mathbf{H_2O}$ has a total oxidation state of 0; thus, according to Rule #6 the oxidation state of oxygen is usually -2, so the oxidation state of hydrogen in $\mathbf{H_2O}$ must be +1.

Note that the autoionization reaction of water is **not** a redox nor decomposition reaction since the oxidation states do not change for any element:

$$\mathbf{H_2O \longrightarrow H^+ + OH^-}$$

Single Replacement Reactions

A **single replacement** reaction involves the "replacing" of an element in the reactants with another element in the products:

$$\mathbf{A + BC \longrightarrow AB + C}$$

Example 8.1.7: Single Replacement Reaction

Equation:

$$\mathbf{Cl_2 + NaBr \rightarrow NaCl + Br_2}$$

Calculation:

$$(0) + ((+1) + (-1) = 0) \text{ -> } ((+1) + (-1) = 0) + 0$$

In this equation, $\mathbf{Br}$ is replaced with $\mathbf{Cl}$, and the $\mathbf{Cl}$ atoms in $\mathbf{Cl_2}$ are reduced, while the $\mathbf{Br}$ ion in $\mathbf{NaBr}$ is oxidized.

Double Replacement Reactions

A double replacement reaction is similar to a single replacement reaction, but involves "replacing" two elements in the reactants, with two in the products:

$$\mathrm{AB + CD \longrightarrow AD + CB}$$

An example of a double replacement reaction is the reaction of magnesium sulfate with sodium oxalate

$$\mathrm{MgSO_4\,(aq) + Na_2C_2O_4\,(aq) \longrightarrow MgC_2O_4\,(s) + Na_2SO_4\,(aq)}$$

Combustion Reactions

Combustion is the formal terms for "burning" and typically involves a substance reacts with oxygen to transfer energy to the surroundings as light and heat. Hence, combustion reactions are almost always exothermic. For example, internal combustion engines rely on the combustion of organic hydrocarbons $\mathrm{C_xH_y}$ to generate $\mathrm{CO_2}$ and $\mathrm{H_2O}$:

$$\mathrm{C_xH_y + O_2 \longrightarrow CO_2 + H_2O}$$

Although combustion reactions typically involve redox reactions with a chemical being oxidized by oxygen, many chemicals can "burn" in other environments. For example, both titanium and magnesium metals can burn in nitrogen as well:

$$\mathrm{2\,Ti\,(s) + N_2\,(g) \longrightarrow 2\,TiN\,(s)}$$

$$\mathrm{3\,Mg\,(s) + N_2\,(g) \longrightarrow Mg_3N_2\,(s)}$$

Moreover, chemicals can be oxidized by other chemicals than oxygen, such as $\mathrm{Cl_2}$ or $\mathrm{F_2}$; these processes are also considered combustion reactions.

✔ Example 8.1.8: Identifying Combustion Reactions

Which of the following are combustion reactions?

a. $\mathrm{2\,H_2O \longrightarrow 2\,H_2 + O_2}$
b. $\mathrm{4\,Fe + 3\,O_2 \longrightarrow 2\,Fe_2O_3}$
c. $\mathrm{2\,AgNO_3 + H_2S \longrightarrow Ag_2S + 2\,NHO_3}$
d. $\mathrm{2\,Al + N_2 \longrightarrow 2\,AlN_4}$

Solution

Both reaction b and reaction d are combustion reactions, although with different oxidizing agents. Reaction b is the conventional combustion reaction using $\mathrm{O_2}$ and reaction uses $\mathrm{N_2}$ instead.

Disproportionation Reactions

In disproportionation reactions, a single substance can be both oxidized and reduced. These are known as disproportionation reactions, with the following general equation:

$$\mathrm{2\,A \longrightarrow A^{+}_{n} + A^{-}_{n}}$$

where n is the number of electrons transferred. Disproportionation reactions do not need begin with neutral molecules, and can involve more than two species with differing oxidation states (but rarely).

✔ Example 8.1.9: Disproportionation Reaction

Disproportionation reactions have some practical significance in everyday life, including the reaction of hydrogen peroxide, $\mathrm{H_2O_2}$ poured over a cut. This a decomposition reaction of hydrogen peroxide, which produces oxygen and water. Oxygen is present in all parts of the chemical equation and as a result it is both oxidized and reduced. The reaction is as follows:

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

Dicussion

On the reactant side, **H** has an oxidation state of +1 and **O** has an oxidation state of -1, which changes to -2 for the product $\mathbf{H_2O}$ (oxygen is reduced), and 0 in the product $\mathbf{O_2}$ (oxygen is oxidized).

? Exercise 8.1.9

Which element undergoes a bifurcation of oxidation states in this disproportionation reaction:

$$\mathbf{HNO_2 \longrightarrow HNO_3 + NO + H_2O}$$

Answer

The **N** atom undergoes disproportionation. You can confirm that by identifying the oxidation states of each atom in each species.

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8.2: Balancing Redox Reactions

Oxidation-Reduction Reactions, or redox reactions, are reactions in which one reactant is oxidized and one reactant is reduced simultaneously. This module demonstrates how to balance various redox equations.

Identifying Redox Reactions

The first step in balancing any redox reaction is determining whether or not it is even an oxidation-reduction reaction. This requires that one and typically more species changing oxidation states during the reaction. To maintain charge neutrality in the sample, the redox reaction will entail both a reduction component and an oxidation components. These are often separated into independent two hypothetical **half-reactions** to aid in understanding the reaction. This requires identifying which element is oxidized and which element is reduced. For example, consider this reaction:

$$\mathrm{Cu\,(s) + 2\,Ag^{+}\,(aq)\ \rightarrow Cu^{2+}\,(aq) + 2\,Ag\,(s)}$$

The first step in determining whether the reaction is a redox reaction is to split the equation into two hypothetical *half-reactions*. Let's start with the half-reaction involving the copper atoms:

$$\mathrm{Cu\,(s)\ \rightarrow Cu^{2+}\,(aq)}$$

The oxidation state of copper on the left side is 0 because it is an element on its own. The oxidation state of copper on the right hand side of the equation is +2. The copper in this half-reaction is oxidized as the oxidation states increases from 0 in Cu to +2 in $\mathrm{Cu^{2+}}$. Now consider the silver atoms

$$\mathrm{2\,Ag^{+}\,(aq)\ \rightarrow 2\,Ag\,(s)}$$

In this half-reaction, the oxidation state of silver on the left side is a +1. The oxidation state of silver on the right is 0 because it is an pure element. Because the oxidation state of silver decreases from +1 to 0, this is the reduction half-reaction.

Consequently, this reaction is a redox reaction as both reduction and oxidation half-reactions occur (via the transfer of electrons, that are not explicitly shown in equations 2). Once confirmed, it often necessary to balance the reaction (the reaction in equation 1 is balanced already though), which can be accomplished in two ways because the reaction could take place in neutral, acidic or basic conditions.

Balancing Redox Reactions

Balancing redox reactions is slightly more complex than balancing standard reactions, but still follows a relatively simple set of rules. One major difference is the necessity to know the half-reactions of the involved reactants; a half-reaction table is very useful for this. Half-reactions are often useful in that two half reactions can be added to get a total net equation. Although the half-reactions must be known to complete a redox reaction, it is often possible to figure them out without having to use a half-reaction table. This is demonstrated in the acidic and basic solution examples. Besides the general rules for neutral conditions, additional rules must be applied for aqueous reactions in acidic or basic conditions.

One method used to balance redox reactions is called the **Half-Equation Method**. In this method, the equation is separated into two half-equations; one for oxidation and one for reduction.

Half-Equation Method to Balance redox Reactions in **Acidic** Aqueous Solutions

Each reaction is balanced by adjusting coefficients and adding $\mathrm{H_2O}$, $\mathrm{H^{+}}$, and $\mathrm{e^{-}}$ in this order:

1. Balance elements in the equation other than O and H.
2. Balance the oxygen atoms by adding the appropriate number of water ($\mathrm{H_2O}$) molecules to the opposite side of the equation.
3. Balance the hydrogen atoms (including those added in step 2 to balance the oxygen atom) by adding $\mathrm{H^{+}}$ ions to the opposite side of the equation.
4. Add up the charges on each side. Make them equal by adding enough electrons ($\mathrm{e^{-}}$) to the more positive side. (Rule of thumb: $\mathrm{e^{-}}$ and $\mathrm{H^{+}}$ are almost always on the same side.)

5. The e^- on each side must be made equal; if they are not equal, they must be multiplied by appropriate integers (the lowest common multiple) to be made the same.
6. The half-equations are added together, canceling out the electrons to form one balanced equation. Common terms should also be canceled out.

The equation can now be checked to make sure that it is balanced.

Half-Equation Method to Balance redox Reactions in **Basic** Aqueous Solutions

If the reaction is being balanced in a basic solution, the above steps are modified with the the addition of one step between #3 and #4:

3b Add the appropriate number of OH^- to neutralize all H^+ and to convert into water molecules.

The equation can now be checked to make sure that it is balanced.

Neutral Conditions

The first step to balance any redox reaction is to separate the reaction into half-reactions. The substance being reduced will have electrons as reactants, and the oxidized substance will have electrons as products. (Usually all reactions are written as reduction reactions in half-reaction tables. To switch to oxidation, the whole equation is reversed and the voltage is multiplied by -1.) Sometimes it is necessary to determine which half-reaction will be oxidized and which will be reduced. In this case, whichever half-reaction has a higher reduction potential will by reduced and the other oxidized.

Example 8.2.1: Balancing in a Neutral Solution

Balance the following reaction

$$Cu^+(aq) + Fe(s) \rightarrow Fe^{3+}(aq) + Cu(s)$$

Solution

Step 1: Separate the half-reactions. By searching for the reduction potential, one can find two separate reactions:

$$Cu^+(aq) + e^- \rightarrow Cu(s)$$

and

$$Fe^{3+}(aq) + 3e^- \rightarrow Fe(s)$$

The copper reaction has a higher potential and thus is being reduced. Iron is being oxidized so the half-reaction should be flipped. This yields:

$$Cu^+(aq) + e^- \rightarrow Cu(s)$$

and

$$Fe(s) \rightarrow Fe^{3+}(aq) + 3e^-$$

Step 2: Balance the electrons in the equations. In this case, the electrons are simply balanced by multiplying the entire $Cu^+(aq) + e^- \rightarrow Cu(s)$ half-reaction by 3 and leaving the other half reaction as it is. This gives:

$$3Cu^+(aq) + 3e^- \rightarrow 3Cu(s)$$

and

$$Fe(s) \rightarrow Fe^{3+}(aq) + 3e^-$$

Step 3: Adding the equations give:

$$3Cu^+(aq) + 3e^- + Fe(s) \rightarrow 3Cu(s) + Fe^{3+}(aq) + 3e^-$$

The electrons cancel out and the balanced equation is left.

$$3\,Cu^{+}(aq) + Fe(s) \rightarrow 3\,Cu(s) + Fe^{3+}(aq)$$

Acidic Conditions

Acidic conditions usually implies a solution with an excess of H^+ concentration, hence making the solution acidic. The balancing starts by separating the reaction into half-reactions. However, instead of immediately balancing the electrons, balance all the elements in the half-reactions that are not hydrogen and oxygen. Then, add H_2O molecules to balance any oxygen atoms. Next, balance the hydrogen atoms by adding protons (H^+). Now, balance the *charge* by adding electrons and scale the electrons (multiply by the lowest common multiple) so that they will cancel out when added together. Finally, add the two half-reactions and cancel out common terms.

Example 8.2.2: Balancing in a Acid Solution

Balance the following redox reaction in acidic conditions.

$$Cr_2O_7^{2-}(aq) + HNO_2(aq) \rightarrow Cr^{3+}(aq) + NO_3^{-}(aq)$$

Solution

Step 1: Separate the half-reactions. The table provided does not have acidic or basic half-reactions, so just write out what is known.

$$Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}(aq)$$

$$HNO_2(aq) \rightarrow NO_3^{-}(aq)$$

Step 2: Balance elements other than O and H. In this example, only chromium needs to be balanced. This gives:

$$Cr_2O_7^{2-}(aq) \rightarrow 2\,Cr^{3+}(aq)$$

and

$$HNO_2(aq) \rightarrow NO_3^{-}(aq)$$

Step 3: Add H_2O to balance oxygen. The chromium reaction needs to be balanced by adding 7 H_2O molecules. The other reaction also needs to be balanced by adding one water molecule. This yields:

$$Cr_2O_7^{2-}(aq) \rightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$$

and

$$HNO_2(aq) + H_2O(l) \rightarrow NO_3^{-}(aq)$$

Step 4: Balance hydrogen by adding protons (H^+). 14 protons need to be added to the left side of the chromium reaction to balance the 14 (2 per water molecule * 7 water molecules) hydrogens. 3 protons need to be added to the right side of the other reaction.

$$14\,H^{+}(aq) + Cr_2O_7^{2-}(aq) \rightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$$

and

$$HNO_2(aq) + H_2O(l) \rightarrow 3\,H^{+}(aq) + NO_3^{-}(aq)$$

Step 5: Balance the charge of each equation with electrons. The chromium reaction has (14+) + (2-) = 12+ on the left side and (2 * 3+) = 6+ on the right side. To balance, add 6 electrons (each with a charge of -1) to the left side:

$$6\,e^{-} + 14\,H^{+}(aq) + Cr_2O_7^{2-}(aq) \rightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$$

For the other reaction, there is no charge on the left and a (3+) + (-1) = 2+ charge on the right. So add 2 electrons to the right side:

$$HNO_2(aq) + H_2O(l) \rightarrow 3\,H^{+}(aq) + NO_3^{-}(aq) + 2\,e^{-}$$

Step 6: Scale the reactions so that the electrons are equal. The chromium reaction has $6e^-$ and the other reaction has $2e^-$, so it should be multiplied by 3. This gives:

$$6\,e^- + 14\,H^+(aq) + Cr_2O_7{}^{2-}(aq) \rightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)\cdot$$

and

$$3\times\left[HNO_2(aq) + H_2O(l) \rightarrow 3\,H^+(aq) + NO_3{}^-(aq) + 2\,e^-\right]$$
$$3\,HNO_2(aq) + 3\,H_2O(l) \rightarrow 9\,H^+(aq) + 3\,NO_3{}^-(aq) + 6\,e^-$$

Step 7: Add the reactions and cancel out common terms.

$$\begin{aligned} 3\,HNO_2(aq) + 3\,H_2O(l) &\rightarrow 9\,H^+(aq) + 3\,NO_3{}^-(aq) + 6\,e^- \\ 6\,e^- + 14\,H^+(aq) + Cr_2O_7{}^{2-}(aq) &\rightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l) \\ \hline 3\,HNO_2(aq) + \cancel{3\,H_2O(l)} + \cancel{6e^-} & \\ + 14\,H^+(aq) + Cr_2O_7{}^{2-}(aq) &\rightarrow 9\,H^+(aq) + 3\,NO_3{}^-(aq) + \cancel{6e^-} \\ &\quad + 2\,Cr^{3+}(aq) + \cancel{7}^{4}H_2O(l) \end{aligned}$$

The electrons cancel out as well as 3 water molecules and 9 protons. This leaves the balanced net reaction of:

$$3\,HNO_2(aq) + 5\,H^+(aq) + Cr_2O_7{}^{2-}(aq) \rightarrow 3\,NO_3{}^-(aq) + 2\,Cr^{3+}(aq) + 4\,H_2O(l)$$

Basic Conditions

Bases dissolve into OH^- ions in solution; hence, balancing redox reactions in basic conditions requires OH^-. Follow the same steps as for acidic conditions. The only difference is adding hydroxide ions to each side of the net reaction to balance any H^+. OH^- and H^+ ions on the same side of a reaction should be added together to form water. Again, any common terms can be canceled out.

✔ Example 8.2.1: Balancing in Basic Solution

Balance the following redox reaction in basic conditions.

$$Ag(s) + Zn^{2+}(aq) \rightarrow Ag_2O(aq) + Zn(s)$$

Solution

Go through all the same steps as if it was in acidic conditions.

Step 1: Separate the half-reactions.

$$Ag(s) \rightarrow Ag_2O(aq)$$

$$Zn^{2+}(aq) \rightarrow Zn(s)$$

Step 2: Balance elements other than O and H.

$$2\,Ag(s) \rightarrow Ag_2O(aq)$$

$$Zn^{2+}(aq) \rightarrow Zn(s)$$

Step 3: Add H_2O to balance oxygen.

$$H_2O(l) + 2\,Ag(s) \rightarrow Ag_2O(aq)$$

$$Zn^{2+}(aq) \rightarrow Zn(s)$$

Step 4: Balance hydrogen with protons.

$$H_2O(l) + 2\,Ag(s) \rightarrow Ag_2O(aq) + 2\,H^+(aq)$$

$$Zn^{2+}(aq) \rightarrow Zn(s)$$

Step 5: Balance the charge with e^-.

$$H_2O(l) + 2\,Ag(s) \rightarrow Ag_2O(aq) + 2\,H^+(aq) + 2\,e^-$$

$$Zn^{2+}(aq) + 2\,e^- \rightarrow Zn(s)$$

Step 6: Scale the reactions so that they have an equal amount of electrons. In this case, it is already done.

Step 7: Add the reactions and cancel the electrons.

$$H_2O(l) + 2\,Ag(s) + Zn^{2+}(aq) \rightarrow Zn(s) + Ag_2O(aq) + 2\,H^+(aq)\cdot$$

Step 8: Add OH^- to balance H^+. There are 2 net protons in this equation, so add 2 OH^- ions to each side.

$$H_2O(l) + 2\,Ag(s) + Zn^{2+}(aq) + 2\,OH^-(aq) \rightarrow Zn(s) + Ag_2O(aq) + 2\,H^+(aq) + 2\,OH^-(aq)\cdot$$

Step 9: Combine OH^- ions and H^+ ions that are present on the same side to form water.

$$\cancel{H2O(l)} + 2\,Ag(s) + Zn^{2+}(aq) + 2\,OH^-(aq) \longrightarrow Zn(s) + Ag_2O(aq) + \cancel{2}\,H_2O(l)$$

Step 10: Cancel common terms.

$$2\,Ag(s) + Zn^{2+}(aq) + 2\,OH^-(aq) \rightarrow Zn(s) + Ag_2O(aq) + H_2O(l)$$

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8.3: Galvanic 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 8.3.1). 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 8.3.1). 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.

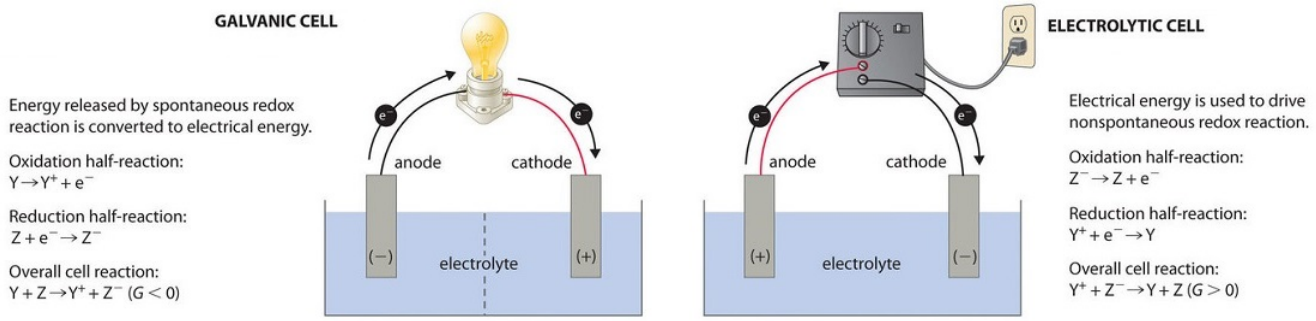


Figure 8.3.1: Electrochemical Cells. A galvanic cell (left) transforms the energy released by a spontaneous redox reaction into electrical energy that can be used to perform work. The oxidative and reductive half-reactions usually occur in separate compartments that are connected by an external electrical 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:

$$\mathrm{Zn\,(s) + Cu^{2+}\,(aq) \rightarrow Zn^{2+}\,(aq) + Cu\,(s)} \tag{8.3.1}$$

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 8.3.2: 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 8.3.3a. To assemble the cell, a copper strip is inserted into a beaker that contains a 1 M solution of $\mathrm{Cu^{2+}}$ ions, and a zinc strip is inserted into a different beaker that contains a 1 M solution of $\mathrm{Zn^{2+}}$ ions. The two metal strips, which serve as electrodes, are connected by a wire, and the compartments are connected by a **salt bridge**, a U-shaped tube inserted into both solutions that contains a concentrated liquid or gelled electrolyte.

The ions in the salt bridge are selected so that they do not interfere with the electrochemical reaction by being oxidized or reduced themselves or by forming a precipitate or complex; commonly used cations and anions are 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 8.3.3*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.

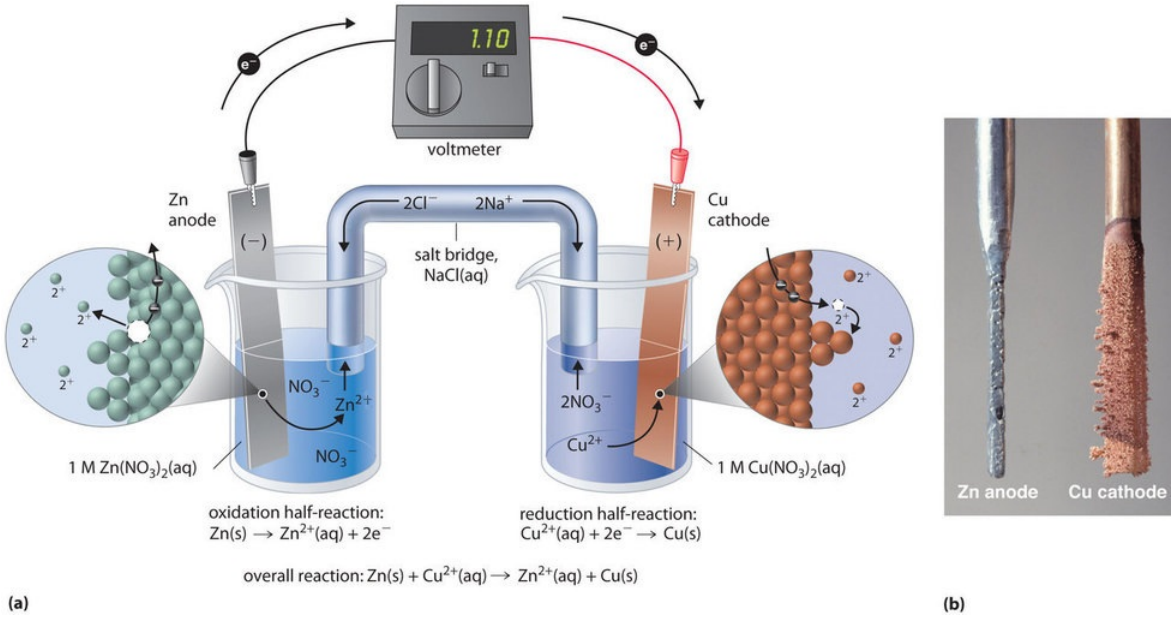


Figure 8.3.3: The Reaction of Metallic Zinc with Aqueous Copper(II) Ions in a Galvanic Cell. (a) A galvanic cell can be constructed by inserting a copper strip into a beaker that contains an aqueous 1 M solution of Cu^{2+} ions and a zinc strip into a different beaker that contains an aqueous 1 M solution 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 8.3.3*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 **8.3.1**.

> *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 8.3.1

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 8.3.1

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 8.3.3*a* is written as follows:

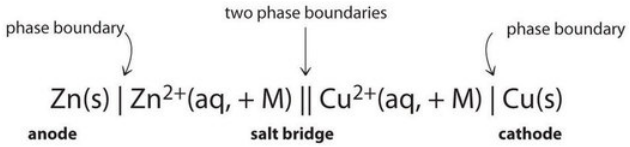


Figure 8.3.4: A cell diagram includes solution concentrations when they are provided. The + M term is meant to indicate the applicable concentration of the species. If the species is a gas, then you substitute the pressure instead.

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 8.3.2

Draw a cell diagram for the galvanic cell described in Example 8.3.1. 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 8.3.2

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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8.4: Standard Electrode Potentials

Skills to Develop

- To use redox potentials to predict whether a reaction is spontaneous.
- To balance redox reactions using half-reactions.

In a galvanic cell, current is produced when electrons flow externally through the circuit from the anode to the cathode because of a difference in potential energy between the two electrodes in the electrochemical cell. In the **Zn/Cu** system, the valence electrons in zinc have a substantially higher potential energy than the valence electrons in copper because of shielding of the s electrons of zinc by the electrons in filled d orbitals. Hence electrons flow spontaneously from zinc to copper(II) ions, forming zinc(II) ions and metallic copper. Just like water flowing spontaneously downhill, which can be made to do work by forcing a waterwheel, the flow of electrons from a higher potential energy to a lower one can also be harnessed to perform work.

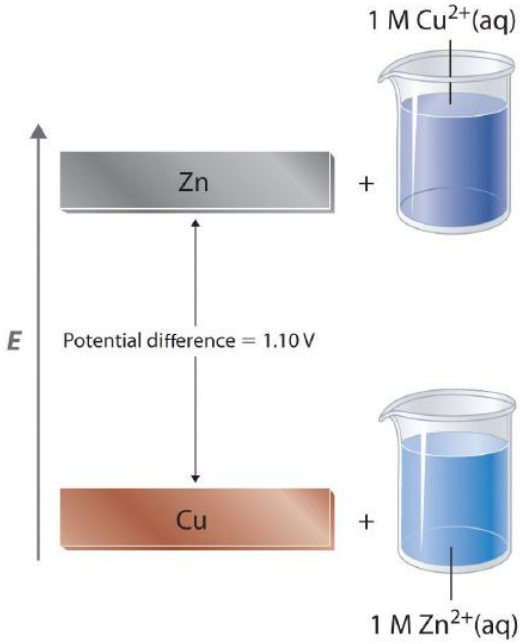


Figure **8.4.1**: Potential Energy Difference in the Zn/Cu System. The potential energy of a system consisting of metallic ***Zn*** and aqueous Cu^{2+} ions is greater than the potential energy of a system consisting of metallic Cu and aqueous Zn^{2+} ions. Much of this potential energy difference is because the valence electrons of metallic Zn are higher in energy than the valence electrons of metallic Cu. Because the Zn(s) + Cu^{2+}(aq) system is higher in energy by 1.10 V than the Cu(s) + Zn^{2+}(aq) system, energy is released when electrons are transferred from Zn to Cu^{2+} to form Cu and Zn^{2+}.

Because the potential energy of valence electrons differs greatly from one substance to another, the voltage of a galvanic cell depends partly on the identity of the reacting substances. If we construct a galvanic cell similar to the one in Figure **8.4.1*a*** but instead of copper use a strip of cobalt metal and 1 M Co^{2+} in the cathode compartment, the measured voltage is not 1.10 V but 0.51 V. Thus we can conclude that the difference in potential energy between the valence electrons of cobalt and zinc is less than the difference between the valence electrons of copper and zinc by 0.59 V.

The measured potential of a cell also depends strongly on the concentrations of the reacting species and the temperature of the system. To develop a scale of relative potentials that will allow us to predict the direction of an electrochemical reaction and the magnitude of the driving force for the reaction, the potentials for oxidations and reductions of different substances must be measured under comparable conditions. To do this, chemists use the **standard cell potential** (E^{o}_{cell}), defined as the potential of a cell measured under standard conditions—that is, with all species in their standard states (1 M for solutions,Concentrated solutions of salts (about 1 M) generally do not exhibit ideal behavior, and the actual standard state corresponds to an activity of 1 rather than a concentration of 1 M. Corrections for nonideal behavior are important for precise quantitative work but not for the more qualitative approach that we are taking here. 1 atm for gases, pure solids or pure liquids for other substances) and at a fixed temperature, usually 25°C.

> *Measured redox potentials depend on the potential energy of valence electrons, the concentrations of the species in the reaction, and the temperature of the system.*

Measuring Standard Electrode Potentials

It is physically impossible to measure the potential of a single electrode: only the difference between the potentials of two electrodes can be measured (this is analogous to measuring **absolute enthalpies** or **free energies** since only differences in enthalpy and free energy can be measured). We can, however, compare the standard cell potentials for two different galvanic cells that have one kind of electrode in common. This allows us to measure the potential difference between two dissimilar electrodes. For example, the measured standard cell potential ($E°$) for the **Zn/Cu** system is 1.10 V, whereas $E°$ for the corresponding **Zn/Co** system is 0.51 V. This implies that the potential difference between the **Co** and **Cu** electrodes is 1.10 V − 0.51 V = 0.59 V. In fact, that is exactly the potential measured under standard conditions if a cell is constructed with the following cell diagram:

$$\mathrm{Co\,(s)\ |\ Co^{2+}\,(aq,\,1\,M)\ ||\ Cu^{2+}\,(aq,\,1\,M)\ |\ Cu\,(s)}\quad E°= 0.59\,V \tag{8.4.1}$$

This cell diagram corresponds to the oxidation of a cobalt anode and the reduction of Cu^{2+} in solution at the copper cathode.

All tabulated values of standard electrode potentials by convention are listed for a reaction written as a reduction, not as an oxidation, to be able to compare standard potentials for different substances (Table P1). The standard cell potential ($E°_{cell}$) is therefore the difference between the tabulated reduction potentials of the two half-reactions, not their sum:

$$E°_{cell} = E°_{cathode} - E°_{anode} \tag{8.4.2}$$

In contrast, recall that half-reactions are written to show the reduction and oxidation reactions that actually occur in the cell, so the overall cell reaction is written as the sum of the two half-reactions. According to Equation 8.4.2, when we know the standard potential for any single half-reaction, we can obtain the value of the standard potential of many other half-reactions by measuring the standard potential of the corresponding cell.

> The overall cell reaction is the sum of the two half-reactions, but the cell potential is the difference between the reduction potentials:
>
> $$E°_{cell} = E°_{cathode} - E°_{anode}$$

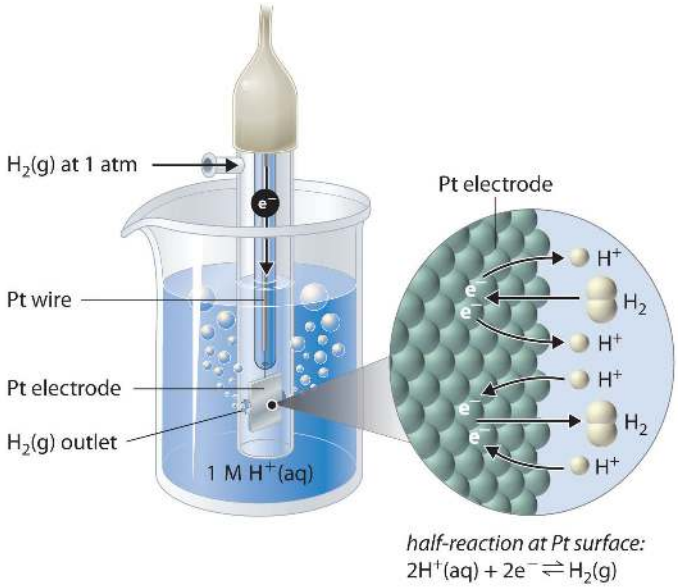


Figure 8.4.2: The Standard Hydrogen Electrode. The SHE consists of platinum wire that is connected to a Pt surface in contact with an aqueous solution containing 1 M H^+ in equilibrium with H_2 gas at a pressure of 1 atm. In the molecular view, the Pt surface catalyzes the oxidation of hydrogen molecules to protons or the reduction of protons to hydrogen gas. (Water is omitted for clarity.) The standard potential of the SHE is arbitrarily assigned a value of 0 V.

Although it is impossible to measure the potential of any electrode directly, we can choose a reference electrode whose potential is defined as 0 V under standard conditions. The **standard hydrogen electrode (SHE)** is universally used for this purpose and is assigned a standard potential of 0 V. It consists of a strip of platinum wire in contact with an aqueous solution containing 1 M $\mathbf{H^+}$ (since it is in standard conditions). The $\mathbf{H^+}$ in solution is in equilibrium with $\mathbf{H_2}$ gas at a pressure of 1 atm at the Pt-solution interface (Figure **8.4.2**). Protons are reduced or hydrogen molecules are oxidized at the **Pt** surface according to the following equation:

$$\mathbf{2\,H^+(aq) + 2\,e^- \rightleftharpoons H_2(g)} \tag{8.4.3}$$

One especially attractive feature of the SHE is that the **Pt** metal electrode is not consumed during the reaction.

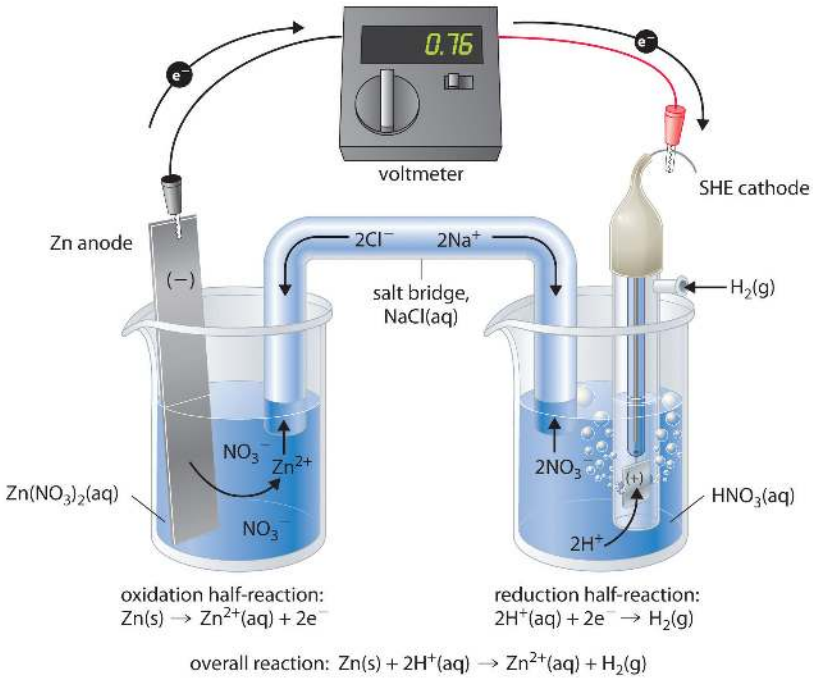


Figure **8.4.3**: Determining a Standard Electrode Potential Using a Standard Hydrogen Electrode. The voltmeter shows that the standard cell potential of a galvanic cell consisting of a SHE and a Zn/Zn^{2+} couple is $E°_{cell}$ = 0.76 V. Because the zinc electrode in this cell dissolves spontaneously to form $Zn^{2+}(aq)$ ions while $H^+(aq)$ ions are reduced to H_2 at the platinum surface, the standard electrode potential of the Zn^{2+}/Zn couple is −0.76 V.

Figure **8.4.3** shows a galvanic cell that consists of a SHE in one beaker and a Zn strip in another beaker containing a solution of Zn^{2+} ions. When the circuit is closed, the voltmeter indicates a potential of 0.76 V. The zinc electrode begins to dissolve to form Zn^{2+}, and H^+ ions are reduced to H_2 in the other compartment. Thus the hydrogen electrode is the cathode, and the zinc electrode is the anode. The diagram for this galvanic cell is as follows:

$$\mathbf{Zn\,(s)\ |\ Zn^{2+}\,(aq)\ ||\ H^+\,(aq,\,1\,M)\ |\ H_2\,(g,\,1\,atm)\ |\ Pt\,(s)}$$

The half-reactions that actually occur in the cell and their corresponding electrode potentials are as follows:

- cathode:

$$\mathbf{2\,H^+\,(aq) + 2\,e^- \longrightarrow H_2\,(g)} \qquad E°_{cathode} = 0\,V$$

- anode:

$$\mathbf{Zn\,(s) \longrightarrow Zn^{2+}\,(aq) + 2\,e^-} \qquad E°_{anode} = -0.76\,V$$

- overall:

$$\mathbf{Zn\,(s) + 2\,H^+\,(aq) \longrightarrow Zn^{2+}\,(aq) + H_2\,(g)}$$

Then via Equation 8.4.2 we can calculate the standard cell potential

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 0.76\ V$$

Caution: Watch the Sign

Although the reaction at the anode is an oxidation, by convention its tabulated E^o value is reported as a reduction potential. The potential of a half-reaction measured against the SHE under standard conditions is called the **standard electrode potential** for that half-reaction. In this example, the standard reduction potential for $Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$ is −0.76 V, which means that the standard electrode potential for the reaction that occurs at the anode, the oxidation of Zn to Zn^{2+}, often called the **Zn/Zn^{2+} redox couple**, or the **Zn/Zn^{2+} couple**, is −(−0.76 V) = 0.76 V.

We must therefore **subtract** E°_{anode} from $E^\circ_{cathode}$ to obtain $E^\circ_{cell} = 0.76\ V$. This is the origin of the negative sign in Equation 8.4.2.

Because electrical potential is the energy needed to move a charged particle in an electric field, standard electrode potentials for half-reactions are intensive properties and do not depend on the amount of substance involved. Consequently, E° values are *independent of the stoichiometric coefficients* for the half-reaction, and, most important, the coefficients used to produce a balanced overall reaction do not affect the value of the cell potential.

> *E° values do NOT depend on the stoichiometric coefficients for a half-reaction, because it is an intensive property.*

Standard Electrode Potentials

To measure the potential of the Cu/Cu^{2+} couple, we can construct a galvanic cell analogous to the one shown in Figure **8.4.3** but containing a Cu/Cu^{2+} couple in the sample compartment instead of Zn/Zn^{2+}. When we close the circuit this time, the measured potential for the cell is negative (−0.34 V) rather than positive. The negative value of E°_{cell} indicates that the direction of spontaneous electron flow is the opposite of that for the Zn/Zn^{2+} couple. Hence the reactions that occur spontaneously, indicated by a positive E°_{cell}, are the reduction of Cu^{2+} to Cu at the copper electrode. The copper electrode gains mass as the reaction proceeds, and H_2 is oxidized to H^+ at the platinum electrode. In this cell, the copper strip is the cathode, and the hydrogen electrode is the anode. The cell diagram therefore is written with the SHE on the left and the Cu^{2+}/Cu couple on the right:

$$Pt(s)\ |\ H_2(g, 1\,atm)\ |\ H^+(aq,\ 1\ M)\ ||\ Cu^{2+}(aq, 1\,M)\ |Cu(s)$$

The half-cell reactions and potentials of the spontaneous reaction are as follows:

- Cathode:

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(g) \qquad E^\circ_{cathode} = 0.34\ V$$

- Anode:

$$H_2(g) \longrightarrow 2H^+(aq) + 2e^- \qquad E^\circ_{anode} = 0\ V$$

- Overall:

$$H_2(g) + Cu^{2+}(aq) \longrightarrow 2H^+(aq) + Cu(s)$$

Then via Equation 8.4.2 we can calculate the standard cell potential

$$\begin{aligned} E^\circ_{cell} &= E^\circ_{cathode} - E^\circ_{anode} \\ &= 0.34\ V \end{aligned}$$

Thus the standard electrode potential for the Cu^{2+}/Cu couple is 0.34 V.

Calculating Standard Cell Potentials

The standard cell potential for a redox reaction (E°_{cell}) is a measure of the tendency of reactants in their standard states to form products in their standard states; consequently, it is a measure of the driving force for the reaction, which earlier we called voltage.

We can use the two standard electrode potentials we found earlier to calculate the standard potential for the Zn/Cu cell represented by the following cell diagram:

$$\mathrm{Zn\,(s)\ |\ Zn^{2+}\,(aq,\,1\,M)\ ||\ Cu^{2+}\,(aq,\,1\,M)\ |\ Cu\,(s)}$$

We know the values of $E°_{anode}$ for the reduction of Zn^{2+} and $E°_{cathode}$ for the reduction of Cu^{2+}, so we can calculate $E°_{cell}$:

- cathode:

$$\mathrm{Cu^{2+}\,(aq) + 2\,e^- \longrightarrow Cu\,(s)} \qquad E°_{cathode} = 0.34\ V$$

- anode:

$$\mathrm{Zn\,(s) \longrightarrow Zn^{2+}\,(aq,\,1\,M) + 2\,e^-} \qquad E°_{anode} = -0.76\ V$$

- overall:

$$\mathrm{Zn\,(s) + Cu^{2+}\,(aq) \longrightarrow Zn^{2+}\,(aq) + Cu\,(s)}$$

Then via Equation 8.4.2 we can calculate the standard cell potential

$$\begin{aligned} E°_{cell} &= E°_{cathode} - E°_{anode} \\ &= 1.10\ V \end{aligned}$$

This is the same value that is observed experimentally. If the value of $E°_{cell}$ is positive, the reaction will occur spontaneously as written. If the value of $E°_{cell}$ is negative, then the reaction is not spontaneous, and it will not occur as written under standard conditions; it will, however, proceed spontaneously in the opposite direction. As we shall see in Section 20.9, this does not mean that the reaction cannot be made to occur at all under standard conditions. With a sufficient input of electrical energy, virtually any reaction can be forced to occur. Example **8.4.2** and its corresponding exercise illustrate how we can use measured cell potentials to calculate standard potentials for redox couples.

> *A positive $E°_{cell}$ means that the reaction will occur spontaneously as written. A negative $E°_{cell}$ means that the reaction will proceed spontaneously in the opposite direction.*

Example 8.4.1

A galvanic cell with a measured standard cell potential of 0.27 V is constructed using two beakers connected by a salt bridge. One beaker contains a strip of gallium metal immersed in a 1 M solution of $GaCl_3$, and the other contains a piece of nickel immersed in a 1 M solution of $\mathbf{NiCl_2}$. The half-reactions that occur when the compartments are connected are as follows:

- cathode:

$$\mathrm{Ni^{2+}\,(aq) + 2\,e^- \longrightarrow Ni\,(s)}$$

- anode:

$$\mathrm{Ga\,(s) \longrightarrow Ga^{3+}\,(aq) + 3\,e^-}$$

If the potential for the oxidation of **Ga** to $\mathbf{Ga^{3+}}$ is 0.55 V under standard conditions, what is the potential for the oxidation of Ni to Ni^{2+}?

Given: galvanic cell, half-reactions, standard cell potential, and potential for the oxidation half-reaction under standard conditions

Asked for: standard electrode potential of reaction occurring at the cathode

Strategy:

A. Write the equation for the half-reaction that occurs at the anode along with the value of the standard electrode potential for the half-reaction.

B. Use Equation 8.4.2 to calculate the standard electrode potential for the half-reaction that occurs at the cathode. Then reverse the sign to obtain the potential for the corresponding oxidation half-reaction under standard conditions.

Solution:

A We have been given the potential for the oxidation of Ga to Ga^{3+} under standard conditions, but to report the standard electrode potential, we must reverse the sign. For the reduction reaction $Ga^{3+}(aq) + 3e^- \rightarrow Ga(s)$, $E°_{anode} = -0.55$ V.

B Using the value given for $E°_{cell}$ and the calculated value of $E°_{anode}$, we can calculate the standard potential for the reduction of Ni^{2+} to Ni from Equation 8.4.2:

$$E°_{cell} = E°_{cathode} - E°_{anode}$$
$$0.27\,V = E°_{cathode} - (-0.55V)$$
$$E°_{cathode} = -0.28\,V$$

This is the standard electrode potential for the reaction $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$. Because we are asked for the potential for the oxidation of Ni to Ni^{2+} under standard conditions, we must reverse the sign of $E°_{cathode}$. Thus $E° = -(-0.28\text{ V}) = 0.28$ V for the oxidation. With three electrons consumed in the reduction and two produced in the oxidation, the overall reaction is not balanced. Recall, however, that standard potentials are independent of stoichiometry.

Exercise 8.4.1

A galvanic cell is constructed with one compartment that contains a mercury electrode immersed in a 1 M aqueous solution of mercuric acetate $Hg(CH_3CO_2)_2$ and one compartment that contains a strip of magnesium immersed in a 1 M aqueous solution of $MgCl_2$. When the compartments are connected, a potential of 3.22 V is measured and the following half-reactions occur:

- cathode:

$$Hg^{2+}(aq) + 2e^- \longrightarrow Hg(l)$$

- anode:

$$Mg(s) \longrightarrow Mg^{2+}(aq) + 2e^-$$

If the potential for the oxidation of Mg to Mg^{2+} is 2.37 V under standard conditions, what is the standard electrode potential for the reaction that occurs at the cathode?

Answer

0.85 V

Reference Electrodes

When using a galvanic cell to measure the concentration of a substance, we are generally interested in the potential of only one of the electrodes of the cell, the so-called **indicator electrode**, whose potential is related to the concentration of the substance being measured. To ensure that any change in the measured potential of the cell is due to only the substance being analyzed, the potential of the other electrode, the **reference electrode**, must be constant. You are already familiar with one example of a reference electrode: the SHE. The potential of a reference electrode must be unaffected by the properties of the solution, and if possible, it should be physically isolated from the solution of interest. To measure the potential of a solution, we select a reference electrode and an appropriate indicator electrode. Whether reduction or oxidation of the substance being analyzed occurs depends on the potential of the half-reaction for the substance of interest (the sample) and the potential of the reference electrode.

> *The potential of any reference electrode should not be affected by the properties of the solution to be analyzed, and it should also be physically isolated.*

There are many possible choices of reference electrode other than the SHE in Figure 8.4.2. The SHE requires a constant flow of highly flammable hydrogen gas, which makes it inconvenient to use. Consequently, two other electrodes are commonly chosen as reference electrodes. One is the **silver–silver chloride electrode**, which consists of a silver wire coated with a very thin layer of AgCl that is dipped into a chloride ion solution with a fixed concentration. The silver–silver chloride electrode cell diagram is

$$Cl^-(aq) \mid AgCl(s) \mid Ag(s)$$

and corresponding half-reaction is

$$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq).$$

If a saturated solution of KCl is used as the chloride solution, the potential of the silver–silver chloride electrode is 0.197 V versus the SHE. That is, 0.197 V must be subtracted from the measured value to obtain the standard electrode potential measured against the SHE.

A second common reference electrode is the **saturated calomel electrode (SCE)**, which has the same general form as the silver–silver chloride electrode. The SCE consists of a platinum wire inserted into a moist paste of liquid mercury (Hg_2Cl_2; called calomel in the old chemical literature) and KCl. This interior cell is surrounded by an aqueous KCl solution, which acts as a salt bridge between the interior cell and the exterior solution (Figure 8.4.5*a*). Although it sounds and looks complex, this cell is actually easy to prepare and maintain, and its potential is highly reproducible. The SCE cell diagram is

$$Pt(s) \mid Hg_2Cl_2(s) \mid KCl(aq, sat)$$

and corresponding half-reaction is

$$Hg_2Cl_2(s) + 2e^- \longrightarrow 2Hg(l) + 2Cl^-(aq).$$

At 25°C, the potential of the SCE is 0.2415 V versus the SHE, which means that 0.2415 V must be subtracted from the potential versus an SCE to obtain the standard electrode potential.

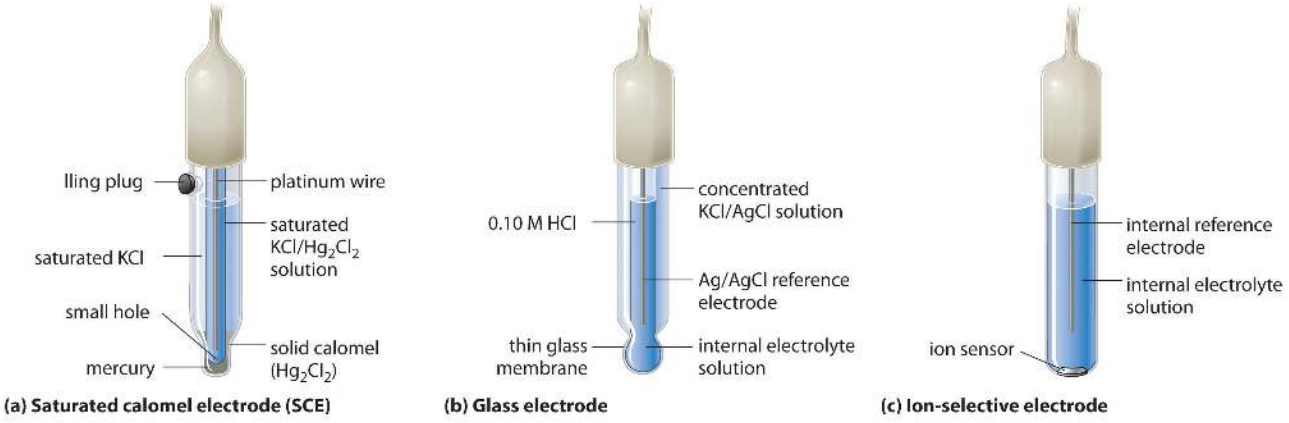


Figure 8.4.5: Three Common Types of Electrodes. (a) The SCE is a reference electrode that consists of a platinum wire inserted into a moist paste of liquid mercury (calomel; Hg_2Cl_2) and KCl. The interior cell is surrounded by an aqueous KCl solution, which acts as a salt bridge between the interior cell and the exterior solution. (b) In a glass electrode, an internal Ag/AgCl electrode is immersed in a 1 M HCl solution that is separated from the sample solution by a very thin glass membrane. The potential of the electrode depends on the H^+ ion concentration of the sample. (c) The potential of an ion-selective electrode depends on the concentration of only a single ionic species in solution.

Using Electrochemistry to Measure Concentrations

One of the most common uses of electrochemistry is to measure the H^+ ion concentration of a solution. A **glass electrode** is generally used for this purpose, in which an internal Ag/AgCl electrode is immersed in a 0.10 M HCl solution that is separated from the solution by a very thin glass membrane (Figure 8.4.5*b*. The glass membrane absorbs protons, which affects the measured potential. The extent of the adsorption on the inner side is fixed because $[H^+]$ is fixed inside the electrode, but the adsorption of protons on the outer surface depends on the pH of the solution. The potential of the glass electrode depends on $[H^+]$ as follows (recall that $pH = -\log[H^+]$):

$$\begin{aligned} E_{glass} &= E' + (0.0591\ V \times \log[H^+]) \\ &= E' - 0.0591\ V \times pH \end{aligned}$$

The voltage E' is a constant that depends on the exact construction of the electrode. Although it can be measured, in practice, a glass electrode is calibrated; that is, it is inserted into a solution of known pH, and the display on the pH meter is adjusted to the

known value (Figure 8.4.7). Once the electrode is properly calibrated, it can be placed in a solution and used to determine an unknown pH.



Figure 8.4.7: A pH meter measures the hydrogen-ion concentration in water-based solutions, indicating its acidity or alkalinity expressed as pH. The pH meter measures the difference in electrical potential between a pH electrode and a reference electrode, and so the pH meter is sometimes referred to as a "potentiometric pH meter". (CC By-SA 2.0 Generic; Sergei Golyshev via Wikipedia)

Ion-selective electrodes are used to measure the concentration of a particular species in solution; they are designed so that their potential depends on only the concentration of the desired species (Figure 8.4.5c). These electrodes usually contain an internal reference electrode that is connected by a solution of an electrolyte to a crystalline inorganic material or a membrane, which acts as the sensor. For example, one type of ion-selective electrode uses a single crystal of Eu-doped LaF_3 as the inorganic material. When fluoride ions in solution diffuse to the surface of the solid, the potential of the electrode changes, resulting in a so-called fluoride electrode. Similar electrodes are used to measure the concentrations of other species in solution. Some of the species whose concentrations can be determined in aqueous solution using ion-selective electrodes and similar devices are listed in Table 8.4.1.

Table 8.4.1: Some Species Whose Aqueous Concentrations Can Be Measured Using Electrochemical Methods

Species	Type of Sample
H^+	laboratory samples, blood, soil, and ground and surface water
NH_3/NH_4^+	wastewater and runoff water
K^+	blood, wine, and soil
CO_2/HCO_3^-	blood and groundwater
F^-	groundwater, drinking water, and soil
Br^-	grains and plant extracts
I^-	milk and pharmaceuticals
NO_3^-	groundwater, drinking water, soil, and fertilizer

Summary

Redox reactions can be balanced using the half-reaction method. The standard cell potential is a measure of the driving force for the reaction.

$$E°_{cell} = E°_{cathode} - E°_{anode}$$

The flow of electrons in an electrochemical cell depends on the identity of the reacting substances, the difference in the potential energy of their valence electrons, and their concentrations. The potential of the cell under standard conditions (1 M for solutions, 1 atm for gases, pure solids or liquids for other substances) and at a fixed temperature (25°C) is called the standard cell potential

($E°_{cell}$). Only the difference between the potentials of two electrodes can be measured. By convention, all tabulated values of standard electrode potentials are listed as standard reduction potentials. The overall cell potential is the reduction potential of the reductive half-reaction minus the reduction potential of the oxidative half-reaction ($E°_{cell} = E°_{cathode} - E°_{anode}$). The potential of the standard hydrogen electrode (SHE) is defined as 0 V under standard conditions. The potential of a half-reaction measured against the SHE under standard conditions is called its standard electrode potential. The standard cell potential is a measure of the driving force for a given redox reaction. All E° values are independent of the stoichiometric coefficients for the half-reaction. Redox reactions can be balanced using the half-reaction method, in which the overall redox reaction is divided into an oxidation half-reaction and a reduction half-reaction, each balanced for mass and charge. The half-reactions selected from tabulated lists must exactly reflect reaction conditions. In an alternative method, the atoms in each half-reaction are balanced, and then the charges are balanced. Whenever a half-reaction is reversed, the sign of E° corresponding to that reaction must also be reversed. If $\boldsymbol{E°_{cell}}$ is positive, the reaction will occur spontaneously under standard conditions. If $\boldsymbol{E°_{cell}}$ is negative, then the reaction is not spontaneous under standard conditions, although it will proceed spontaneously in the opposite direction. The potential of an indicator electrode is related to the concentration of the substance being measured, whereas the potential of the reference electrode is held constant. Whether reduction or oxidation occurs depends on the potential of the sample versus the potential of the reference electrode. In addition to the SHE, other reference electrodes are the silver–silver chloride electrode; the saturated calomel electrode (SCE); the glass electrode, which is commonly used to measure pH; and ion-selective electrodes, which depend on the concentration of a single ionic species in solution. Differences in potential between the SHE and other reference electrodes must be included when calculating values for E°.

8.4: Standard Electrode Potentials is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

8.5: Strengths of Oxidants and Reductants

Learning Objectives

- Identify how to view Standard Reduction Potentials from the perspective of viable reducing and oxidizing agents in REDOX reactions.

We can measure the standard potentials for a wide variety of chemical substances, some of which are listed in Table P2. These data allow us to compare the oxidative and reductive strengths of a variety of substances. The half-reaction for the standard hydrogen electrode (SHE) lies more than halfway down the list in Table **8.5.1**. All reactants that lie below the SHE in the table are stronger oxidants than H^+, and all those that lie above the SHE are weaker. The strongest oxidant in the table is F_2, with a standard electrode potential of 2.87 V. This high value is consistent with the high electronegativity of fluorine and tells us that fluorine has a stronger tendency to accept electrons (it is a stronger oxidant) than any other element.

Table **8.5.1**: Standard Potentials for Selected Reduction Half-Reactions at 25°C

Half-Reaction	E° (V)
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	–3.040
$Be^{2+}(aq) + 2e^- \rightleftharpoons Be(s)$	–1.99
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	–1.676
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	–0.7618
$Ag_2S(s) + 2e^- \rightleftharpoons 2Ag(s) + S^{2-}(aq)$	–0.71
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	–0.44
$Cr^{3+}(aq) + e^- \rightleftharpoons Cr^{2+}(aq)$	–0.424
$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s)$	–0.4030
$PbSO_4(s) + 2e^- \rightleftharpoons Pb(s) + SO_4^{2-}(aq)$	–0.356
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	–0.257
$2SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons S_2O_6^{2-}(aq) + 2H_2O(l)$	–0.25
$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$	−0.14
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00
$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq)$	0.154
$Cu^{2+}(aq) + e^- \rightleftharpoons Cu^+(aq)$	0.159
$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-(aq)$	0.2223
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	0.3419
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$	0.401
$H_2SO_3(aq) + 4H^+(aq) + 4e^- \rightleftharpoons S(s) + 3H_2O(l)$	0.45
$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	0.5355
$MnO_4^{2-}(aq) + 2H_2O(l) + 2e^- \rightleftharpoons MnO_2(s) + 4OH^-(aq)$	0.60
$O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O_2(aq)$	0.695
$H_2SeO_3(aq) + 4H^+ + 4e^- \rightleftharpoons Se(s) + 3H_2O(l)$	0.74
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	0.771
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	0.7996
$NO_3^-(aq) + 3H^+(aq) + 2e^- \rightleftharpoons HNO_2(aq) + H_2O(l)$	0.94
$Br_2(aq) + 2e^- \rightleftharpoons 2Br^-(aq)$	1.087
$MnO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Mn^{2+}(aq) + 2H_2O(l)$	1.23
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	1.229
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$	1.36
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	1.396
$Ce^{4+}(aq) + e^- \rightleftharpoons Ce^{3+}(aq)$	1.61
$PbO_2(s) + HSO_4^-(aq) + 3H^+(aq) + 2e^- \rightleftharpoons PbSO_4(s) + 2H_2O(l)$	1.690

Half-Reaction	E° (V)
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$	1.763
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	2.87

Not all oxidizers and reducers are created equal. The standard reduction potentials in Table **8.5.1** can be interpreted as a ranking of substances according to their oxidizing and reducing power. Strong oxidizing agents are typically compounds with elements in high oxidation states or with high electronegativity, which gain electrons in the redox reaction (Figure **8.5.1**). Examples of strong oxidizers include hydrogen peroxide, permanganate, and osmium tetroxide. Reducing agents are typically electropositive elements such as hydrogen, lithium, sodium, iron, and aluminum, which lose electrons in redox reactions. Hydrides (compounds that contain hydrogen in the formal -1 oxidation state), such as sodium hydride, sodium borohydride and lithium aluminum hydride, are often used as reducing agents in organic and organometallic reactions.

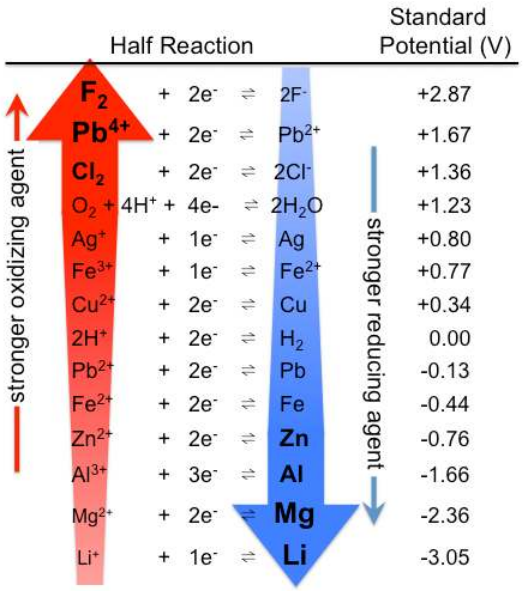


Figure **8.5.1**: Table of standard electrode potentials. **Note that the ranking is the opposite here**, with strong oxidizing agents at the top and strong reducing agents at the bottom, than in Table **8.5.1**. The actual standard potentials are the same of course. (CC BY-SA 3.0; Tem5psu).

Similarly, all species in Table **8.5.1** that lie above H_2 are stronger reductants than H_2, and those that lie below H_2 are weaker. The strongest reductant in the table is thus metallic lithium, with a standard electrode potential of −3.04 V. This fact might be surprising because cesium, not lithium, is the least electronegative element. The apparent anomaly can be explained by the fact that electrode potentials are measured in aqueous solution, where intermolecular interactions are important, whereas ionization potentials and electron affinities are measured in the gas phase. Due to its small size, the Li^+ ion is stabilized in aqueous solution by strong electrostatic interactions with the negative dipole end of water molecules. These interactions result in a significantly greater $\Delta H_{hydration}$ for Li^+ compared with Cs^+. Lithium metal is therefore the strongest reductant (most easily oxidized) of the alkali metals in aqueous solution.

> *The standard reduction potentials can be interpreted as a ranking of substances according to their oxidizing and reducing power. Species in Table* **8.5.1** *that lie above* H_2 *are stronger reducing agents (more easily oxidized) than* H_2*. Species that lie below* $\mathbf{H_2}$ *are stronger oxidizing agents.*

Because the half-reactions shown in Table **8.5.1** are arranged in order of their E° values, we can use the table to quickly predict the relative strengths of various oxidants and reductants. Any species on the left side of a half-reaction will spontaneously oxidize any species on the right side of another half-reaction that lies below it in the table. Conversely, any species on the right side of a half-

reaction will spontaneously reduce any species on the left side of another half-reaction that lies above it in the table. We can use these generalizations to predict the spontaneity of a wide variety of redox reactions ($E°_{cell} > 0$), as illustrated in Example **8.5.1**.

Example 8.5.1: Silver Sulfide

The black tarnish that forms on silver objects is primarily Ag_2S. The half-reaction for reversing the tarnishing process is as follows:

$$Ag_2S(s) + 2e^- \longrightarrow 2Ag(s) + S^{2-}(aq) \qquad E° = -0.69\,V$$

a. Referring to Table **8.5.1**, predict which species—H_2O_2(aq), Zn(s), I^-(aq), Sn^{2+}(aq)—can reduce Ag_2S to Ag under standard conditions.
b. Of these species—H_2O_2(aq), Zn(s), I^-(aq), Sn^{2+}(aq), identify which is the strongest reducing agent in aqueous solution and thus the best candidate for a commercial product.
c. From the data in Table **8.5.1**, suggest an alternative reducing agent that is readily available, inexpensive, and possibly more effective at removing tarnish.



Given: reduction half-reaction, standard electrode potential, and list of possible reductants

Asked for: reductants for Ag_2S, strongest reductant, and potential reducing agent for removing tarnish

Strategy:

A From their positions in Table **8.5.1**, decide which species can reduce Ag_2S. Determine which species is the strongest reductant.

B Use Table **8.5.1** to identify a reductant for Ag_2S that is a common household product.

Solution

We can solve the problem in one of two ways: (1) compare the relative positions of the four possible reductants with that of the Ag_2S/Ag couple in Table **8.5.1** or (2) compare E° for each species with E° for the Ag_2S/Ag couple (−0.69 V).

a. **A** The species in Table **8.5.1** are arranged from top to bottom in order of increasing reducing strength. Of the four species given in the problem, I^-(aq), Sn^{2+}(aq), and H_2O_2(aq) lie above Ag_2S, and one [Zn(s)] lies below it. We can therefore conclude that Zn(s) can reduce Ag_2S(s) under standard conditions, whereas I^-(aq), Sn^{2+}(aq), and H_2O_2(aq) cannot. Sn^{2+}(aq) and H_2O_2(aq) appear twice in the table: on the left side (oxidant) in one half-reaction and on the right side (reductant) in another.
b. The strongest reductant is Zn(s), the species on the right side of the half-reaction that lies closer to the bottom of Table **8.5.1** than the half-reactions involving I^-(aq), Sn^{2+}(aq), and H_2O_2(aq). (Commercial products that use a piece of zinc are often marketed as a “miracle product” for removing tarnish from silver. All that is required is to add warm water and salt for electrical conductivity.)
c. **B** Of the reductants that lie below Zn(s) in Table **8.5.1**, and therefore are stronger reductants, only one is commonly available in household products: Al(s), which is sold as aluminum foil for wrapping foods.

Example 8.5.2

Use the data in Table 8.5.1 to determine whether each reaction is likely to occur spontaneously under standard conditions:

a. $\mathrm{Sn(s) + Be^{2+}(aq) \longrightarrow Sn^{2+}(aq) + Be(s)}$
b. $\mathrm{MnO_2(s) + H_2O_2(aq) + 2H^+(aq) \longrightarrow O_2(g) + Mn^{2+}(aq) + 2H_2O(l)}$

Given: redox reaction and list of standard electrode potentials (Table 8.5.1)

Asked for: reaction spontaneity

Strategy:

A. Identify the half-reactions in each equation. Using Table 8.5.1, determine the standard potentials for the half-reactions in the appropriate direction.
B. Use the $E_{cell} = E^{\circ}_{srp}(cathode) - E^{\circ}_{srp}(anode)$ equation to calculate the standard cell potential for the overall reaction. From this value, determine whether the overall reaction is spontaneous.

Solution

a. **A** Metallic tin is oxidized to $\mathrm{Sn^{2+}(aq)}$, and $\mathrm{Be^{2+}(aq)}$ is reduced to elemental beryllium. We can find the standard electrode potentials for the latter (reduction) half-reaction (−1.99 V) and for the former (oxidation) half-reaction (−0.14 V) directly from Table 8.5.1.

B Adding the two half-reactions gives the overall reaction:

$$\begin{aligned} \mathrm{cathode: Be^{2+}(aq) + 2e^- \rightarrow Be(s)} \\ \mathrm{anode: Sn(s) \rightarrow Sn^{2+}(s) + 2e^-} \\ \hline \mathrm{overall: Sn(s) + Be^{2+}(aq) \rightarrow Sn^{2+}(aq) + Be(s)} \end{aligned}$$

with

$$\begin{aligned} E^{\circ}_{\text{cathode}} &= \text{-1.99 V} \\ E^{\circ}_{\text{anode}} &= \text{-0.14 V} \\ E^{\circ}_{\text{cell}} &= E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} \\ &= -1.85 \text{ V} \end{aligned}$$

The standard cell potential is quite negative, so the reaction will not occur spontaneously as written. That is, metallic tin cannot reduce Be^{2+} to beryllium metal under standard conditions. Instead, the reverse process, the reduction of stannous ions (Sn^{2+}) by metallic beryllium, which has a positive value of E°_{cell}, will occur spontaneously.

b. **A** $\mathrm{MnO_2}$ is the oxidant ($\mathrm{Mn^{4+}}$ is reduced to $\mathrm{Mn^{2+}}$), while $\mathrm{H_2O_2}$ is the reductant ($\mathrm{O^{2-}}$ is oxidized to $\mathrm{O_2}$). We can obtain the standard electrode potentials for the reduction and oxidation half-reactions directly from Table 8.5.1.

B The two half-reactions and their corresponding potentials are as follows:

$$\begin{aligned} \mathrm{cathode: MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O(l)} \\ \mathrm{anode: H_2O_2(aq) \rightarrow O_2(g) + 2H^+(aq) + 2e^-} \\ \hline \mathrm{overall: MnO_2(s) + H_2O_2(aq) + 2H^+(aq) \rightarrow O_2(g) + Mn^{2+}(aq) + 2H_2O(l)} \end{aligned}$$

with

$$\begin{aligned} E^{\circ}_{\text{cathode}} &= 1.23 \text{ V} \\ E^{\circ}_{\text{anode}} &= 0.70 \text{ V} \\ E^{\circ}_{\text{cell}} &= E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} \\ &= +0.52 \text{ V} \end{aligned}$$

The standard potential for the reaction is positive, indicating that under standard conditions, it will occur spontaneously as written. Hydrogen peroxide will reduce $\mathrm{MnO_2}$, and oxygen gas will evolve from the solution.

? Exercise 8.5.2

Use the data in Table 8.5.1 to determine whether each reaction is likely to occur spontaneously under standard conditions:

a. $2\,Ce^{4+}(aq) + 2\,Cl^{-}(aq) \longrightarrow 2\,Ce^{3+}(aq) + Cl_2(g)$
b. $4\,MnO_2(s) + 3\,O_2(g) + 4\,OH^{-}(aq) \longrightarrow 4\,MnO_4^{-}(aq) + 2\,H_2O$

Answer a

spontaneous with $E^{o}_{cell} = 1.61\,V - 1.396\,V = 0.214\,V$

Answer b

nonspontaneous with $E^{\circ}_{cell} = -0.20\,V$

Although the sign of E^{o}_{cell} tells us whether a particular redox reaction will occur spontaneously under standard conditions, it does not tell us to what extent the reaction proceeds, and it does not tell us what will happen under nonstandard conditions. To answer these questions requires a more quantitative understanding of the relationship between electrochemical cell potential and chemical thermodynamics.

Summary

The relative strengths of various oxidants and reductants can be predicted using E^{o} values. The oxidative and reductive strengths of a variety of substances can be compared using standard electrode potentials. Apparent anomalies can be explained by the fact that electrode potentials are measured in aqueous solution, which allows for strong intermolecular electrostatic interactions, and not in the gas phase.

Conceptual Problems

1. The order of electrode potentials cannot always be predicted by ionization potentials and electron affinities. Why? Do you expect sodium metal to have a higher or a lower electrode potential than predicted from its ionization potential? What is its approximate electrode potential?
2. Without referring to tabulated data, of Br_2/Br^-, Ca^{2+}/Ca, O_2/OH^-, and Al^{3+}/Al, which would you expect to have the least negative electrode potential and which the most negative? Why?
3. Because of the sulfur-containing amino acids present in egg whites, eating eggs with a silver fork will tarnish the fork. As a chemist, you have all kinds of interesting cleaning products in your cabinet, including a 1 M solution of oxalic acid ($H_2C_2O_4$). Would you choose this solution to clean the fork that you have tarnished from eating scrambled eggs?
4. The electrode potential for the reaction $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ is 0.34 V under standard conditions. Is the potential for the oxidation of 0.5 mol of Cu equal to −0.34/2 V? Explain your answer.
5. Refer to Table 8.5.1 to predict
   A. Which species—$Sn^{4+}(aq)$, $Cl^-(aq)$, $Ag^+(aq)$, $Cr^{3+}(aq)$, and/or $H_2O_2(aq)$—can oxidize $MnO_2(s)$ to MNO_4^- under standard conditions.
   B. Which species—$Sn^{4+}(aq)$, $Cl^-(aq)$, $Ag^+(aq)$, $Cr^{3+}(aq)$, and/or $H_2O_2(aq)$—is the strongest oxidizing agent in aqueous solution.

Conceptual Answer

3. No; E° = −0.691 V for $Ag_2S(s) + 2e^- \rightarrow Ag(s) + S^{2-}(aq)$, which is too negative for Ag_2S to be spontaneously reduced by oxalic acid [E° = 0.49 V for $2CO_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2C_2O_4(aq)$]

5.

A. $Ag^+(aq)$; $H_2O_2(aq)$
B. $H_2O_2(aq)$

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8.6: E, ΔG, and K (The Big Triangle of Chemistry)

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:

$$\Delta G^\circ = -nFE^\circ_{cell} \tag{8.6.1}$$

A spontaneous redox reaction is characterized by a negative value of ΔG°, which corresponds to a positive value of E°_{cell}.

Example 8.6.1

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 8.6.1 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 8.6.1. Because six electrons are transferred in the overall reaction, the value of n is 6:

$$\begin{aligned}\Delta G^\circ &= -(n)(F)(E^\circ_{cell}) \\ &= -(6\text{ mole})[96,485\text{ J/(V}\cdot\text{mol)}(0.27\text{ V})] \\ &= -15.6 \times 10^4\text{ J} \\ &= -156\text{ kJ/mol } Cr_2O_7^{2-}\end{aligned}$$

Thus ΔG^o is −168 kJ/mol for the reaction as written, and the reaction is spontaneous.

Exercise 8.6.1

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 8.6.1 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 8.6.1), we can write

$$-nFE^\circ_{cell} = -RT \ln K$$

Rearranging this equation,

$$E^\circ_{\text{cell}} = \left(\frac{RT}{nF}\right) \ln K \tag{8.6.2}$$

For $T = 298\,K$, Equation 8.6.2 can be simplified as follows:

$$\begin{aligned} E^\circ_{\text{cell}} &= \left(\frac{RT}{nF}\right) \ln K \\ &= \left[\frac{[8.314\ \text{J/(mol}\cdot\text{K)}(298\ \text{K})]}{n[96,485\ \text{J/(V}\cdot\text{mol)}]}\right] 2.303 \log K \\ &= \left(\frac{0.0592\ \text{V}}{n}\right) \log K \end{aligned} \tag{8.6.3}$$

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 8.6.2

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 8.6.3 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 8.6.3 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 8.6.2

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:

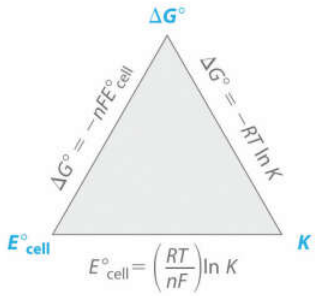
$$2\,Sn^{2+}(aq) + O_2(g) + 4\,H^+(aq) \rightleftharpoons 2\,Sn^{4+}(aq) + 2\,H_2O(l)$$

Answer

5.7×10^{72}

Figure 8.6.1 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 **8.6.1**: 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°.

8.6: E, ΔG, and K (The Big Triangle of Chemistry) is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

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8.7: Cell Potential as a Function of Concentrations

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:

$$\Delta G = \Delta G^\circ + RT \ln Q \tag{8.7.1}$$

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 8.7.1, we obtain

$$-nFE_{cell} = -nFE^o_{cell} + RT \ln Q \tag{8.7.2}$$

Dividing both sides of this equation by $-nF$,

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{RT}{nF}\right) \ln Q \tag{8.7.3}$$

Equation 8.7.3 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 8.7.3 reduces to Equation 8.7.4 and 8.7.5 because $Q = K$, and there is no net transfer of electrons (i.e., E_{cell} = 0).

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{RT}{nF}\right) \ln K = 0 \tag{8.7.4}$$

since

$$E^\circ_{\text{cell}} = \left(\frac{RT}{nF}\right) \ln K \tag{8.7.5}$$

Substituting the values of the constants into Equation 8.7.3 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):

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right) \log Q \tag{8.7.6}$$

The Power of the Nernst Equation

The Nernst Equation (8.7.3) 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 8.7.6 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 8.7.6 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 8.7.1

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 8.7.6 instead of Equation 8.7.3. 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 8.7.6,

$$\begin{aligned} E_{cell} &= E°_{cell} - \left(\frac{0.0591\ \text{V}}{n}\right)\log Q \\ &= 0.25\ \text{V} - \left(\frac{0.0591\ \text{V}}{2}\right)\log\left(\frac{[Ce^{3+}]^2 P_{Cl_2}}{[Ce^{4+}]^2[Cl^-]^2}\right) \\ &= 0.25\ \text{V} - [(0.0296\ \text{V})(8.37)] = 0.00\ \text{V} \end{aligned}$$

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 8.7.1

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:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s) \quad E°cell = 1.10V \tag{8.7.7}$$

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 8.7.6:

$$E_{cell} = E^\circ_{cell} - \left(\frac{0.0591\ V}{n}\right) \log \frac{[Zn^{2+}]}{[Cu^{2+}]} \tag{8.7.8}$$

$$= 1.10\ V - \left(\frac{0.0591\ V}{2}\right) \log \left(\frac{1.0 \times 10^{-6}}{1.0}\right) = 1.28\ V \tag{8.7.9}$$

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+}), $Q = 1.0 \times 10^6$, and the cell potential will be reduced to 0.92 V.

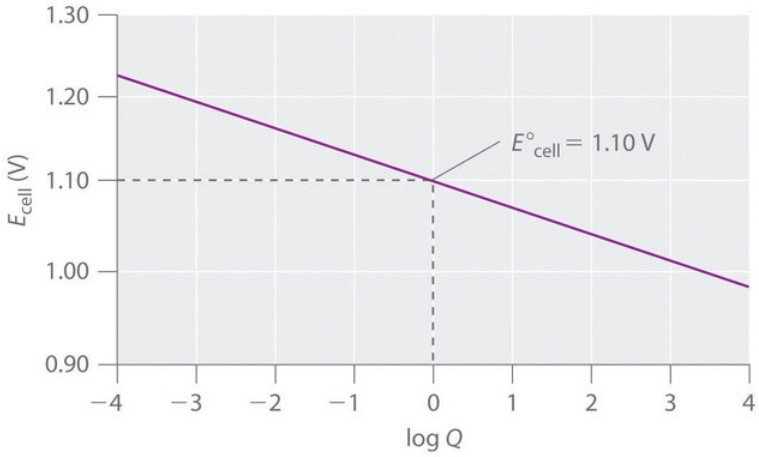


Figure 8.7.1: The Variation of E_{cell} with Log Q for a Zn/Cu Cell. Initially, log Q < 0, and the voltage of the cell is greater than $E°_{cell}$. As the reaction progresses, log Q increases, and E_{cell} decreases. When $[Zn^{2+}] = [Cu^{2+}]$, log Q = 0 and $E_{cell} = E°_{cell} = 1.10$ V. As long 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 8.7.1. 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:

$$E_{cell} = E^\circ_{cell} - \left(\frac{0.0591\ V}{n}\right) \log Q = 0 \tag{8.7.10}$$

$$E^\circ = \left(\frac{0.0591\ V}{n}\right) \log Q \tag{8.7.11}$$

$$\log Q = \frac{E°n}{0.0591\ V} = \frac{(1.10\ V)(2)}{0.0591\ V} = 37.23 \tag{8.7.12}$$

$$Q = 10^{37.23} = 1.7 \times 10^{37} \tag{8.7.13}$$

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:

$$\mathrm{Ag(s)\,|\,Ag^+}(aq, 0.010\ M)\ ||\ \mathrm{Ag^+}(aq, 1.0\ M)\,|\,\mathrm{Ag\,(s)} \tag{8.7.14}$$

cathode:

$$\mathrm{Ag^+}(aq, 1.0\ M) + \mathrm{e^-} \rightarrow \mathrm{Ag\,(s)} \tag{8.7.15}$$

anode:

$$\mathrm{Ag\,(s)} \rightarrow \mathrm{Ag^+}(aq, 0.010\ M) + \mathrm{e^-} \tag{8.7.16}$$

Overall

$$\mathrm{Ag^+}(aq, 1.0\ M) \rightarrow \mathrm{Ag^+}(aq, 0.010\ M) \tag{8.7.17}$$

As the reaction progresses, the concentration of Ag^+ will increase in the left (oxidation) compartment as the silver electrode dissolves, while the Ag^+ concentration in the right (reduction) compartment decreases as the electrode in that compartment gains mass. The total mass of $Ag(s)$ in the cell will remain constant, however. We can calculate the potential of the cell using the Nernst equation, inserting 0 for $E°_{cell}$ because $E°_{cathode} = -E°_{anode}$:

$$\begin{aligned} E_{\text{cell}} &= E^\circ_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right)\log Q \\ &= 0 - \left(\frac{0.0591\ \text{V}}{1}\right)\log\left(\frac{0.010}{1.0}\right) \\ &= 0.12\ \text{V} \end{aligned}$$

An electrochemical cell of this type, in which the anode and cathode compartments are identical except for the concentration of a reactant, is called a **concentration cell**. As the reaction proceeds, the difference between the concentrations of Ag^+ in the two compartments will decrease, as will E_{cell}. Finally, when the concentration of Ag^+ is the same in both compartments, equilibrium will have been reached, and the measured potential difference between the two compartments will be zero ($E_{cell} = 0$).

✔ Example 8.7.2

Calculate the voltage in a galvanic cell that contains a manganese electrode immersed in a 2.0 M solution of $MnCl_2$ as the cathode, and a manganese electrode immersed in a 5.2×10^{-2} M solution of $MnSO_4$ as the anode (T = 25°C).

Given: galvanic cell, identities of the electrodes, and solution concentrations

Asked for: voltage

Strategy:

A. Write the overall reaction that occurs in the cell.

B. Determine the number of electrons transferred. Substitute this value into the Nernst equation to calculate the voltage.

Solution

A This is a concentration cell, in which the electrode compartments contain the same redox active substance but at different concentrations. The anions (Cl^- and SO_4^{2-}) do not participate in the reaction, so their identity is not important. The overall reaction is as follows:

$$Mn^{2+}(aq, 2.0\,M) \rightarrow Mn^{2+}(aq, 5.2 \times 10^{-2}\,M)$$

B For the reduction of Mn^{2+}(aq) to Mn(s), n = 2. We substitute this value and the given Mn^{2+} concentrations into Equation 8.7.6:

$$\begin{aligned} E_{cell} &= E^\circ_{cell} - \left(\frac{0.0591\ V}{n}\right) \log Q \\ &= 0\ V - \left(\frac{0.0591\ V}{2}\right) \log\left(\frac{5.2 \times 10^{-2}}{2.0}\right) \\ &= 0.047\ V \end{aligned}$$

Thus manganese will dissolve from the electrode in the compartment that contains the more dilute solution and will be deposited on the electrode in the compartment that contains the more concentrated solution.

? Exercise 8.7.2

Suppose we construct a galvanic cell by placing two identical platinum electrodes in two beakers that are connected by a salt bridge. One beaker contains 1.0 M HCl, and the other a 0.010 M solution of Na_2SO_4 at pH 7.00. Both cells are in contact with the atmosphere, with P_{O_2} = 0.20 atm. If the relevant electrochemical reaction in both compartments is the four-electron reduction of oxygen to water:

$$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$$

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.

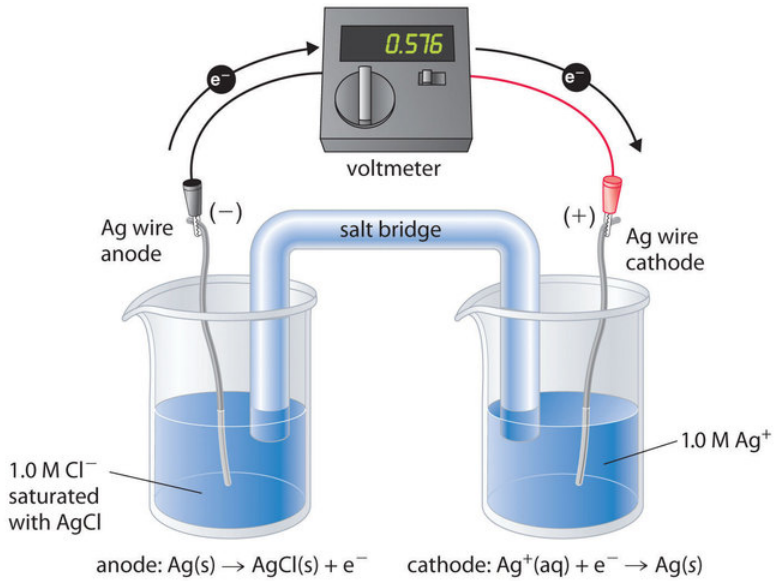


Figure 8.7.1: A Galvanic ("Concentration") Cell for Measuring the Solubility Product of AgCl. One compartment contains a silver wire inserted into a 1.0 M solution of Ag^+, and the other compartment contains a silver wire inserted into a 1.0 M Cl^- solution saturated with AgCl. The potential due to the 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 8.7.1, 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:

$$\begin{aligned}E_{cell} &= 0\ V - \left(\frac{0.0591\ V}{1}\right) \log\left(\frac{[Ag^+]_{dilute}}{[Ag^+]_{concentrated}}\right) \\ &= -0.0591\ V\ \log\left(\frac{K_{sp}}{1.0}\right) \\ &= -0.0591\ V\ \log K_{sp} \qquad (8.7.18)\end{aligned}$$

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 8.7.18 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 8.7.3: 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 **8.7.1**, 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 8.7.3

A concentration cell similar to the one described in Example **8.7.3** 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 **8.7.3**, 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 8.7.4: 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:

$$\mathrm{Zn\,(s)\,|Zn^{2+}}(aq, 1.0\,M)\,\big|\,\big|\,\mathrm{H^+}(aq, ?\,M)\,\big|\,\mathrm{H_2}(g, 1.0\,atm)|Pt(s)$$

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 8.7.6), 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 8.7.4

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.

8.7: Cell Potential as a Function of Concentrations is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

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8.8: Batteries- Producing Electricity Through Chemical Reactions

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 8.8.1). 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.

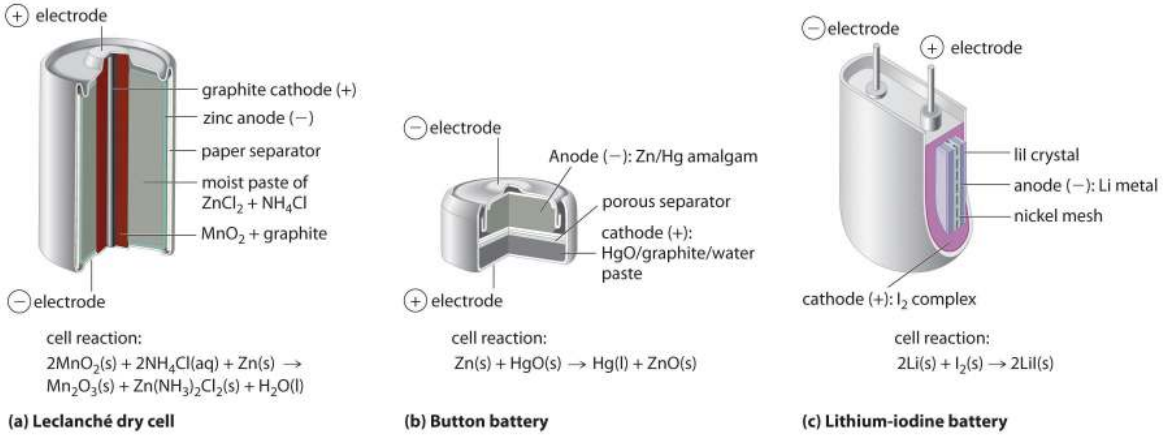


Figure 8.8.1: Three Kinds of Primary (Nonrechargeable) Batteries. (a) A Leclanché dry cell is actually a "wet cell," in which the electrolyte is an acidic water-based paste containing MnO_2, NH_4Cl, $ZnCl_2$, graphite, and starch. Though inexpensive to manufacture, the cell is not very efficient in producing 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 8.8.1). The half-reactions at the anode and the cathode can be summarized as follows:

- cathode (reduction):

$$2\,MnO_2\,(s) + 2\,NH_4^+\,(aq) + 2\,e^- \longrightarrow Mn_2O_3\,(s) + 2\,NH_3\,(aq) + H_2O\,(l)$$

- anode (oxidation):

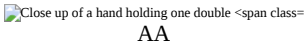
$$Zn\,(s) \longrightarrow Zn^{2+}\,(aq) + 2\,e^-$$

The Zn^{2+} ions formed by the oxidation of $Zn(s)$ at the anode react with NH_3 formed at the cathode and Cl^- ions present in solution, so the overall cell reaction is as follows:

- overall reaction:

$$2\,MnO_2(s) + 2\,NH_4Cl(aq) + Zn(s) \longrightarrow Mn_2O_3(s) + Zn(NH_3)_2Cl_2(s) + H_2O(l) \tag{8.8.1}$$

The dry cell produces about 1.55 V and is inexpensive to manufacture. It is not, however, very efficient in producing electrical energy because only the relatively small fraction of the MnO_2 that is near the cathode is actually reduced and only a small fraction of the zinc cathode is actually consumed as the cell discharges. In addition, dry cells have a limited shelf life because the Zn anode reacts spontaneously with NH_4Cl in the electrolyte, causing the case to corrode and allowing the contents to leak out.



AA

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Source: Photo courtesy of Mitchclanky2008, www.flickr.com/photos/25597837@N05/2422765479/.

The **alkaline battery** is essentially a Leclanché cell adapted to operate under alkaline, or basic, conditions. The half-reactions that occur in an alkaline battery are as follows:

- cathode (reduction)

$$2\,MnO_2(s) + H_2O(l) + 2\,e^- \longrightarrow Mn_2O_3(s) + 2\,OH^-(aq)$$

- anode (oxidation):

$$Zn(s) + 2\,OH^-(aq) \longrightarrow ZnO(s) + H_2O(l) + 2\,e^-$$

- overall reaction:

$$Zn(s) + 2\,MnO_2(s) \longrightarrow ZnO(s) + Mn_2O_3(s)$$

This battery also produces about 1.5 V, but it has a longer shelf life and more constant output voltage as the cell is discharged than the Leclanché dry cell. Although the alkaline battery is more expensive to produce than the Leclanché dry cell, the improved performance makes this battery more cost-effective.

Button Batteries

Although some of the small button batteries used to power watches, calculators, and cameras are miniature alkaline cells, most are based on a completely different chemistry. In these "button" batteries, the anode is a zinc–mercury amalgam rather than pure zinc, and the cathode uses either HgO or Ag_2O as the oxidant rather than MnO_2 in Figure 8.8.1*b*).



Button batteries. (Gerhard H Wrodnigg via Wikipedia)

The cathode, anode and overall reactions and cell output for these two types of button batteries are as follows (two half-reactions occur at the anode, but the overall oxidation half-reaction is shown):

- cathode (mercury battery):

$$HgO(s) + H_2O(l) + 2\,e^- \longrightarrow Hg(l) + 2\,OH^-(aq)$$

- Anode (mercury battery):

$$Zn + 2\,OH^- \longrightarrow ZnO + H_2O + 2\,e^-$$

- overall reaction (mercury battery):

$$Zn(s) + 2\,HgO(s) \longrightarrow 2\,Hg(l) + ZnO(s)$$

with $E_{cell} = 1.35\,V$.

- cathode reaction (silver battery):

$$Ag_2O(s) + H_2O(l) + 2e^- \longrightarrow 2Ag(s) + 2OH^-(aq)$$

- 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):

$$I_{2(s)} + 2e^- \rightarrow 2I^-_{(LiI)} \tag{8.8.2}$$

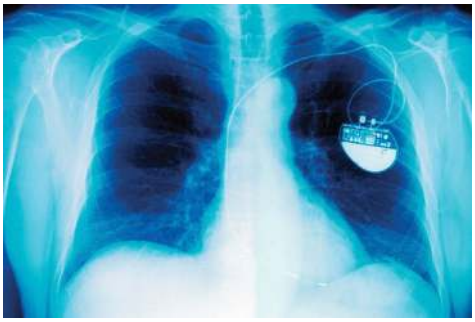
- anode (oxidation):

$$2Li_{(s)} \rightarrow 2Li^+_{(LiI)} + 2e^- \tag{8.8.3}$$

- overall:

$$2Li_{(s)} + I_{2(s)} \rightarrow 2LiI_{(s)} \tag{8.8.4}$$

with $E_{cell} = 3.5\,V$



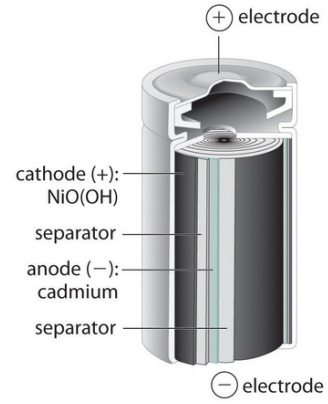
Cardiac pacemaker: An x-ray of a patient showing the location and size of a pacemaker powered by a lithium–iodine battery.

As shown in part (c) in Figure 8.8.1, 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 8.8.2, 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.



cell reaction:

$Cd(s) + 2NiO(OH)(s) + 2H_2O(l) \rightarrow Cd(OH)_2(s) + 2Ni(OH)_2(s)$

Figure 8.8.2: 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):

$$2NiO(OH)_{(s)} + 2H_2O_{(l)} + 2e^- \rightarrow 2Ni(OH)_{2(s)} + 2OH^-_{(aq)} \tag{8.8.5}$$

- anode (oxidation):

$$Cd_{(s)} + 2OH^-_{(aq)} \rightarrow Cd(OH)_{2(s)} + 2e^- \tag{8.8.6}$$

- overall:

$$Cd_{(s)} + 2NiO(OH)_{(s)} + 2H_2O_{(l)} \rightarrow Cd(OH)_{2(s)} + 2Ni(OH)_{2(s)} \tag{8.8.7}$$

$$E_{cell} = 1.4V$$

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:

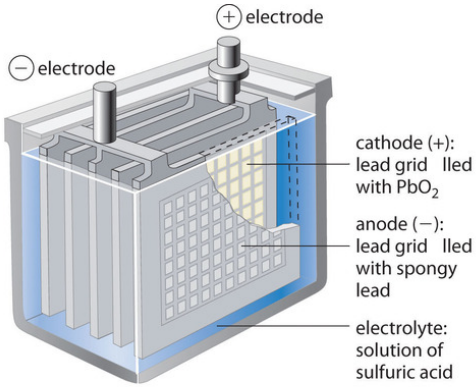
\[NiO(OH)_{(s)} + MH \rightarrow Ni(OH)_{2(s)} + M_{(s)} \label{Eq16} \]

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.



cell reaction:

$Pb(s) + PbO_2(s) + 2HSO_4^-(aq) + 2H^+(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$

Figure 8.8.3: 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 8.8.3, 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):

$$Pb_{(s)} + HSO^-_{4(aq)} \rightarrow PbSO_{4(s)} + H^+_{(aq)} + 2e^- \tag{8.8.8}$$

with $E^\circ_{anode} = -0.356\ V$

- overall:

$$Pb_{(s)} + PbO_{2(s)} + 2HSO^-_{4(aq)} + 2H^+_{(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(l)} \tag{8.8.9}$$

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:

$$2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2(g)} \tag{8.8.10}$$

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.

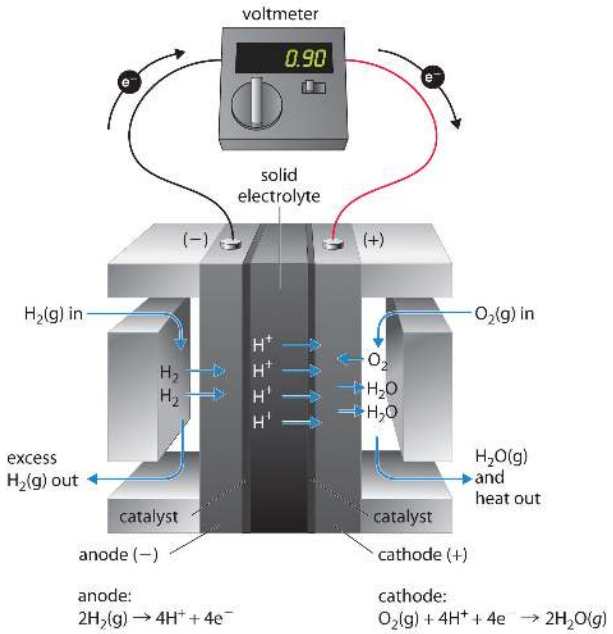


Figure **8.8.4**: A Hydrogen Fuel Cell Produces Electrical Energy Directly from a Chemical Reaction. Hydrogen is oxidized to protons at the anode, and the electrons are transferred through an external circuit to the cathode, where oxygen is reduced and combines with H^+ to form water. A solid electrolyte 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 **8.8.4**. The electrode reactions are as follows:

- cathode (reduction):

$$O_{2(g)} + 4H^+ + 4e^- \rightarrow 2H_2O_{(g)} \tag{8.8.11}$$

- anode (oxidation):

$$2H_{2(g)} \rightarrow 4H^+ + 4e^- \tag{8.8.12}$$

- overall:

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)} \tag{8.8.13}$$

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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8.9: Corrosion- Unwanted Voltaic Cells

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 **8.9.1**). 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.

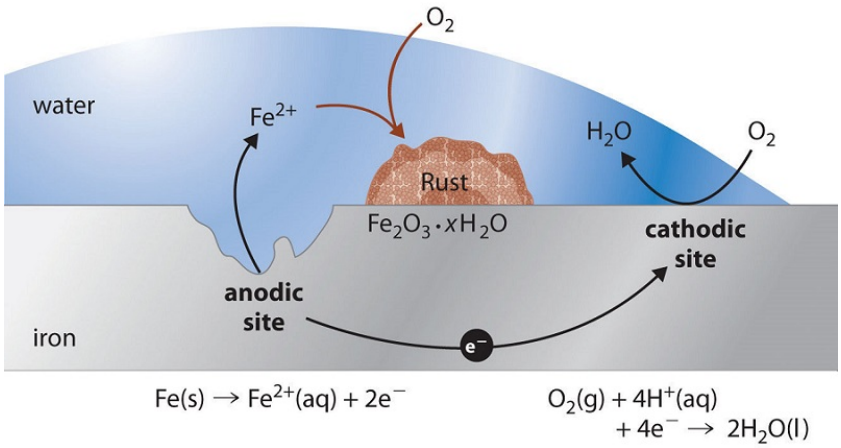


Figure **8.9.1**: Rust, the Result of Corrosion of Metallic Iron. Iron is oxidized to $Fe^{2+}(aq)$ at an anodic site on the surface of the iron, which is often an impurity or a lattice defect. Oxygen is reduced to water at a different site on the surface of the iron, which acts as the cathode. Electrons 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:

$$\mathrm{Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-}$$

with $E^o_{SRP} = -0.45\ V$.

- overall:

$$\mathrm{2Fe(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^{2+}(aq) + 2H_2O(l)} \tag{8.9.1}$$

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:

$$\mathrm{4Fe^{2+}(aq) + O_2(g) + (2 + 4x)H_2O \ \rightarrow 2Fe_2O_3 \cdot xH_2O + 4H^+(aq)} \tag{8.9.2}$$

The sign and magnitude of E^o_{cell} for the corrosion process (Equation 8.9.1) 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 8.9.2).

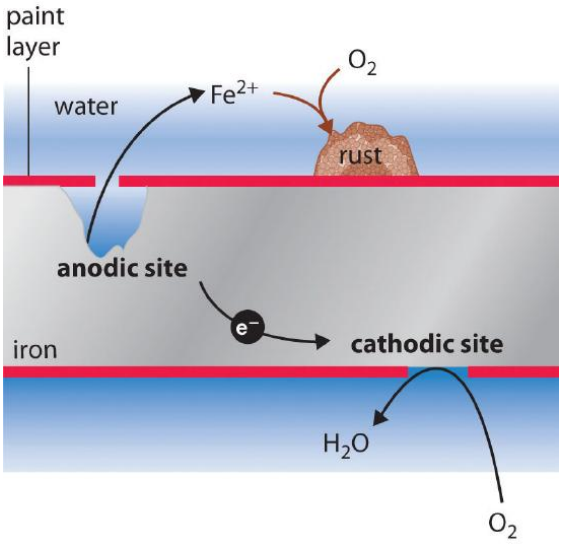


Figure 8.9.2: Small Scratches in a Protective Paint Coating Can Lead to the Rapid Corrosion of Iron. Holes in a protective coating allow oxygen to be reduced at the surface with the greater exposure to air (the cathode), while metallic iron is oxidized to Fe^{2+}(aq) at the less exposed site (the anode). 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).

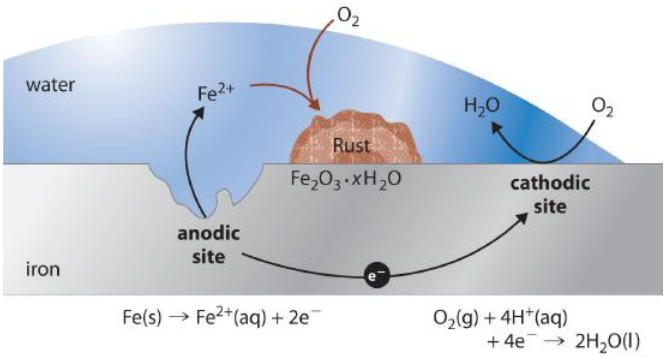


Figure 8.9.3: Galvanic Corrosion. If iron is in contact with a more corrosion-resistant metal such as tin, copper, or lead, the other metal can act as a large cathode that greatly increases the rate of reduction of oxygen. Because the reduction of oxygen is coupled to the oxidation of iron, this can 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 8.9.3). 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:

$$\underbrace{O_{2(g)} + 4e^- + 4H^+_{(aq)} \rightarrow 2H_2O_{(l)}}_{\text{reduction at cathode}} \tag{8.9.3}$$

$$\underbrace{Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-}_{\text{oxidation at anode}} \tag{8.9.4}$$

$$\underbrace{2Zn_{(s)} + O_{2(g)} + 4H^+_{(aq)} \rightarrow 2Zn^{2+}_{(aq)} + 2H_2O_{(l)}}_{\text{overall}} \tag{8.9.5}$$

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 8.9.4). Replacing the sacrificial electrodes is more cost-effective than replacing the iron objects they are protecting.

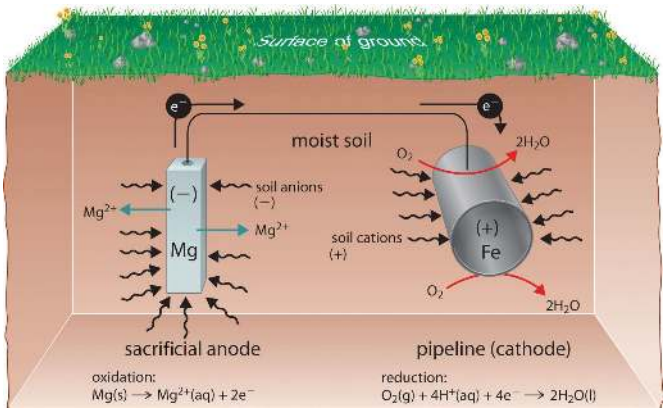


Figure **8.9.4**: The Use of a Sacrificial Electrode to Protect Against Corrosion. Connecting a magnesium rod to an underground steel pipeline protects the pipeline from corrosion. Because magnesium (E° = −2.37 V) is much more easily oxidized than iron (E° = −0.45 V), the Mg rod acts as the anode in 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 8.9.1

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 $E^{\circ\circ}_{cell}$?
b. How could you prevent this corrosion from occurring?

Given: identity of metals

Asked for: corrosion reaction, $E^{\circ\circ}_{cell}$, and preventive measures

Strategy:

A. Write the reactions that occur at the anode and the cathode. From these, write the overall cell reaction and calculate $E^{\circ\circ}_{cell}$.
B. Based on the relative redox activity of various substances, suggest possible preventive measures.

Solution

a. **A** According to Table P2, both copper and tin are less active metals than iron (i.e., they have higher positive values of $E^{\circ\circ}_{cell}$ than iron). Thus if tin or copper is brought into electrical contact by seawater with iron in the presence of oxygen, corrosion will occur. We therefore anticipate that the bronze propeller will act as the cathode at which O_2 is reduced, and the iron screws will act as anodes at which iron dissolves:

$$\begin{aligned}
&\text{cathode:} && O_2(s) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l) && E^\circ_{\text{cathode}} = 1.23\ \text{V}\\
&\text{anode:} && Fe(s) \rightarrow Fe^{2+} + 2e^- && E^\circ_{\text{anode}} = -0.45\ \text{V}\\
&\text{overall:} && 2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l) && E^\circ_{\text{overall}} = 1.68\ \text{V}
\end{aligned}$$

Over time, the iron screws will dissolve, and the boat will fall apart.

b. **B** Possible ways to prevent corrosion, in order of decreasing cost and inconvenience, are as follows: disassembling the boat and rebuilding it with bronze screws; removing the boat from the water and storing it in a dry place; or attaching an inexpensive piece of zinc metal to the propeller shaft to act as a sacrificial electrode and replacing it once or twice a year. Because zinc is a more active metal than iron, it will act as the sacrificial anode in the electrochemical cell and dissolve (Equation 8.9.5).



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 8.9.1

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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8.10: Electrolysis- Causing Nonspontaneous Reactions to Occur

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 **8.10.1***a*).

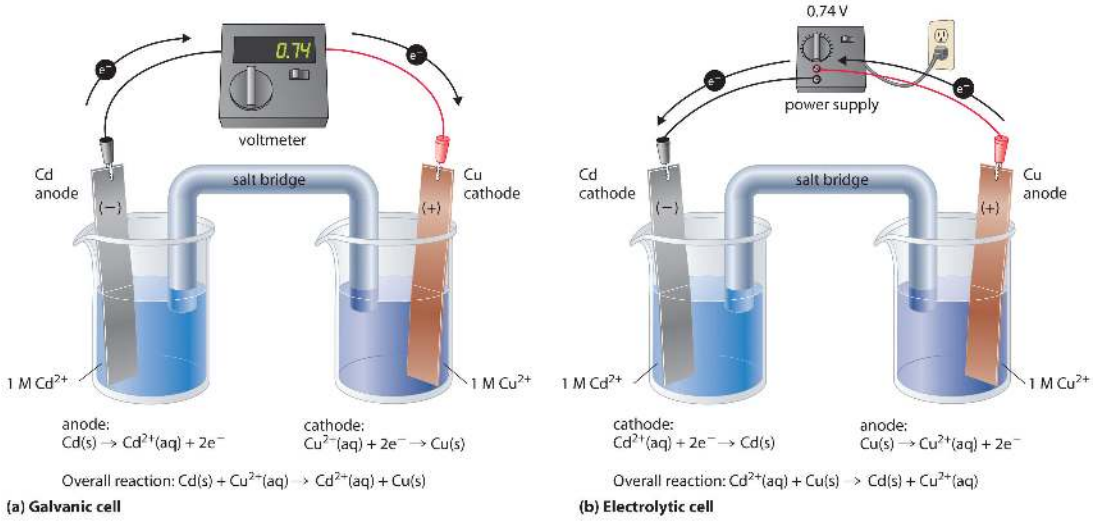


Figure **8.10.1**: An Applied Voltage Can Reverse the Flow of Electrons in a Galvanic Cd/Cu Cell. (a) When compartments that contain a Cd electrode immersed in 1 M Cd^{2+}(aq) and a Cu electrode immersed in 1 M Cu^{2+}(aq) are connected to create a galvanic cell, Cd(s) is spontaneously oxidized to Cd^{2+}(aq) 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 8.10.1*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:

$$\mathrm{Cd^{2+}(aq) + 2\,e^- \rightarrow Cd(s)} \tag{8.10.1}$$

with $E^\circ_{cathode} = -0.40\,V$

- half-reaction at the anode:

$$\mathrm{Cu(s) \rightarrow Cu^{2+}(aq) + 2\,e^-} \tag{8.10.2}$$

with $E^\circ_{anode} = 0.34\,V$

- Overall Reaction:

$$\mathrm{Cd^{2+}(aq) + Cu(s) \rightarrow Cd(s) + Cu^{2+}(aq)} \tag{8.10.3}$$

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 8.10.1.

Table 8.10.1: 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:

$$\mathrm{2\,NaCl(l) \rightarrow 2\,Na(l) + Cl_2(g)} \tag{8.10.4}$$

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 8.10.2). 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.

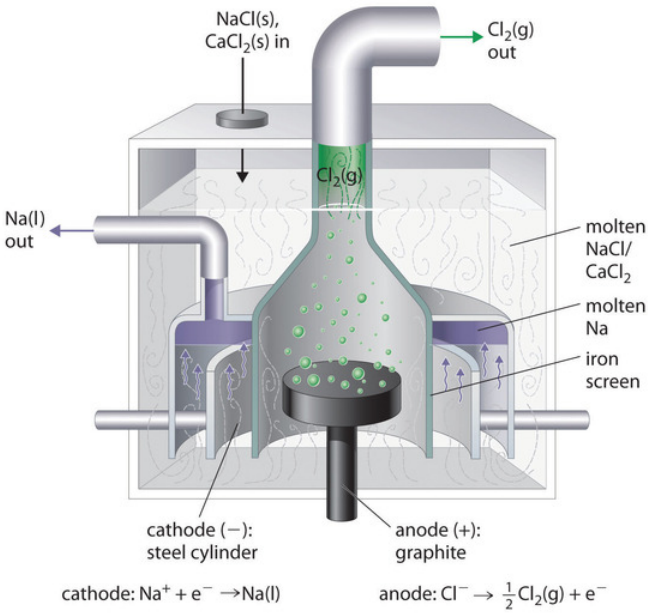


Figure 8.10.2: A Downs Cell for the Electrolysis of Molten NaCl. The electrolysis of a molten mixture of NaCl and $CaCl_2$ results in the formation of elemental sodium and chlorine gas. Because sodium is a liquid under these conditions and liquid sodium is less dense than molten sodium chloride, the 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:

$$2\,Al_2O_3\,(l) + 3\,C\,(s) \longrightarrow 4\,Al\,(l) + 3\,CO_2\,(g) \tag{8.10.5}$$

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 8.10.1

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 8.10.1

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 **8.10.3**).

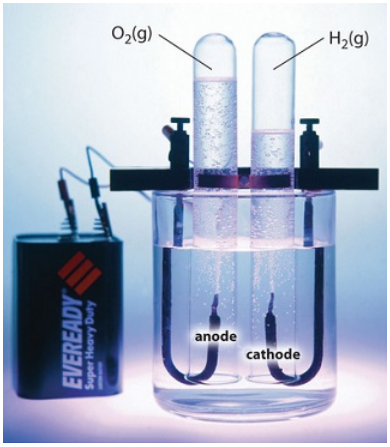


Figure **8.10.3**: The Electrolysis of Water. Applying an external potential of about 1.7–1.9 V to two inert electrodes immersed in an aqueous solution of an electrolyte such as H_2SO_4 or Na_2SO_4 drives the thermodynamically nonspontaneous decomposition of water into H_2 at the cathode and O_2 at the anode. (CC BY-SA-NC; anonymous)

The reactions that occur are as follows:

- cathode:

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} \qquad E^\circ_{cathode} = 0V \tag{8.10.6}$$

- anode:

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^- \qquad E^\circ_{anode} = 1.23\ V \tag{8.10.7}$$

- overall:

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 2H_{2(g)} \qquad E^\circ_{cell} = -1.23\ V \tag{8.10.8}$$

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:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right)\log(P_{\text{O}_2}P^2_{\text{H}_2}) \tag{8.10.9}$$

$$= -1.23\ \text{V} - \left(\frac{0.0591\ \text{V}}{4}\right)\log(1) = -1.23\ \text{V} \tag{8.10.10}$$

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 8.10.4.

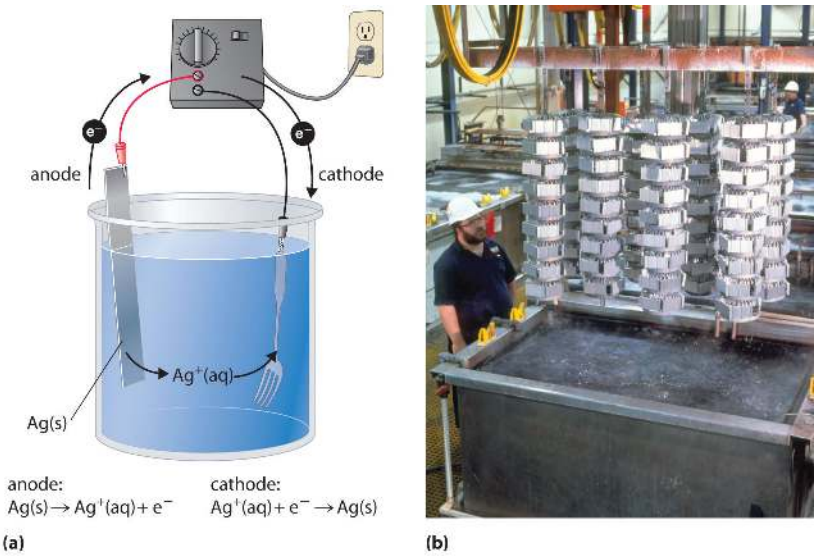


Figure 8.10.3: Electroplating. (a) Electroplating uses an electrolytic cell in which the object to be plated, such as a fork, is immersed in a solution of the metal to be deposited. The object being plated acts as the cathode, on which the desired metal is deposited in a thin layer, while the anode usually 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):

$$q = I \times t \tag{8.10.11}$$

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 8.10.2

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 8.10.2

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.

8.10: Electrolysis- Causing Nonspontaneous Reactions to Occur is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

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CHAPTER OVERVIEW

9: Coordination Chemistry

Complexes or **coordination compounds** are molecules that posess a metal center that is bound to ligands (atoms, ions, or molecules that donate electrons to the metal). These complexes can be neutral or charged. When the complex is charged, it is stabilized by neighboring counter-ions.

9.1: Werner’s Theory of Coordination Compounds
9.2: Ligands
9.3: Nomenclature
9.4: Isomerism
9.5: Optical Isomerism in Metal Complexes
9.6: Stability Aspects of Complex-Ion Equilibria
9.7: Chelation
9.8: Bonding in Octahedral Complex Ions- Crystal Field Theory
9.9: Bonding in Non-Octahedral Complex Ions- Crystal Field Theory
9.10: Magnetic Behavior of Atoms, Molecules, and Materials
9.11: Magnetic Behavior of Complex Ions
9.12: Optical Properties of Coordination Compounds (Color)

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9.1: Werner's Theory of Coordination Compounds

Learning Objectives

- To know the most common structures observed for metal complexes.
- To predict the relative stabilities of metal complexes with different ligands

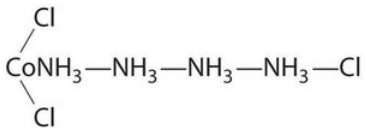
One of the most important properties of metallic elements is their ability to act as Lewis acids that form complexes with a variety of Lewis bases. A metal complex consists of a central metal atom or ion that is bonded to one or more ligands (from the Latin ligare, meaning "to bind"), which are ions or molecules that contain one or more pairs of electrons that can be shared with the metal. Metal complexes can be neutral, such as $Co(NH_3)_3Cl_3$; positively charged, such as $[Nd(H_2O)_9]^{3+}$; or negatively charged, such as $[UF_8]^{4-}$. Electrically charged metal complexes are sometimes called *complex ions*. A *coordination compound* contains one or more metal complexes.

Coordination compounds are important for at least three reasons. First, most of the elements in the periodic table are metals, and almost all metals form complexes, so metal complexes are a feature of the chemistry of more than half the elements. Second, many industrial catalysts are metal complexes, and such catalysts are steadily becoming more important as a way to control reactivity. For example, a mixture of a titanium complex and an organometallic compound of aluminum is the catalyst used to produce most of the polyethylene and polypropylene "plastic" items we use every day. Finally, transition-metal complexes are essential in biochemistry. Examples include hemoglobin, an iron complex that transports oxygen in our blood; cytochromes, iron complexes that transfer electrons in our cells; and complexes of Fe, Zn, Cu, and Mo that are crucial components of certain enzymes, the catalysts for all biological reactions.

History of the Coordination Compounds

Coordination compounds have been known and used since antiquity; probably the oldest is the deep blue pigment called Prussian blue: $\mathbf{KFe_2(CN)_6}$. The chemical nature of these substances, however, was unclear for a number of reasons. For example, many compounds called "double salts" were known, such as $\mathbf{AlF_3 \cdot 3\,KF}$, $\mathbf{Fe(CN)_2 \cdot 4\,KCN}$, and $\mathbf{ZnCl_2 \cdot 2\,CsCl}$, which were combinations of simple salts in fixed and apparently arbitrary ratios. Why should $\mathbf{AlF_3 \cdot 3\,KF}$ exist but not $\mathbf{AlF_3 \cdot 4\,KF}$ or $\mathbf{AlF_3 \cdot 2\,KF}$? And why should a 3:1 KF:AlF3 mixture have different chemical and physical properties than either of its components? Similarly, adducts of metal salts with neutral molecules such as ammonia were also known—for example, $\mathbf{CoCl_3 \cdot 6\,NH_3}$, which was first prepared sometime before 1798. Like the double salts, the compositions of these adducts exhibited fixed and apparently arbitrary ratios of the components. For example, $\mathbf{CoCl_3 \cdot 6\,NH_3}$, $\mathbf{CoCl_3 \cdot 5\,NH_3}$, $\mathbf{CoCl_3 \cdot 4\,NH_3}$, and $\mathbf{CoCl_3 \cdot 3\,NH_3}$ were all known and had very different properties, but despite all attempts, chemists could not prepare $\mathbf{CoCl_3 \cdot 2\,NH_3}$ or $\mathbf{CoCl_3 \cdot NH_3}$.

Although the chemical composition of such compounds was readily established by existing analytical methods, their chemical nature was puzzling and highly controversial. The major problem was that what we now call valence (i.e., the oxidation state) and coordination number were thought to be identical. As a result, highly implausible (to modern eyes at least) structures were proposed for such compounds, including the "Chattanooga choo-choo" model for $CoCl_3 \cdot 4NH_3$ shown here.



$\mathbf{CoCl_3 \cdot 4NH_3}$

The modern theory of coordination chemistry is based largely on the work of Alfred Werner (1866–1919; Nobel Prize in Chemistry in 1913). In a series of careful experiments carried out in the late 1880s and early 1890s, he examined the properties of several series of metal halide complexes with ammonia. For example, five different "adducts" of ammonia with $PtCl_4$ were known at the time: $PtCl_4 \cdot nNH_3$ (n = 2–6). Some of Werner's original data on these compounds are shown in Table **9.1.1**. The electrical conductivity of aqueous solutions of these compounds was roughly proportional to the number of ions formed per mole, while the number of chloride ions that could be precipitated as AgCl after adding $Ag^+(aq)$ was a measure of the number of "free" chloride

ions present. For example, Werner's data on $PtCl_4 \cdot 6NH_3$ in Table **9.1.1** showed that all the chloride ions were present as free chloride. In contrast, $PtCl_4 \cdot 2NH_3$ was a neutral molecule that contained no free chloride ions.

Alfred Werner (1866–1919)

Werner, the son of a factory worker, was born in Alsace. He developed an interest in chemistry at an early age, and he did his first independent research experiments at age 18. While doing his military service in southern Germany, he attended a series of chemistry lectures, and he subsequently received his PhD at the University of Zurich in Switzerland, where he was appointed professor of chemistry at age 29. He won the Nobel Prize in Chemistry in 1913 for his work on coordination compounds, which he performed as a graduate student and first presented at age 26. Apparently, Werner was so obsessed with solving the riddle of the structure of coordination compounds that his brain continued to work on the problem even while he was asleep. In 1891, when he was only 25, he woke up in the middle of the night and, in only a few hours, had laid the foundation for modern coordination chemistry.

Table **9.1.1**: Werner's Data on Complexes of Ammonia with $PtCl_4$

Complex	Conductivity (ohm^{-1})	Number of Ions per Formula Unit	Number of Cl^- Ions Precipitated by Ag^+
$PtCl_4 \cdot 6NH_3$	523	5	4
$PtCl_4 \cdot 5NH_3$	404	4	3
$PtCl_4 \cdot 4NH_3$	299	3	2
$PtCl_4 \cdot 3NH_3$	97	2	1
$PtCl_4 \cdot 2NH_3$	0	0	0

These data led Werner to postulate that metal ions have two different kinds of valence: (1) a primary valence (**oxidation state**) that corresponds to the positive charge on the metal ion and (2) a secondary valence (**coordination number**) that is the total number of ligand-metal bonds bound to the metal ion. If **Pt** had a primary valence of 4 and a secondary valence of 6, Werner could explain the properties of the $\mathbf{PtCl_4 \cdot NH_3}$ adducts by the following reactions, where the metal complex is enclosed in square brackets:

$$[Pt(NH_3)_6]Cl_4 \rightarrow [Pt(NH_3)_6]^{4+}(aq) + 4Cl^-(aq)$$
$$[Pt(NH_3)_5Cl]Cl_3 \rightarrow [Pt(NH_3)_5Cl]^{3+}(aq) + 3Cl^-(aq)$$
$$[Pt(NH_3)_4Cl_2]Cl_2 \rightarrow [Pt(NH_3)_4Cl_2]^{2+}(aq) + 2Cl^-(aq)$$
$$[Pt(NH_3)_3Cl_3]Cl \rightarrow [Pt(NH_3)_3Cl_3]^{+}(aq) + Cl^-(aq)$$
$$[Pt(NH_3)_2Cl_4] \rightarrow [Pt(NH_3)_2Cl_4]^{0}(aq)$$

Further work showed that the two missing members of the series—$[Pt(NH_3)Cl_5]^-$ and $[PtCl_6]^{2-}$—could be prepared as their mono- and dipotassium salts, respectively. Similar studies established coordination numbers of 6 for Co^{3+} and Cr^{3+} and 4 for Pt^{2+} and Pd^{2+}.

Werner's studies on the analogous Co^{3+} complexes also allowed him to propose a structural model for metal complexes with a coordination number of 6. Thus he found that $[Co(NH_3)_6]Cl_3$ (yellow) and $[Co(NH_3)_5Cl]Cl_2$ (purple) were 1:3 and 1:2 electrolytes. Unexpectedly, however, two different $[Co(NH_3)_4Cl_2]Cl$ compounds were known: one was red, and the other was green (Figure **9.1.1*a***). Because both compounds had the same chemical composition and the same number of groups of the same kind attached to the same metal, there had to be something different about the arrangement of the ligands around the metal ion. Werner's key insight was that the six ligands in $[Co(NH_3)_4Cl_2]Cl$ had to be arranged at the vertices of an octahedron because that was the only structure consistent with the existence of two, and only two, arrangements of ligands (Figure **9.1.1*b***. His conclusion was corroborated by the existence of only two different forms of the next compound in the series: $Co(NH_3)_3Cl_3$.

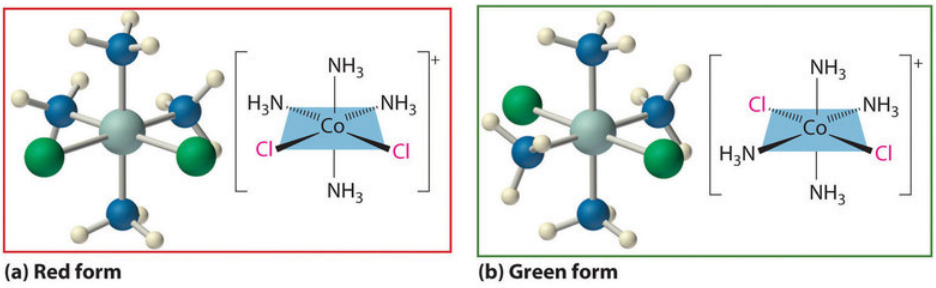


Figure **9.1.1**: Complexes with Different Arrangements of the Same Ligands Have Different Properties. The $[Co(NH_3)_4Cl_2]^+$ ion can have two different arrangements of the ligands, which results in different colors: if the two Cl^- ligands are next to each other, the complex is red (a), but if they are opposite each other, the complex is green (b).

Example 9.1.1

In Werner's time, many complexes of the general formula MA_4B_2 were known, but no more than two different compounds with the same composition had been prepared for any metal. To confirm Werner's reasoning, calculate the maximum number of different structures that are possible for six-coordinate MA_4B_2 complexes with each of the three most symmetrical possible structures: a hexagon, a trigonal prism, and an octahedron. What does the fact that no more than two forms of any MA_4B_2 complex were known tell you about the three-dimensional structures of these complexes?

Given: three possible structures and the number of different forms known for MA_4B_2 complexes

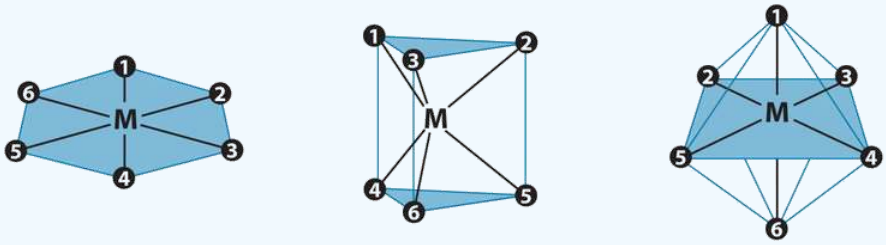
Asked for: number of different arrangements of ligands for MA_4B_2 complex for each structure

Strategy:

Sketch each structure, place a B ligand at one vertex, and see how many different positions are available for the second B ligand.

Solution

The three regular six-coordinate structures are shown here, with each coordination position numbered so that we can keep track of the different arrangements of ligands. For each structure, all vertices are equivalent. We begin with a symmetrical MA_6 complex and simply replace two of the A ligands in each structure to give an MA_4B_2 complex:



For the hexagon, we place the first B ligand at position 1. There are now three possible places for the second B ligand: at position 2 (or 6), position 3 (or 5), or position 4. These are the only possible arrangements. The (1, 2) and (1, 6) arrangements are chemically identical because the two B ligands are adjacent to each other. The (1, 3) and (1, 5) arrangements are also identical because in both cases the two B ligands are separated by an A ligand.

Turning to the trigonal prism, we place the first B ligand at position 1. Again, there are three possible choices for the second B ligand: at position 2 or 3 on the same triangular face, position 4 (on the other triangular face but adjacent to 1), or position 5 or 6 (on the other triangular face but not adjacent to 1). The (1, 2) and (1, 3) arrangements are chemically identical, as are the (1, 5) and (1, 6) arrangements.

In the octahedron, however, if we place the first B ligand at position 1, then we have only two choices for the second B ligand: at position 2 (or 3 or 4 or 5) or position 6. In the latter, the two B ligands are at opposite vertices of the octahedron, with the

metal lying directly between them. Although there are four possible arrangements for the former, they are chemically identical because in all cases the two B ligands are adjacent to each other.

The number of possible MA_4B_2 arrangements for the three geometries is thus: hexagon, 3; trigonal prism, 3; and octahedron, 2. The fact that only two different forms were known for all MA_4B_2 complexes that had been prepared suggested that the correct structure was the octahedron but did not prove it. For some reason one of the three arrangements possible for the other two structures could have been less stable or harder to prepare and had simply not yet been synthesized. When combined with analogous results for other types of complexes (e.g., MA_3B_3), however, the data were best explained by an octahedral structure for six-coordinate metal complexes.

? Exercise 9.1.1

Determine the maximum number of structures that are possible for a four-coordinate MA_2B_2 complex with either a square planar or a tetrahedral symmetrical structure.

Answer

square planar, 2; tetrahedral, 1

Structures of Metal Complexes

The coordination numbers of metal ions in metal complexes can range from 2 to at least 9. In general, the differences in energy between different arrangements of ligands are greatest for complexes with low coordination numbers and decrease as the coordination number increases. Usually only one or two structures are possible for complexes with low coordination numbers, whereas several different energetically equivalent structures are possible for complexes with high coordination numbers (n > 6). The following presents the most commonly encountered structures for coordination numbers 2–9. Many of these structures should be familiar to you from our discussion of the valence-shell electron-pair repulsion (VSEPR) model because they correspond to the lowest-energy arrangements of n electron pairs around a central atom.

> *Compounds with low coordination numbers exhibit the greatest differences in energy between different arrangements of ligands.*

Coordination Number 2

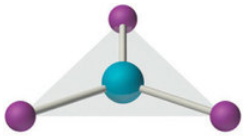
Although it is rare for most metals, this coordination number is surprisingly common for d^{10} metal ions, especially Cu^+, Ag^+, Au^+, and Hg^{2+}. An example is the $[Au(CN)_2]^-$ ion, which is used to extract gold from its ores. As expected based on VSEPR considerations, these complexes have the linear L–M–L structure shown here.



Linear ML_2

Coordination Number 3

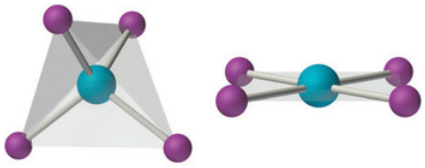
Although it is also rare, this coordination number is encountered with d^{10} metal ions such as Cu^+ and Hg^{2+}. Among the few known examples is the HgI_3^- ion. Three-coordinate complexes almost always have the trigonal planar structure expected from the VSEPR model.



Trigonal planar ML_3

Coordination Number 4

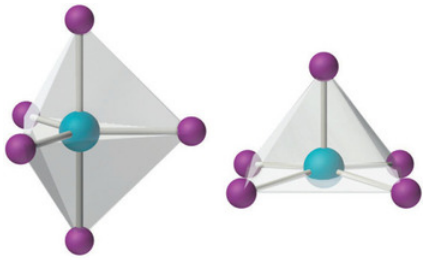
Two common structures are observed for four-coordinate metal complexes: tetrahedral and square planar. The tetrahedral structure is observed for all four-coordinate complexes of nontransition metals, such as $[BeF_4]^{2-}$, and d^{10} ions, such as $[ZnCl_4]^{2-}$. It is also found for four-coordinate complexes of the first-row transition metals, especially those with halide ligands (e.g., $[FeCl_4]^-$ and $[FeCl_4]^{2-}$). In contrast, square planar structures are routinely observed for four-coordinate complexes of second- and third-row transition metals with d^8 electron configurations, such as Rh^+ and Pd^{2+}, and they are also encountered in some complexes of Ni^{2+} and Cu^{2+}.



Tetrahedral and square planar ML_4

Coordination Number 5

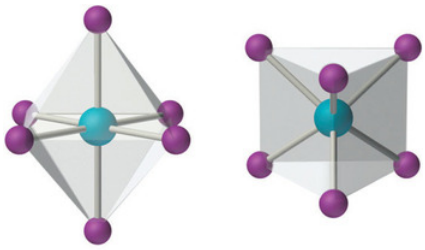
This coordination number is less common than 4 and 6, but it is still found frequently in two different structures: trigonal bipyramidal and square pyramidal. Because the energies of these structures are usually rather similar for most ligands, many five-coordinate complexes have distorted structures that lie somewhere between the two extremes.



Trigonal bipyramidal and square pyramidal ML_5

Coordination Number 6

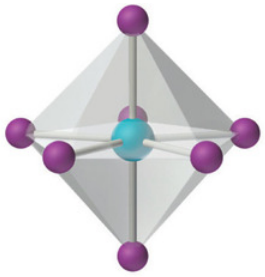
This coordination number is by far the most common. The six ligands are almost always at the vertices of an octahedron or a distorted octahedron. The only other six-coordinate structure is the trigonal prism, which is very uncommon in simple metal complexes.



Octahedral and trigonal prismatic ML_6

Coordination Number 7

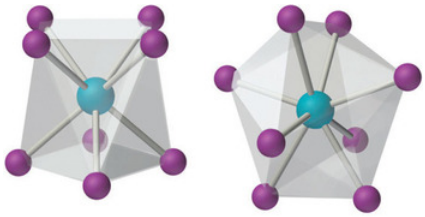
This relatively uncommon coordination number is generally encountered for only large metals (such as the second- and third-row transition metals, lanthanides, and actinides). At least three different structures are known, two of which are derived from an octahedron or a trigonal prism by adding a ligand to one face of the polyhedron to give a “capped” octahedron or trigonal prism. By far the most common, however, is the pentagonal bipyramid.



Pentagonal bipyramidal ML_7

Coordination Number 8

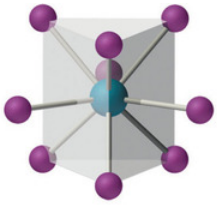
This coordination number is relatively common for larger metal ions. The simplest structure is the cube, which is rare because it does not minimize interligand repulsive interactions. Common structures are the square antiprism and the dodecahedron, both of which can be generated from the cube.



Square antiprismatic and trigonal dodecahedral ML_8

Coordination Number 9

This coordination number is found in larger metal ions, and the most common structure is the tricapped trigonal prism, as in $[Nd(H_2O)_9]^{3+}$.



Tricapped trigonal prismatic ML_9

Key Takeaways

- Coordination compounds are a major feature of the chemistry of over half the elements.
- Coordination compounds have important roles as industrial catalysts in controlling reactivity, and they are essential in biochemical processes.

Summary

Transition metals form metal complexes, polyatomic species in which a metal ion is bound to one or more ligands, which are groups bound to a metal ion. Complex ions are electrically charged metal complexes, and a coordination compound contains one or more metal complexes. Metal complexes with low coordination numbers generally have only one or two possible structures, whereas those with coordination numbers greater than six can have several different structures. Coordination numbers of two and three are common for d^{10} metal ions. Tetrahedral and square planar complexes have a coordination number of four; trigonal bipyramidal and square pyramidal complexes have a coordination number of five; and octahedral complexes have a coordination

number of six. At least three structures are known for a coordination number of seven, which is generally found for only large metal ions. Coordination numbers of eight and nine are also found for larger metal ions.

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9.2: Ligands

A metal ion in solution does not exist in isolation, but in combination with ligands (such as solvent molecules or simple ions) or chelating groups, giving rise to complex ions or coordination compounds. These complexes contain a central atom or ion, often a transition metal, and a cluster of ions or neutral molecules surrounding it. Ligands are ions or neutral molecules that bond to a central metal atom or ion. Ligands act as Lewis bases (electron pair donors), and the central atom acts as a Lewis acid (electron pair acceptor). Ligands have at least one donor atom with an electron pair used to form covalent bonds with the central atom.

The term ligand come from the latin word *ligare* (which meaning to bind) was first used by Alfred Stock in 1916 in relation to silicon chemistry. Ligands can be anions, cations, or neutral molecules. Ligands can be further characterized as monodentate, bidentate, tridentate etc. where the concept of teeth **(dent)** is introduced, hence the idea of bite angle etc. A monodentate ligand has only one donor atom used to bond to the central metal atom or ion.

Monodentate Ligands

The term "monodentate" can be translated as "one tooth," referring to the ligand binding to the center through only one atom. Some examples of monodentate ligands are: chloride ions (referred to as chloro when it is a ligand), water (referred to as aqua when it is a ligand), hydroxide ions (referred to as hydroxo when it is a ligand), and ammonia (referred to as ammine when it is a ligand).

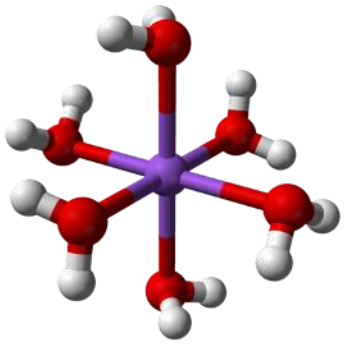


Figure **9.2.1**: Central atom with six monodentate ligands attached. (Image courtesy of Wikimedia Commons.)

Bidentate Ligands

Bidentate ligands have two donor atoms which allow them to bind to a central metal atom or ion at two points. Common examples of bidentate ligands are ethylenediamine (en), and the oxalate ion (ox). Shown below is a diagram of ethylenediamine: the nitrogen (blue) atoms on the edges each have two free electrons that can be used to bond to a central metal atom or ion.

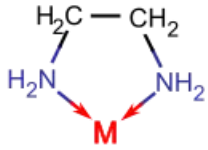


Figure **9.2.2**: Ethylenediamine (en) is an example of a bidentate ligand. (Image courtesy of Wikimedia Commons.). Ethylenediamine (en) is a bidentate ligand that forms a five-membered ring in coordinating to a metal ion M

Polydentate Ligands

Polydentate ligands range in the number of atoms used to bond to a central metal atom or ion. EDTA, a hexadentate ligand, is an example of a polydentate ligand that has six donor atoms with electron pairs that can be used to bond to a central metal atom or ion.

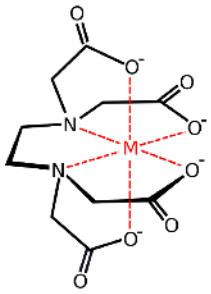
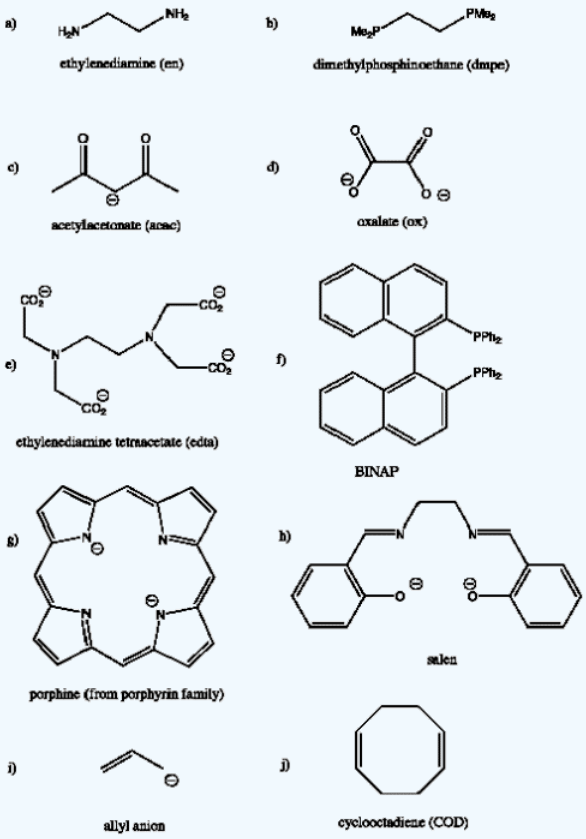


Figure **9.2.3**: Ethylenediaminetetraaceticacid acid (EDTA) is a hexadentate ligand and can bind a Metal via multiple "teeth" (left) Unbound EDTA ion and (right) EDTA bound to a generic transition metal. (Images courtesy of Wikimedia Commons.)

Unlike polydentate ligands, ambidentate ligands can attach to the central atom in two places. A good example of this is thiocyanate, SCN^-, which can attach at either the sulfur atom or the nitrogen atom.

Example 9.2.1

Draw metal complexes using the ligands below and metal ions of your choice.



Chelation

Chelation is a process in which a polydentate ligand bonds to a metal ion, forming a ring. The complex produced by this process is called a chelate, and the polydentate ligand is referred to as a chelating agent. The term chelate was first applied in 1920 by Sir Gilbert T. Morgan and H.D.K. Drew, who stated: "The adjective chelate, derived from the great claw or chela (chely- Greek) of the lobster or other crustaceans, is suggested for the caliperlike groups which function as two associating units and fasten to the central atom so as to produce heterocyclic rings." As the name implies, chelating ligands have high affinity for metal ions relative to ligands with only one binding group (which are called monodentate = "single tooth") ligands. Both Ethylenediamine (Figure **9.2.2**) and Ethylenediaminetetraaceticacid acid (Figure **9.2.3**) are examples of chelating agents, but many others are commonly found in the inorganic laboratory.

The Chelate Effect

The chelate effect is the enhanced affinity of chelating ligands for a metal ion compared to the affinity of a collection of similar nonchelating (monodentate) ligands for the same metal.

The **macrocyclic effect** follows the same principle as the chelate effect, but the effect is further enhanced by the cyclic conformation of the ligand. Macrocyclic ligands are not only multi-dentate, but because they are covalently constrained to their cyclic form, they allow less conformational freedom. The ligand is said to be "pre-organized" for binding, and there is little entropy penalty for wrapping it around the metal ion. For example heme b is a tetradentate cyclic ligand that strongly complexes transition metal ions, including Fe^{+2} in hemogloben (Figure **9.2.4**).

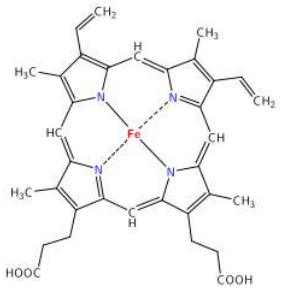
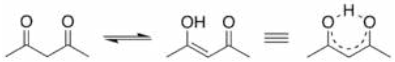


Figure **9.2.4**: Heme b macrocyclic ligand that binds iron in hemoglobin

Some other common chelating and cyclic ligands are shown below:

- **Acetylacetonate** ($acac^-$, top) is an anionic bidentate ligand that coordinates metal ions through two oxygen atoms. $Acac^-$ is a hard base so it prefers hard acid cations. With divalent metal ions, $acac^-$forms neutral, volatile complexes such as $Cu(acac)_2$ and $Mo(acac)_2$ that are useful for chemical vapor deposition (CVD) of metal thin films.



- **2,2'-Bipyridine 2,2'-Bipyridine** (Figure **9.2.5***:* left) and related bidentate ligands such as 1,10-phenanthroline form propeller-shaped complexes with metals such as Ru^{2+}. The $[Ru(bpy)_3]^{2+}$ complex is photoluminescent and can also undergo photoredox reactions, making it an interesting compound for both photocatalysis and artificial photosynthesis.
- **Crown ethers** such as 18-crown-6 **2,2'-Bipyridine** (Figure **9.2.5**: center) are cyclic hard bases that can complex alkali metal cations. Crowns can selectively bind Li^+, Na^+, or K^+ depending on the number of ethylene oxide units in the ring.
- The chelating properties of crown ethers are mimetic of the natural antibiotic **valinomycin** (**2,2'-Bipyridine** (Figure **9.2.5**: right), which selectively transports K^+ ions across bacterial cell membranes, killing the bacterium by dissipating its membrane potential. Like crown ethers, valinomycin is a cyclic hard base.

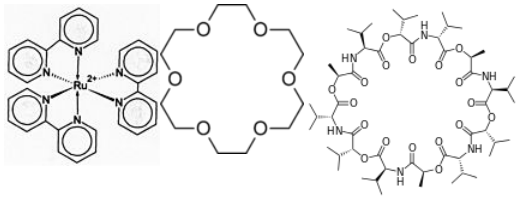


Figure **9.2.5**: (let) 2,2'-Bipyridine, (center) 18-crown-6 2,2'-Bipyridine (right) valinomycin

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9.3: Nomenclature

Learning Objectives

- To learn the basis for complex ion and compound nomenclature

Coordination complexes have their own classes of isomers, different magnetic properties and colors, and various applications (photography, cancer treatment, etc), so it makes sense that they would have a naming system as well. Consisting of a metal and ligands, their formulas follow the pattern [Metal ligands]$^{\pm Charge}$, while names are written Prefix Ligands Metal (Oxidation State).

Introduction

According to the Lewis Acid-Base theory, ligands are Lewis bases since they can donate electrons to the central metal atom. The metals, in turn, are Lewis acids since they accept electrons. **Coordination complexes** consist of a ligand and a metal center cation and their charge can be positive, negative, or neutral. **Coordination compounds** are neutral compounds that contain at least one complex ions. Example of coordination complexes and compounds are:

- Complex Cation: $[Co(NH_3)_6]^{3+}$
- Complex Anion: $[CoCl_4(NH_3)_2]^-$
- Neutral Complex: $[CoCl_3(NH_3)_3]$
- Coordination Compound: $K_4[Fe(CN)_6]$

A ligand can be an anion or a neutral molecule that *donates an electron pair* to the complex (NH_3, H_2O, Cl^-). The number of ligands that attach to a metal depends on whether the ligand is **monodentate** or **polydentate**.

Rules to Complex Ion Nomenclature

To begin naming coordination complexes, here are some things to keep in mind.

1. Ligands are named first in alphabetical order.
2. The name of the metal comes next.
3. The oxidation state of the metal follows, noted by a Roman numeral in parentheses (II, IV).

Rule 1: Anionic Ligands

Ligands that act as anions which end in "-ide" are replaced with an ending "-o" (e.g., Chloride → Chloro). Anions ending with "-ite" and "-ate" are replaced with endings "-ito" and "-ato" respectively (e.g., Nitrite → Nitrito, Nitrate → Nitrato).

Table **9.3.1**: Anionic Monodentate Ligands

Molecular Formula	Ligand Name	Molecular Formula	Ligand Name
F^-	Fluoro	OH^-	Hydroxo
Cl^-	Chloro	SO_4^{2-}	Sulfato
Br^-	Bromo	$S_2O_3^{2-}$	Thiosulfato
I^-	Iodo	NO_2^-	Nitrito-N-; Nitro
O^{2-}	Oxo	ONO^-	Nitrito-O-; Nitrito
CN^-	Cyano	SCN^-	Thiocyanato-S-; Thiocyanato
NC^-	Isocyano	NCS^-	Thiocyanato-N-; Isothiocyanato

Rule 2: Neutral Ligands

Most neutral molecules that are ligands carry their normal name. The few exceptions are the first four on the chart: ammine, aqua, carbonyl, and nitrosyl.

Table **9.3.2**: Select Neutral Monodentate Ligands. Note: Ammine is spelled with two m's when referring to a ligand. Amines are a class of organic nitrogen-containing compounds.

Molecular Formula of Ligand	Ligand Name
NH_3	Ammine
H_2O	Aqua
CO	Carbonyl
NO	Nitrosyl
CH_3NH_2	Methylamine
C_5H_5N	Pyridine

Polydentate ligands follow the same rules for anions and neutral molecules.

Table **9.3.3**: Select Polydentate ligands

Short name	Extended name
en	Ethylenediamine
ox^{2-}	Oxalato
$EDTA^{4-}$	Ethylenediaminetetraacetato

Rule 3: Ligand Multiplicity

The number of ligands present in the complex is indicated with the prefixes di, tri, etc. The exceptions are polydentates that have a prefix already in their name (en and $EDTA^{4-}$ are the most common). When indicating how many of these are present in a coordination complex, put the ligand's name in parentheses and use *bis* (for two ligands), *tris* (for three ligands), and *tetrakis* (for four ligands).

Table **9.3.4**: Prefixes for indicating number of ligands in a complex.

Number of Ligands	Monodentate Ligands	Polydentate Ligands
1	mono	-
2	di	bis
3	tri	tris
4	tetra	tetrakis
5	penta	pentakis
6	hexa	hexakis

Prefixes always go before the ligand name; they are not taken into account when putting ligands in alphabetical order. Note that "mono" often is not used. For example, $[FeCl(CO)_2(NH_3)_3]^{2+}$ would be called triamminedicarbonylchloroiron(III) ion. Remember that ligands are always named first, before the metal is.

Example 9.3.1

What is the name of this complex ion: $[CrCl_2(H_2O)_4]^+$?

Solution

Let's start by identifying the ligands. The ligands here are Cl and H_2O. Therefore, we will use the monodentate ligand names of "chloro" and "aqua". Alphabetically, aqua comes before chloro, so this will be their order in the complex's name. There are 4

aqua's and 2 chloro's, so we will add the number prefixes before the names. Since both are monodentate ligands, we will say "tetra[aqua]di[chloro]".

Now that the ligands are named, we will name the metal itself. The metal is Cr, which is chromium. Therefore, this coordination complex is called tetraaquadichlorochromium(III) ion. See the next section for an explanation of the (III).

? Exercise 9.3.1

What is the name of this complex ion: $[CoCl_2(en)_2]^+$?

Answer

We take the same approach. There are two chloro and ethylenediamine ligands. The metal is Co, cobalt. We follow the same steps, except that *en* is a polydentate ligand with a prefix in its name (ethylene**di**amine), so "bis" is used instead of "di", and parentheses are added. Therefore, this coordination complex is called dichlorobis(ethylenediamine)cobalt(III) ion.

Rule 4: The Metals

When naming the metal center, you must know the formal metal name and the oxidation state. To show the oxidation state, we use Roman numerals inside parenthesis. For example, in the problems above, chromium and cobalt have the oxidation state of +3, so that is why they have (III) after them. Copper, with an oxidation state of +2, is denoted as copper(II). If the overall coordination complex is an anion, the ending "-ate" is attached to the metal center. Some metals also change to their Latin names in this situation. Copper +2 will change into cuprate(II). The following change to their Latin names when part of an anion complex:

Table **9.3.5**: Latin terms for Select Metal Ion

Transition Metal	Latin
Iron	Ferrate
Copper	Cuprate
Tin	Stannate
Silver	Argentate
Lead	Plumbate
Gold	Aurate

The rest of the metals simply have -ate added to the end (cobaltate, nickelate, zincate, osmate, cadmate, platinate, mercurate, etc. Note that the -ate tends to replace -um or -ium, if present).

Finally, when a complex has an overall charge, "ion" is written after it. This is not necessary if it is neutral or part of a coordination compound (Example **9.3.3**). Here are some examples with determining oxidation states, naming a metal in an anion complex, and naming coordination compounds.

✓ Example 9.3.2

What is the name of $[Cr(OH)_4]^-$?

Solution

Immediately we know that this complex is an anion. There is only one monodentate ligand, hydroxide. There are four of them, so we will use the name "tetrahydroxo". The metal is chromium, but since the complex is an anion, we will have to use the "-ate" ending, yielding "chromate". The oxidation state of the metal is 3 (x+(-1)4=-1). Write this with Roman numerals and parentheses (III) and place it after the metal to get tetrahydroxochromate(III) ion.

? Exercise 9.3.2

What is the name of $[CuCl_4]^{2-}$?

Answer

tetrachlorocuprate(II) ion

A last little side note: when naming a coordination compound, it is important that you name the cation first, then the anion. You base this on the charge of the ligand. Foe xample, for $NaCl$. The the positive Na cation comes first and the negative Cl^- anion follows.

✓ Example 9.3.3

What is the name of $[Pt(NH_3)_4][Pt(Cl)_4]$?

Solution

NH_3 is neutral, making the first complex positively charged overall. Cl has a -1 charge, making the second complex the anion. Therefore, you will write the complex with NH_3 first, followed by the one with Cl (the same order as the formula). This coordination compound is called tetraammineplatinum(II) tetrachloroplatinate(II).

✓ Exercise 9.3.3: The Nitro/Nitrito Ambidentate Ligand

What is the name of $[CoCl(NO_2)(NH_3)_4]^+$?

Answer

This coordination complex is called tetraamminechloronitrito-N-cobalt(III). N comes before the O in the symbol for the nitrite ligand, so it is called nitrito-N. If an O came first, as in $[CoCl(ONO)(NH_3)_4]^+$, the ligand would be called nitrito-O, yielding the name tetraamminechloronitrito-O-cobalt(III).

Nitro (for NO_2) and nitrito (for ONO) can also be used to describe the nitrite ligand, yielding the names tetraamminechloronitrocobalt(III) and tetraamminechloronitritocobalt(III).

Writing Formulas of Coordination Complexes

While chemistry typically follow the nomenclature rules for naming complexes and compounds, there is disagreement with the rules for constructing formulas of inorganic complexes. For example, the order of ligand names in their formula has been ambiguous with different conventions being used (charged vs neutral, number of each ligand, etc.). In 2005, IUPAC adopted the recommendation that all ligand names in formulas be listed **alphabetically** (in the same way as in the naming convention) irrespective of the charge or number of each ligand type.

However, this rule is not adhered to in many chemistry laboratories. For practice, the order of the ligands in chemical formulas does not matter as long as you write the transition metal first, which is the stance taken here.

✓ Examples 9.3.4

Write the chemical formulas for:

a. Amminetetraaquachromium(II) ion
b. Amminesulfatochromium(II)

Solution

a. Amminetetraaquachromium(II) ion could be written as $[Cr(H_2O)_4(NH_3)]^{+2}$ or $[Cr(NH_3)(H_2O)_4]^{+2}$.
b. Amminesulfatochromium (II) could be written as $[Cr(SO_4)(NH_3)]$ or $[Cr(NH_3)(SO_4)]$.

? Exercise 9.3.4

Write the chemical formulas for

a. Amminetetraaquachromium (II) sulfate
b. Potassium hexacyanoferrate (III)

Answer

a. Amminetetraaquachromium (II) sulfate can be written as $[Cr(H_2O)_4(NH_3)]SO_4$. Although $[Cr(NH_3)(H_2O)_4]SO_4$ is also acceptable.
b. Potassium hexacyanoferrate (III) is be written as $K_3[Fe(CN)_6]$

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9.4: Isomerism

Learning Objectives

- Explain the differences of Structural and Geometric isomerization in a coordination complexes or complex ions.
- Define Ionization, Linkage, and Coordination Isomerization (structural isomer classes)
- Define cis/tran and mer/fac isomerization (geometric isomer classes)

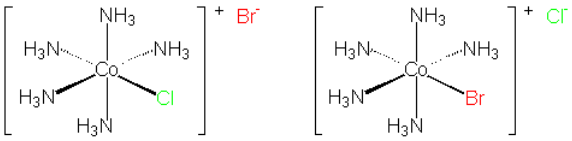
The existence of coordination compounds with the same formula but different arrangements of the ligands was crucial in the development of coordination chemistry. Two or more compounds with the same formula but different arrangements of the atoms are called **isomers**. Because isomers usually have different physical and chemical properties, it is important to know which isomer we are dealing with if more than one isomer is possible. As we will see, coordination compounds exhibit the same types of isomers as organic compounds, as well as several kinds of isomers that are unique. Isomers are compounds with the same molecular formula but different structural formulas and do not necessarily share similar properties. There are many different classes of isomers, like stereoisomers, enantiomers, and geometrical isomers. There are two main forms of isomerism: **structural isomerism** and **stereoisomerism** (spatial isomerism).

Class I: Structural Isomers

Isomers that contain the same number of atoms of each kind but differ in which atoms are bonded to one another are called structural isomers, which differ in structure or bond type. For inorganic complexes, there are three types of structural isomers: *ionization*, *coordination* and *linkage*. Structural isomers, as their name implies, differ in their structure or bonding, which are separate from stereoisomers that differ in the spatial arrangement of the ligands are attached, but still have the bonding properties. The different chemical formulas in structural isomers are caused either by a difference in what ligands are bonded to the central atoms or how the individual ligands are bonded to the central atoms. When determining a structural isomer, you look at (1) the ligands that are bonded to the central metal and (2) which atom of the ligands attach to the central metal.

Ionization Isomerism

Ionization isomers occur when a ligand that is bound to the metal center exchanges places with an anion or neutral molecule that was originally outside the coordination complex. The geometry of the central metal ion and the identity of other ligands are identical. For example, an octahedral isomer will have five ligands that are identical, but the sixth will differ. The non-matching ligand in one compound will be outside of the coordination sphere of the other compound. Because the anion or molecule outside the coordination sphere is different, the chemical properties of these isomers is different. A hydrate isomer is a specific kind of ionization isomer where a water molecule is one of the molecules that exchanges places.



[Co(NH3)5Cl]Br [Co(NH3)5Br]Cl

Figure 9.4.1: Ionization isomerism. The two isomers differ only in which ligands are bound to the center metal and which are counter ions in the second coordination sphere. (left) The chloride ion is bound to the cobalt as a chloro-ligand with the bromide ion as the counter ion. (right) In the other ionization isomer the bromide is acting as a bromo-ligand to the cobalt with the chloride acting as the counter ion. These two isomers are called pentaamminechlorocobalt(II) bromide (left) and pentaamminebromocobalt(II) chloride (right).

The difference between the ionization isomers can be view within the context of the ions generated when each are dissolved in solution. For example, when pentaamminebromocobalt(II) chloride is dissolved in water, $\mathbf{Cl^-}$ ions are generated:

$$\mathbf{CoBr(NH_3)_5Cl\ (s)\ \rightarrow CoBr(NH_3)_5^+\ (aq) + Cl^-\ (aq)} \tag{9.4.1}$$

whereas when pentaamminechlorocobalt(II) bromide is dissolved, $\mathbf{Br^-}$ ions are generated:

$$\mathbf{CoCl(NH_3)_5Br\ (s)\ \rightarrow CoCl(NH_3)_5^+\ (aq) + Br^-\ (aq)} \tag{9.4.2}$$

Notice that both anions are necessary to balance the charge of the complex, and that they differ in that one ion is directly attached to the central metal, but the other is not.

Solvate and Hydrate Isomerism: A special Type of Ionization Isomers

A very similar type of isomerism results from replacement of a coordinated group by a solvent molecule (*Solvate Isomerism*), which in the case of water is called *Hydrate Isomerism*. The best known example of this occurs for chromium chloride ($CrCl_3 \cdot 6H_2O$) which may contain 4, 5, or 6 coordinated water molecules (assuming a coordination number of 6). The dot here is used essentially as an expression of ignorance to indicate that, though the parts of the molecule separated by the dot are bonded to one another in some fashion, the exact structural details of that interaction are not fully expressed in the resulting formula. Alfred Werner's coordination theory indicates that several of the water molecules are actually bonded directly (via coordinate covalent bonds) to the central chromium ion. In fact, there are several possible compounds that use the brackets to signify bonding in the complex and the dots to signify "water molecules that are not bound to the central metal, but are part of the lattice:

- $[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$: bright-green colored
- $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$: grey-green colored
- $[Cr(H_2O)_6]Cl_3$: violet colored

These isomers have very different chemical properties and on reaction with $AgNO_3$ to test for Cl^- ions, would find 1, 2, and 3 Cl^- ions in solution, respectively.

Upon crystallization from water, many compounds incorporate water molecules in their crystalline frameworks. These "waters of crystallization" refers to water that is found in the crystalline framework of a metal complex or a salt, which is **not directly bonded** to the metal cation. In the first two hydrate isomers, there are water molecules that are artifacts of the crystallization and occur inside crystals. These waters of crystallization contribute to the total weight of water in a substance and are mostly present in a definite (stoichiometric) ratio.

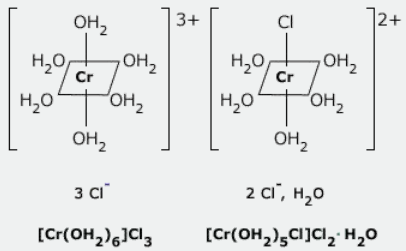


Figure 9.4.2: Hydrate iosomerisim. The $[Cr(H_2O)_6]Cl_3$ hydrate isomer (left) is violet colored and the $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$ hydrate isomer is green-grey colored.

What are "Waters of Crystallization"?

A compound with associated water of crystallization is known as a hydrate. The structure of hydrates can be quite elaborate, because of the existence of hydrogen bonds that define polymeric structures. For example, consider the aquo complex $NiCl_2 \cdot 6H_2O$ that consists of separated *trans*-$[NiCl_2(H_2O)_4]$ molecules linked more weakly to adjacent water molecules. Only four of the six water molecules in the formula are bound to the nickel (II) cation, and the remaining two are waters of crystallization as the crystal structure resolves (Figure 9.4.3).

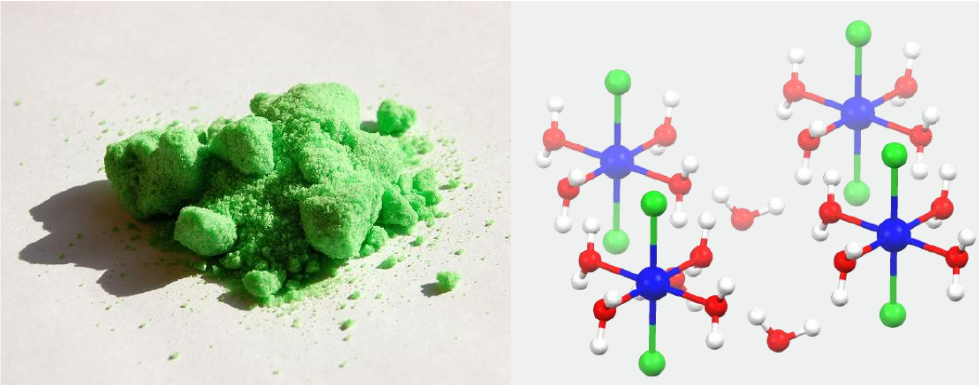


Figure 9.4.3: Water of hydration. (left) Image of $NiCl_2 \cdot 6H_2O$ salt (Public Domain; Benjah-bmm27 via Wikipedia). (right) Crystal Structure of $NiCl_2 \cdot 6H_2O$ with chlorine atoms (green), water molecules (red), and Ni metals (blue) indicated. Note that only four of the waters are bound as ligands to the nickel ions and two are outside of the coordination sphere. (CC BY-SA 4.0; Smokefoot).

Water is particularly common solvent to be found in crystals because it is small and polar. But *all* solvents can be found in some host crystals. Water is noteworthy because it is reactive, whereas other solvents such as benzene are considered to be chemically innocuous.

Coordination Isomerism

Coordination isomerism occurs in compounds containing complex anionic and complex cationic parts and can be viewed as an interchange of some ligands from the cation to the anion. Hence, there are two complex compounds bound together, one with a negative charge and the other with a positive charge. In coordination isomers, the anion and cation complexes of a coordination compound exchange one or more ligands. For example, the $[Zn(NH_3)_4]\,[Cu(Cl_4)]$ and $[Cu(NH_3)_4]\,[Zn(Cl_4)]$ compounds are coordination isomers (Figure 9.4.4).

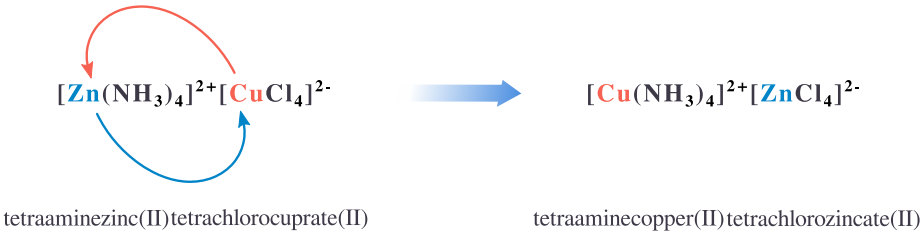


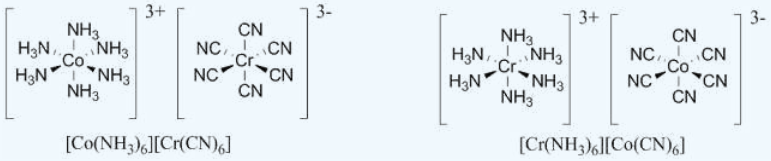
Figure 9.4.4: Coordination Isomerism. (CC BY-NC; Ümit Kaya)

Example 9.4.2: Coordination Isomers

What is the coordination isomer for the $[Co(NH_3)_6]\,[Cr(CN)_6]$ compound?

Solution

Coordination isomerism involves switching the metals between the cation and anion spheres.



Hence the $[Cr(NH_3)_6][Co(CN)_6]$ compound is a coordination isomer of $[Co(NH_3)_6]\,[Cr(CN)_6]$.

Linkage Isomerism

Linkage isomerism occurs with *ambidentate* ligands that are capable of coordinating in more than one way. The best known cases involve the monodentate ligands: SCN^- / NCS^- and NO_2^- / ONO^-. The only difference is what **atoms the molecular ligands bind to the central ion**. The ligand(s) must have more than one donor atom, but bind to ion in only one place. For example, the (NO_2^-) ion is a ligand that can bind to the central atom through the nitrogen or the oxygen atom, but cannot bind to the central atom with both oxygen and nitrogen at once, in which case it would be called a **polydentate ligand** rather than an **ambidentate ligand**.

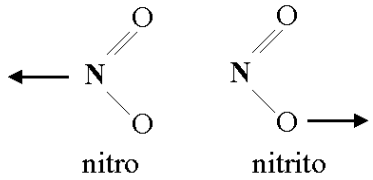


Figure 9.4.5: Linkage Isomerism in the NO_2 ligand. This occurs when a particular ligand is capable of coordinating to a metal in two different and distinct ways. from Angel C. de Dios.

As with all structural isomers, the formula of the complex is unchanged for each isomer, but the properties may differ. The names used to specify the changed ligands are changed as well. For example, the NO_2^- ion is called *nitro* when it binds with the **N** atom and is called *nitrito* when it binds with the **O** atom.

Example 9.4.3: Linkage Isomerization

The cationic cobalt complex $[Co(NH_3)_5(NO_2)]Cl_2$ exists in two separable linkage isomers of the complex ion: $(NH_3)_5(NO_2)]^{2+}$.

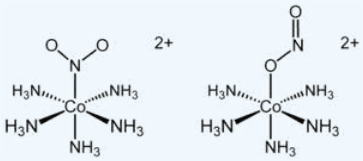


Figure 9.4.6: Linkage Isomerization. (left) The nitro isomer (Co-NO2) and (right) the nitrito isomer (Co-ONO)

When donation is from nitrogen to a metal center, the complex is known as a *nitro-* complex and when donation is from one oxygen to a metal center, the complex is known as a *nitrito-* complex. An alternative formula structure to emphasize the different coordinate covalent bond for the two isomers

- $[Co(ONO)(NH_3)_5]Cl$: the *nitrito* isomer -O attached
- $[Co(NO_2)(NH_3)_5]Cl$: the *nitro* isomer - N attached.

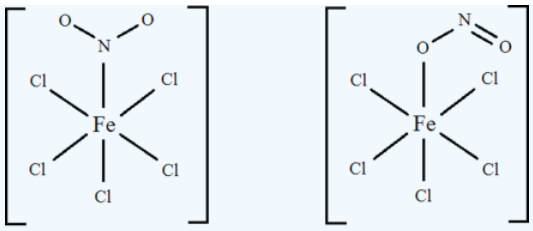
Another example of an ambidentate ligand is thiocyanate, SCN^-, which can attach to the transition metal at either the sulfur atom or the nitrogen atom. Such compounds give rise to linkage isomerism. Other ligands that give rise to linkage isomers include selenocyanate, $SeCN^-$ – isoselenocyanate, $NCSe^-$ and sulfite, SO_3^{2-}.

Exercise 9.4.3

Are $[FeCl_5(NO_2)]^{3-}$ and $[FeCl_5(ONO)]^{3-}$ complex ions linkage isomers of each other?

Answer

Here, the difference is in how the ligand bonds to the metal. In the first isomer, the ligand bonds to the metal through an electron pair on the nitrogen. In the second isomer, the ligand bonds to the metal through an electron pair on one of the oxygen atoms. It's easier to see it:



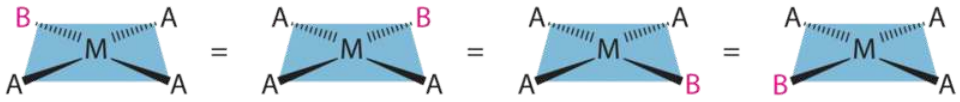
Class 2: Geometric Isomers

The existence of coordination compounds with the same formula but different arrangements of the ligands was crucial in the development of coordination chemistry. Two or more compounds with the same formula but different arrangements of the atoms are called **isomers**. Because isomers usually have different physical and chemical properties, it is important to know which isomer we are dealing with if more than one isomer is possible. Recall that in many cases more than one structure is possible for organic compounds with the same molecular formula; examples discussed previously include n-butane versus isobutane and cis-2-butene versus trans-2-butene. As we will see, coordination compounds exhibit the same types of isomers as organic compounds, as well as several kinds of isomers that are unique.

Planar Isomers

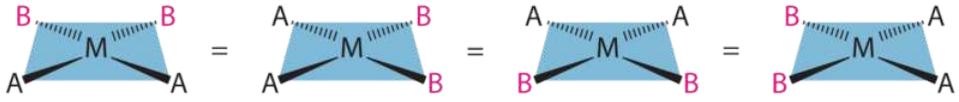
Metal complexes that differ only in which ligands are adjacent to one another (**cis**) or directly across from one another (**trans**) in the coordination sphere of the metal are called geometrical isomers. They are most important for square planar and octahedral complexes.

Because all vertices of a square are equivalent, it does not matter which vertex is occupied by the ligand B in a square planar MA_3B complex; hence only a single geometrical isomer is possible in this case (and in the analogous MAB_3 case). All four structures shown here are chemically identical because they can be superimposed simply by rotating the complex in space:

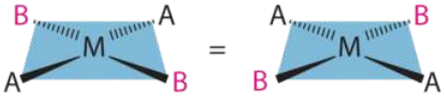


MA_3B square planar complex

For an MA_2B_2 complex, there are two possible isomers: either the A ligands can be adjacent to one another (cis), in which case the B ligands must also be cis, or the A ligands can be across from one another (trans), in which case the B ligands must also be trans. Even though it is possible to draw the cis isomer in four different ways and the trans isomer in two different ways, all members of each set are chemically equivalent:

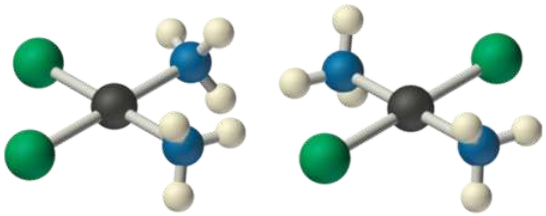


MA_2B_2 square planar complex, *cis* isomer



MA_2B_2 square planar complex, *trans* isomer

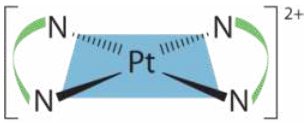
Because there is no way to convert the cis structure to the trans by rotating or flipping the molecule in space, they are fundamentally different arrangements of atoms in space. Probably the best-known examples of cis and trans isomers of an MA_2B_2 square planar complex are cis-$Pt(NH_3)_2Cl_2$, also known as cisplatin, and trans-$Pt(NH_3)_2Cl_2$, which is actually toxic rather than therapeutic.



cis-$Pt(NH_3)_2Cl_2$ *trans*-$Pt(NH_3)_2Cl_2$

The anticancer drug cisplatin and its inactive trans isomer. Cisplatin is especially effective against tumors of the reproductive organs, which primarily affect individuals in their 20s and were notoriously difficult to cure. For example, after being diagnosed with metastasized testicular cancer in 1991 and given only a 50% chance of survival, Lance Armstrong was cured by treatment with cisplatin.

Square planar complexes that contain symmetrical bidentate ligands, such as $[Pt(en)_2]^{2+}$, have only one possible structure, in which curved lines linking the two N atoms indicate the ethylenediamine ligands:



$[Pt(en)_2]^{2+}$

? Exercise 9.4.4

Draw the cis and trans isomers of the following compounds:

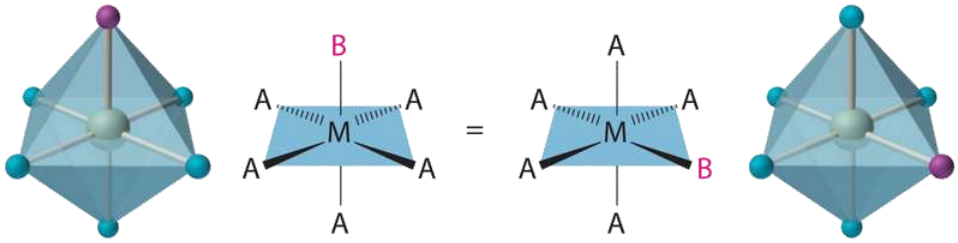
a. $(NH_3)_2IrCl(CO)$
b. $(H_3P)_2PtHBr$
c. $(AsH_3)_2PtH(CO)$

? Exercise 9.4.5

Only one isomer of $(tmeda)PtCl_2$ is possible [tmeda = $(CH_3)_2NCH_2CH_2N(CH_3)_2$; both nitrogens connect to the platinum]. Draw this isomer and explain why the other isomer is not possible.

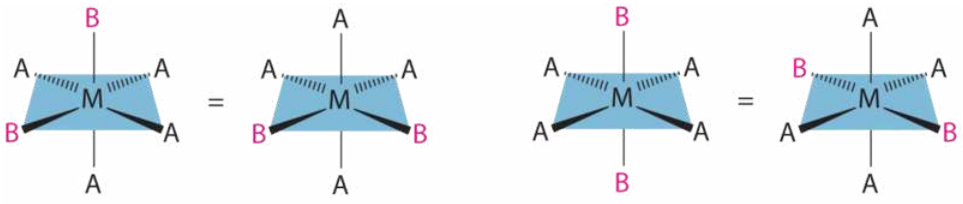
Octahedral Isomers

Octahedral complexes also exhibit cis and trans isomers. Like square planar complexes, only one structure is possible for octahedral complexes in which only one ligand is different from the other five (MA_5B). Even though we usually draw an octahedron in a way that suggests that the four "in-plane" ligands are different from the two "axial" ligands, in fact all six vertices of an octahedron are equivalent. Consequently, no matter how we draw an MA_5B structure, it can be superimposed on any other representation simply by rotating the molecule in space. Two of the many possible orientations of an MA_5B structure are as follows:



MA_5B octahedral complex

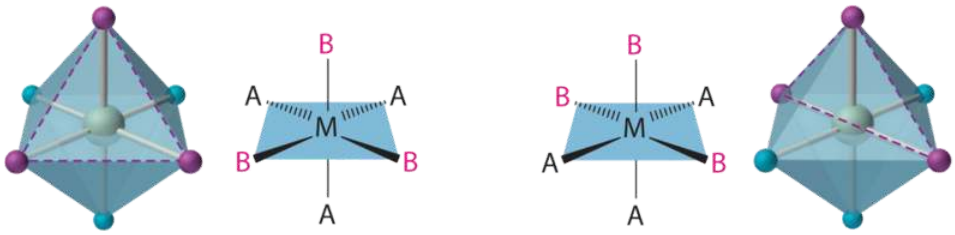
If two ligands in an octahedral complex are different from the other four, giving an MA_4B_2 complex, two isomers are possible. The two B ligands can be cis or trans. Cis- and trans-$[Co(NH_3)_4Cl_2]Cl$ are examples of this type of system:



MA_4B_2 octahedral complex, *cis* isomer

MA_4B_2 octahedral complex, *trans* isomer

Replacing another A ligand by B gives an MA_3B_3 complex for which there are also two possible isomers. In one, the three ligands of each kind occupy opposite triangular faces of the octahedron; this is called the fac isomer (for facial). In the other, the three ligands of each kind lie on what would be the meridian if the complex were viewed as a sphere; this is called the mer isomer (for meridional):



MA_3B_3 octahedral complex, *fac* isomer

MA_3B_3 octahedral complex, *mer* isomer

Example 9.4.4

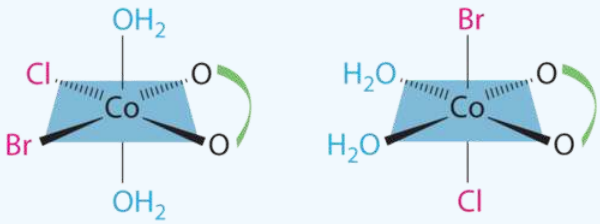
Draw all the possible geometrical isomers for the complex $[Co(H_2O)_2(ox)BrCl]^-$, where ox is $^-O_2CCO_2^-$, which stands for oxalate.

Solution

Given: formula of complex

Asked for: structures of geometrical isomers

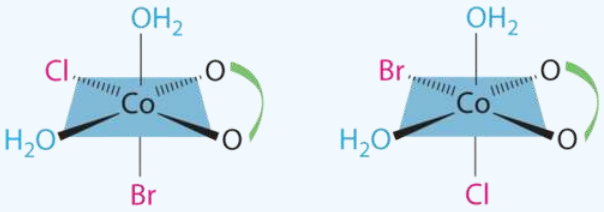
This complex contains one bidentate ligand (oxalate), which can occupy only adjacent (cis) positions, and four monodentate ligands, two of which are identical (H_2O). The easiest way to attack the problem is to go through the various combinations of ligands systematically to determine which ligands can be trans. Thus either the water ligands can be trans to one another or the two halide ligands can be trans to one another, giving the two geometrical isomers shown here:



H_2O's *trans*

Br, Cl *trans*

In addition, two structures are possible in which one of the halides is trans to a water ligand. In the first, the chloride ligand is in the same plane as the oxalate ligand and trans to one of the oxalate oxygens. Exchanging the chloride and bromide ligands gives the other, in which the bromide ligand is in the same plane as the oxalate ligand and trans to one of the oxalate oxygens:

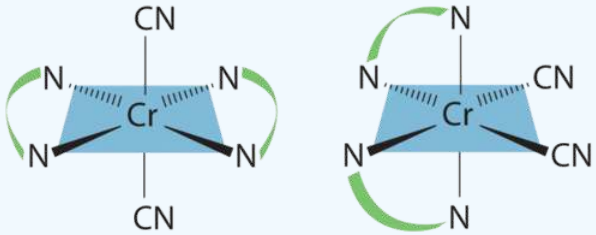


This complex can therefore exist as four different geometrical isomers.

? Exercise 9.4.6

Draw all the possible geometrical isomers for the complex $[Cr(en)_2(CN)_2]^+$.

Answer



Two geometrical isomers are possible: *trans* and *cis*.

Summary

The existence of coordination compounds with the same formula but different arrangements of the ligands was crucial in the development of coordination chemistry. Two or more compounds with the same formula but different arrangements of the atoms are called **isomers**. Many metal complexes form isomers, which are two or more compounds with the same formula but different arrangements of atoms. Structural isomers differ in which atoms are bonded to one another, while geometrical isomers differ only in the arrangement of ligands around the metal ion. Ligands adjacent to one another are cis, while ligands across from one another are trans.

Table **9.4.1** emphasizes the key differences of the three classes of structural isomers discussed below. The highlighted ions are the ions that switch or change somehow to make the type of structural isomer it is.

Table **9.4.1**: Overview of Structural Isomer Classes

Structural Isomer	Examples
Ionization	$[CoBr(H_2O)_5]^+Cl^-$ and $[CoCl(H_2O)_5]^+Br^-$
Coordination	$[Zn(NH_3)_4]^+[CuCl_4]^{2-}$ and $[Cu(NH_3)_4]^+[ZnCl_4]^{2-}$
Linkage	$[Co(NO_2)_6]^{3-}$ and $[Co(ONO)_6]^{3-}$

References

1. Petrucci, Harwood, Herring, and Madura. General Chemistry: Principles and Modern Applications: Ninth Edition. New Jersey: Pearson, 2007.
2. Atkins, Peter, and Loretta Jones. Chemical Principles: The Quest for Insight: Fourth Edition. W. H. Freeman and Company, 2008. Print.

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9.5: Optical Isomerism in Metal Complexes

Optical isomers are stereoisomers that are related via non-superimposable mirror images of each other. They differ from geometric stereoisomers in that they rotate the polarization of plane-polarized light. These isomers are referred to as *enantiomers* or *chiral*.

Introduction

Optical activity refers to whether or not a compound has optical isomers. A coordinate compound that is optically active **has** optical isomers and a coordinate compound that is not optically active does **not have** optical isomers. As we will discuss later, optical isomers have the unique property of rotating light. When light is shot through a polarimeter, optical isomers can rotate the light so it comes out in with a different polarization on the other end. Armed with the knowledge of symmetry and mirror images, optical isomers should not be very difficult. There are two ways optical isomers can be determined: using mirror images or using planes of symmetry.

Optical isomers do not exhibit symmetry and do not have identical mirror images. Let's go through a quick review of symmetry and mirror images. A *mirror image* of an object is that object flipped or the way the object would look in front of a mirror. For example, the mirror image of your left hand would be your right hand. Symmetry on the other hand refers to when an object looks exactly the same when sliced in a certain direction with a plane. For example imagine the shape of a square. No matter in what direction it is sliced, the two resulting images will be the same.

What is a Polarimeter?

A polarimeter is a scientific instrument used to measure the angle of rotation caused by passing polarized light through an optically active substance. Some chemical substances are optically active, and polarized (uni-directional) light will rotate either to the left (counter-clockwise) or right (clockwise) when passed through these substances. The amount by which the light is rotated is known as the **angle of rotation**. The polarimeter is made up of a polarizer (#3 on Figure **9.5.1**) and an analyzer (#7 on Figure **9.5.1**). The polarizer allows only those light waves which move in a single plane. This causes the light to become plane polarized. When the analyzer is also placed in a similar position it allows the light waves coming from the polarizer to pass through it. When it is rotated through the right angle no waves can pass through the right angle and the field appears to be dark. If now a glass tube containing an optically active solution is placed between the polarizer and analyzer the light now rotates through the plane of polarization through a certain angle, the analyzer will have to be rotated in same angle.

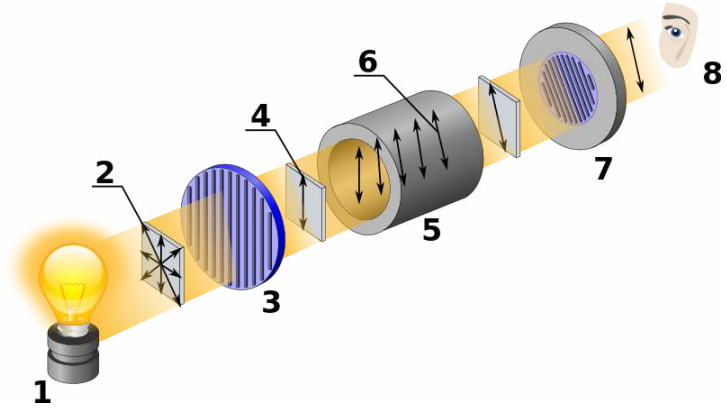


Figure **9.5.1**: Schematic of a polarimeter showing the principles behind it's operation.The plane of polarization of plane polarised light (4) rotates (6) as it passes through an optically active sample (5). This angle is determined with a rotatable polarizing filter (7). (CC BY-SA 3.0; Kaidor via Wikipedia)

Chemists use polarimeters to investigate the influence of compounds (in the sample cell) on plane polarized light. Samples composed only of achiral molecules (e.g. water or hexane), have no effect on the polarized light beam. However, if a single enantiomer is examined (all sample molecules being right-handed, or all being left-handed), the plane of polarization is rotated in either a clockwise (positive) or counter-clockwise (negative) direction, and the analyzer must be turned an appropriate matching angle, **α**, if full light intensity is to reach the detector. In the above illustration, the sample has rotated the polarization plane clockwise by +90º, and the analyzer has been turned this amount to permit maximum light transmission.

The observed rotations (α) of enantiomers are opposite in direction. One enantiomer will rotate polarized light in a clockwise direction, termed **dextrorotatory** or (+), and its mirror-image partner in a counter-clockwise manner, termed **levorotatory** or (–). The prefixes dextro and levo come from the Latin *dexter*, meaning right, and *laevus*, for left, and are abbreviated *d* and *l* respectively. A 50:50 mixture of enantiomers has no observable optical activity. Such mixtures are called **racemates** or **racemic modifications**.

The "Mirror Image Method" to Determine Optical Isomers

Optical isomers do not exhibit symmetry and do not have identical mirror images. Let's go through a quick review of symmetry and mirror images. A *mirror image* of an object is that object flipped or the way the object would look in front of a mirror. For example, the mirror image of your left hand would be your right hand. Symmetry on the other hand refers to when an object looks exactly the same when sliced in a certain direction with a plane. For example imagine the shape of a square. No matter in what direction it is sliced, the two resulting images will be the same.

The **mirror image method** uses a mirror image of the molecule to determine whether optical isomers exist or not. If the mirror image **can** be rotated in such a way that it looks identical to the original molecule, then the molecule is said to be superimposable and has no optical isomers. On the other hand, if the mirror image **cannot** be rotated in any way such that it looks identical to the original molecule, then the molecule is said to be non-superimposable and the molecule has optical isomers. Once again, if the mirror image is superimposable, then no optical isomers, but if the mirror image is non-superimposable, then optical isomers exist.

Non-superimposable means the structure cannot be rotated in a way that one can be put on top of another. This means that no matter how the structure is rotated, it cannot be put on top of another with all points matching. An example of this is your hands. Both left and right hands are identical, but they cannot be put on top of each other with all points matching.

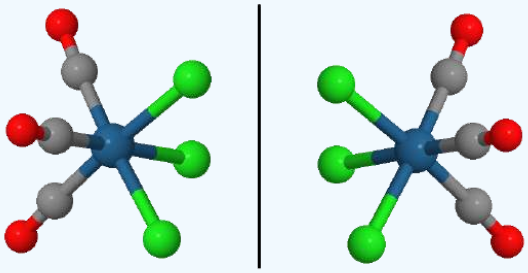
> *Non-superimposable means the structure cannot be rotated in a way that one can be put on top of another.*

Example 9.5.1: The $[OsCl_3(CO)_3]^-$ Ion

Are there enantiomers for the $fac-[OsCl_3(CO)_3]^-$ complex ion?

Solution

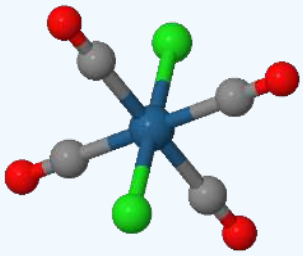
To use mirror image method, we draw the 3D structure for this geometric isomer (not the mer isomer) and then take a mirror image like below.



The left image can be rotated by 180° through a vertical axis to superimpose on the orginal. So the mer-$[OsCl_3(CO)_3]^-$ complex ion is not optically active or we can call it achiral.

Exercise 9.5.1

Use the mirror image method to determine if there are enantiomers for the $mer-[OsCl_3(CO)_3]^-$ complex ion.



Example 9.5.2

Consider the octahedral complex with six monodentate ligands $\mathbf{MA_2B_2C_2}$ have both cis and trans isomers. However, the cis isomer will also have two optical isomers (Figure 9.5.2). No matter how one rotates one of the mirror images, they are are **not** superimposable.

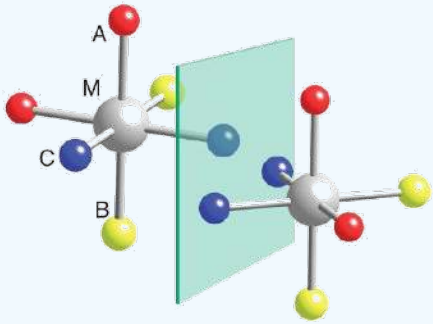


Figure 9.5.2: Two $\mathbf{MA_2B_2C_2}$ enantiomers. (CC BY-SA-NC 4.0; ChemTube3D via Nick Greeves)

Exercise 9.5.1: $\mathbf{MA_2B_2C_2}$

Confirm to yourself that if two like ligands in $\mathbf{MA_2B_2C_2}$ are *trans* to each other, then the complex will not have an optical isomer.

Answer

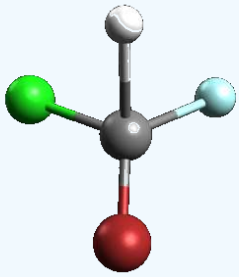
If two like ligands are *trans* then there will be a mirror plane of symmetry normal to the line connecting the ligands that are *trans* to each other. The presence of the mirror plane means this complex will not have an optical isomer.

The "Plane of Symmetry Method" to Determine Optical Isomers

The plane of symmetry method uses symmetry also to identify optical isomers. In this method, one tries to see if such a plane exists which when cut through the coordinate compound produces two exact images. In other words, one looks for the existence of a plane of symmetry within the coordinate compound. If a plane of symmetry exists, then no optical isomers exist for that complex and it is called **achiral**.

Example 9.5.3: A Tetrahedral Complex

Consider the tetrahedral molecule, CHBrClF. Is this molecule optically active?

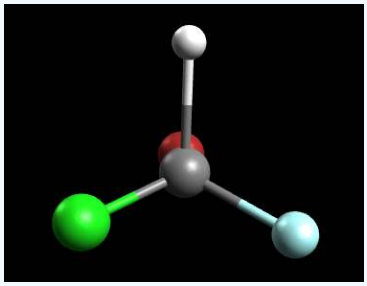


The CHBrClF molecule (note the color scheme: grey=carbon, white=hydrogen, green=chlorine, blue=fluorine, red=bromine)

Solution

- *Mirror-image method*

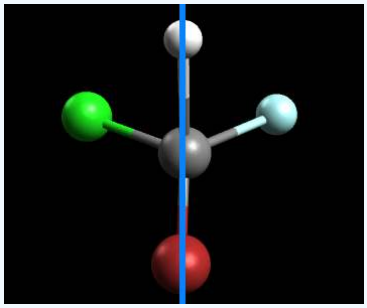
First take the Mirror-image method. The mirror image of the molecule is:



Note that this mirror image is not superimposable. In other words, the mirror image above cannot be rotated in any such way that it looks identical to the original molecule. Remember, if the mirror image is not superimposable, then optical isomers exist. Thus we know that this molecule has optical isomers.

- *Plane of Symmetry Method*

Let's try approaching this problem using the symmetry method. If we take the original molecule and draw an axis or plane of symmetry down the middle, this is what we get:



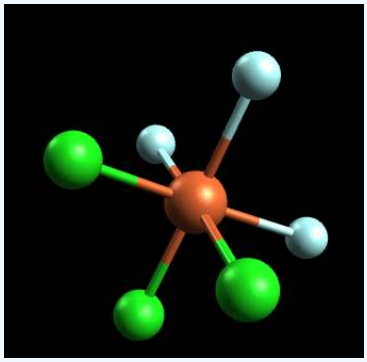
Since the left side is not identical to the right, this molecule does not have a symmetrical center and thus can be called chiral.Additionally, because it does not have a symmetrical center, we can conclude that this molecule has optical isomers. In general, when dealing with a tetrahedral molecule that has 4 different ligands, optical isomers will exist most of the time.

No matter which method you use, the answer will end up being the same.

Optical isomers have no plane of symmetry. For tetrahedral complexes, this is fairly easy to recognize the possibility of this by looking for a center atom with **four** different things attached to it. Unfortunately, this is not quite so easy with more complicated geometries!

Example 9.5.4: An Octahedral Complex

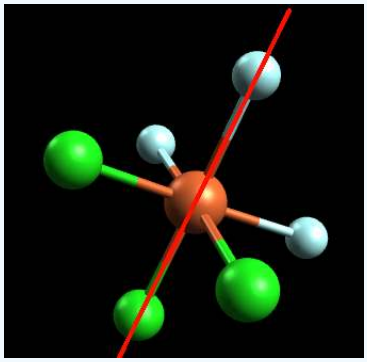
Is the octahedral compound $FeCl_3F_3$ optically active?



(note the color scheme: orange=iron, blue=fluorine, green=chlorine):

Solution

If we try to attempt this problem using the mirror image method, we notice that the mirror image is essentially identical to the original molecule. In other words, the mirror image can be placed on top of the original molecule and is thus superimposable. Since the mirror image is superimposable, this molecule does not have any optical isomers. Let's attempt this same problem using the symmetry method. If we draw an axis or plane of symmetry, this is what we get:



Since the left side is identical to the right side, this molecule has a symmetrical center and is an achiral molecule. Thus, it has no optical isomers.

Enantiomers in Octahedral Complexes with Bidentate Ligands

The examples you are most likely to need occur in octahedral complexes that contain bidentate ligands, e.g., complex ions like $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$ or $[Cr(C_2O_4)_3]^{3-}$. In bidentate complexes or chelating complexes, a ligand binds very tightly to the metal because it holds onto the metal via more than one atom. Ethylenediamine is one example of a bidentate ligand.

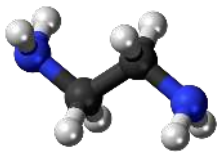
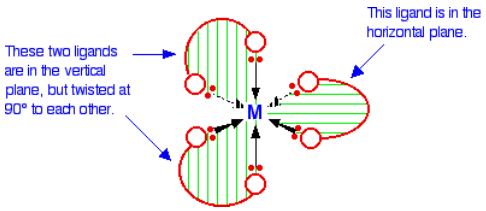


Figure 9.5.3: Ethylenediamine (sometimes abbreviated en) is an example of a bidentate ligand

As you may expect, bidentate ligands bind tightly to metals because they form two bonds with it, rather than just one. It is also important to recognize that in an octahedral complex, the two donor atoms in most bidentate ligand bind *cis* to each other and **cannot** reach all the way around the molecule to bind *trans* to each other (see below). The diagram below shows a simplified view of one of the complex ions with three oxalato ligands (also a bidentate ligand), however, they all have the same shape - all that differs is the nature of the "headphones".



A substance with *no plane of symmetry is going to have optical isomers* - one of which is the mirror image of the other. One of the isomers will rotate the plane of polarization of plane polarized light clockwise; the other rotates it counter-clockwise. In this case, the two isomers are:

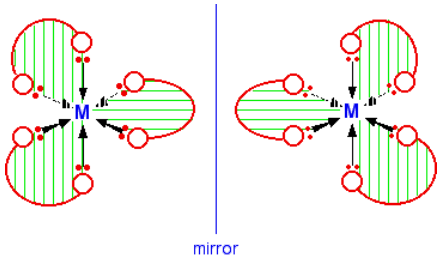
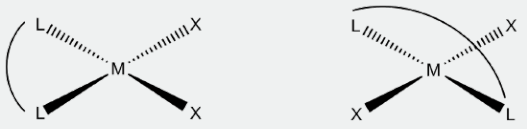


Figure **9.5.4**: A left-handed propeller shape (left) is seen in one optical isomers of the $M(ox)_3^{+}$ octahedral complex. The other optical isomer is a right-handed propeller (right). These shapes are alternatively described as a left-handed screw and a right handed screw. If you can picture turning the shape so that it screws into the page behind it, which direction would you turn the screwdriver? If you would twist the screwdriver clockwise, then you have a right handed screw. If you would twist the screwdriver counter-clockwise, then you have a left handed screw.

Most, but not all, Bidentate Ligands Bind to Metals in the cis Orientation

A wide variety of bidentate ligands bind to metals in the cis fashion, but few can bind in the trans geometry. These are called trans-spanning ligands and required building a bridge between the bonding atoms (e.g. methylene brindges $-CH_2CH_2CH_2CH_2-$).



cis-chelating ligand trans-chelating ligand

Trans vs cis ligands in square planar complexes. (CC BY-SA 3.0; via Wikipedia)

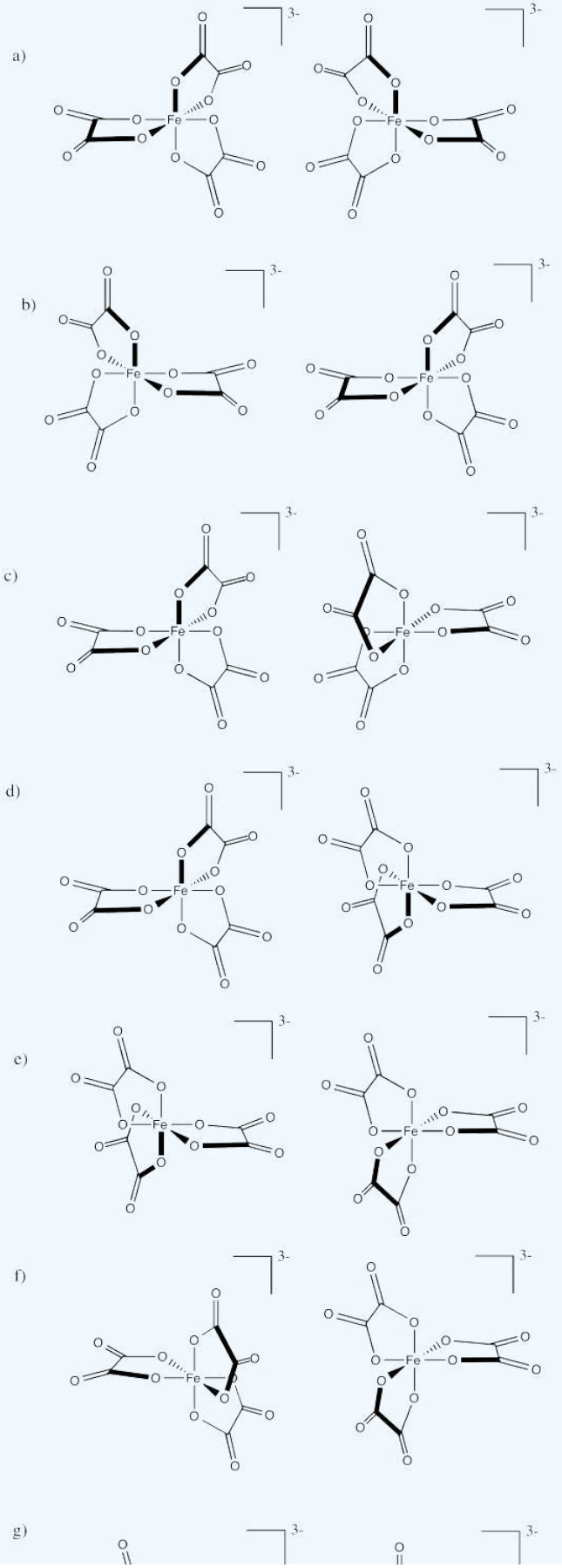
We will not consider any trans-spanning ligands in this text.

A complex containing three bidentate ligands can take on the shape of a left-handed propeller or a right-handed propeller. You may be able to see that there is no way of rotating the second isomer in space so that it looks exactly the same as the first one. As long as you draw the isomers carefully, with the second one a true reflection of the first, the two structures will be different.

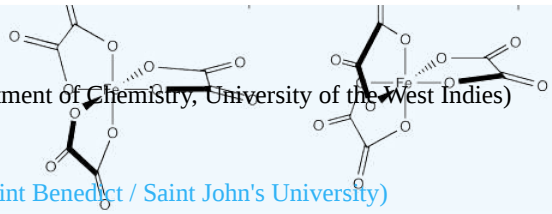
These kinds of complexes were historically important in demonstrating how small molecules and ions bound to metal cations. By showing that some metal complexes were chiral and displayed optical activity, early 20th century workers such as Alfred Werner were able to rule out some competing ideas about the structures of metal compounds. Today, we know that metal complexes play important roles in enzymes in biology, and Werner's work on metal complexes laid the groundwork for how we think about these complexes. In addition, stereochemistry in metal complexes became very important in the late 20th century, especially as pharmaceutical companies looked for catalysts that could aid in the production of one enantiomer of a drug, and not the other, in order to maximize pharmaceutical effectiveness and minimize side effects.

Exercise 9.5.1

Identify the relationships (types of isomers) between the following pairs of iron(III) oxalate ions.


a)
b)
c)
d)
e)
f)
g)
3-

Contributors and Attributions



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9.6: Stability Aspects of Complex-Ion Equilibria

Learning Objectives

- To be introduced to complex ions, including ligands.

Previously, you learned that metal ions in aqueous solution are hydrated—that is, surrounded by a shell of usually four or six water molecules. A hydrated ion is one kind of a complex ion (or, simply, complex), a species formed between a central metal ion and one or more surrounding ligands, molecules or ions that contain at least one lone pair of electrons, such as the $[Al(H_2O)_6]^{3+}$ ion.

A complex ion forms from a metal ion and a ligand because of a Lewis acid–base interaction. The positively charged metal ion acts as a Lewis acid, and the ligand, with one or more lone pairs of electrons, acts as a Lewis base. Small, highly charged metal ions, such as Cu^{2+} or Ru^{3+}, have the greatest tendency to act as Lewis acids, and consequently, they have the greatest tendency to form complex ions.



Figure **9.6.1**: The Formation of Complex Ions. An aqueous solution of $CuSO_4$ consists of hydrated Cu^{2+} ions in the form of pale blue $[Cu(H_2O)_6]^{2+}$ (left). The addition of aqueous ammonia to the solution results in the formation of the intensely blue-violet $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ions, usually written as $[Cu(NH_3)_4]^{2+}$ ion (right) because ammonia, a stronger base than H_2O, replaces water molecules from the hydrated Cu^{2+} ion. For a more complete description, see https://www.youtube.com/watch?v=IQNcLH6OZK0.

As an example of the formation of complex ions, consider the addition of ammonia to an aqueous solution of the hydrated Cu^{2+} ion $\{[Cu(H_2O)_6]^{2+}\}$. Because it is a stronger base than H_2O, ammonia replaces the water molecules in the hydrated ion to form the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ion. Formation of the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex is accompanied by a dramatic color change, as shown in Figure **9.6.1**. The solution changes from the light blue of $[Cu(H_2O)_6]^{2+}$ to the blue-violet characteristic of the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ion.

The Formation Constant

The replacement of water molecules from $[Cu(H_2O)_6]^{2+}$ by ammonia occurs in sequential steps. Omitting the water molecules bound to Cu^{2+} for simplicity, we can write the equilibrium reactions as follows:

$$Cu^{2+}(aq) + NH_3(aq) \rightleftharpoons [Cu(NH_3)]^{2+}(aq) \quad \text{(step 1)}$$

with

$$K_1 = \frac{[Cu(NH_3)]^{2+}(aq)}{[Cu^{2+}(aq)][NH_3(aq)]}$$

$$[Cu(NH_3)]^{2+}(aq) + NH_3(aq) \rightleftharpoons [Cu(NH_3)_2]^{2+}(aq) \quad \text{(step 2)}$$

with

$$K_2 = \frac{[Cu(NH_3)_2]^{2+}(aq)}{[[Cu(NH_3)]^{2+}(aq)][NH_3(aq)]}$$

$$[Cu(NH_3)_2]^{2+}(aq) + NH_3(aq) \rightleftharpoons [Cu(NH_3)_3]^{2+}(aq) \quad \text{(step 3)}$$

with

$$K_3 = \frac{[Cu(NH_3)_3]^{2+}(aq)}{[[Cu(NH_3)_2]^{2+}(aq)][NH_3(aq)]}$$

$$[Cu(NH_3)_3]^{2+}(aq) + NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq) \quad \text{(step 4)}$$

with

$$K_4 = \frac{[Cu(NH_3)_4]^{2+}(aq)}{[[Cu(NH_3)_3]^{2+}(aq)][NH_3(aq)]}$$

The sum of the stepwise reactions is the overall equation for the formation of the complex ion: The hydrated Cu^{2+} ion contains six H_2O ligands, but the complex ion that is produced contains only four NH_3 ligands, not six.

$$Cu^{2+}(aq) + 4\,NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq) \quad (9.6.1)$$

The equilibrium constant for the formation of the complex ion from the hydrated ion is called the **formation constant** (K_f). The equilibrium constant expression for K_f has the same general form as any other equilibrium constant expression. In this case, the expression is as follows:

$$\begin{aligned} K_f &= \frac{[Cu(NH_3)_4]^{2+}]}{[Cu^{2+}][NH_3]^4} \\ &= 2.1 \times 10^{13} \\ &= K_1 \times K_2 \times K_3 \times K_4 \end{aligned}$$

> *The formation constant (K_f) has the same general form as any other equilibrium constant expression.*

Water, a pure liquid, does not appear explicitly in the equilibrium constant expression, and the hydrated $Cu^{2+}(aq)$ ion is represented as Cu^{2+} for simplicity. As for any equilibrium, the larger the value of the equilibrium constant (in this case, K_f), the more stable the product. With $K_f = 2.1 \times 10^{13}$, the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex ion is very stable. The formation constants for some common complex ions are listed in Table **9.6.1**.

Table **9.6.1**: Formation Constants for Selected Complex Ions in Aqueous Solution*

	Complex Ion	Equilibrium Equation	K_f
Ammonia Complexes	$[Ag(NH_3)_2]^+$	$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$	1.1×10^7
	$[Cu(NH_3)_4]^{2+}$	$Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$	2.1×10^{13}
	$[Ni(NH_3)_6]^{2+}$	$Ni^{2+} + 6NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+}$	5.5×10^8
Cyanide Complexes	$[Ag(CN)_2]^-$	$Ag^+ + 2CN^- \rightleftharpoons [Ag(CN)_2]^-$	1.1×10^{18}
	$[Ni(CN)_4]^{2-}$	$Ni^{2+} + 4CN^- \rightleftharpoons [Ni(CN)_4]^{2-}$	2.2×10^{31}
	$[Fe(CN)_6]^{3-}$	$Fe^{3+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{3-}$	1×10^{42}
Hydroxide Complexes	$[Zn(OH)_4]^{2-}$	$Zn^{2+} + 4OH^- \rightleftharpoons [Zn(OH)_4]^{2-}$	4.6×10^{17}
	$[Cr(OH)_4]^-$	$Cr^{3+} + 4OH^- \rightleftharpoons [Cr(OH)_4]^-$	8.0×10^{29}
Halide Complexes	$[HgCl_4]^{2-}$	$Hg^{2+} + 4Cl^- \rightleftharpoons [HgCl_4]^{2-}$	1.2×10^{15}
	$[CdI_4]^{2-}$	$Cd^{2+} + 4I \rightleftharpoons [CdI_4]^{2-}$	2.6×10^5
	$[AlF_6]^{3-}$	$Al^{3+} + 6F^- \rightleftharpoons [AlF_6]^{3-}$	6.9×10^{19}
Other Complexes	$[Ag(S_2O_3)_2]^{3-}$	$Ag^+ + 2S_2O_3^{2-} \rightleftharpoons [Ag(S_2O_3)_2]^{3-}$	2.9×10^{13}
	$[Fe(C_2O_4)_3]^{3-}$	$Fe^{3+} + 3C_2O_4^{2-} \rightleftharpoons [Fe(C_2O_4)_3]^{3-}$	2.0×10^{20}

*Reported values are overall formation constants. Source: Data from *Lange's Handbook of Chemistry*, 15th ed. (1999).

Example 9.6.1

If 12.5 g of $Cu(NO_3)_2 \cdot 6H_2O$ is added to 500 mL of 1.00 M aqueous ammonia, what is the equilibrium concentration of $Cu^{2+}(aq)$?

Given: mass of Cu^{2+} salt and volume and concentration of ammonia solution

Asked for: equilibrium concentration of $Cu^{2+}(aq)$

Strategy:

A. Calculate the initial concentration of $Cu^{2+}(aq)$ due to the addition of copper(II) nitrate hexahydrate. Use the stoichiometry of the reaction shown in Equation 9.6.1 to construct a table showing the initial concentrations, the changes in concentrations, and the final concentrations of all species in solution.

B. Substitute the final concentrations into the expression for the formation constant (K_f) to calculate the equilibrium concentration of $Cu^{2+}(aq)$.

Solution

Adding an ionic compound that contains $Cu^{2+}(aq)$ to an aqueous ammonia solution will result in the formation of $[Cu(NH_3)_4]^{2+}(aq)$, as shown in Equation 9.6.1 We assume that the volume change caused by adding solid copper(II) nitrate to aqueous ammonia is negligible.

A The initial concentration of $Cu^{2+}(aq)$ from the amount of added copper nitrate prior to any reaction is as follows:

$$12.5 \cancel{g}\ Cu(NO_3)_2 \cdot 6H_2O \left(\frac{1\ mol}{295.65 \cancel{g}}\right)\left(\frac{1}{500\ \cancel{mL}}\right)\left(\frac{1000\ \cancel{mL}}{1\ L}\right) = 0.0846\ M$$

Because the stoichiometry of the reaction is four NH_3 to one Cu^{2+}, the amount of NH_3 required to react completely with the Cu^{2+} is 4(0.0846) = 0.338 M. The concentration of ammonia after complete reaction is 1.00 M − 0.338 M = 0.66 M. These results are summarized in the first two lines of the following table. Because the equilibrium constant for the reaction is large (2.1×10^{13}), the equilibrium will lie far to the right. Thus we will assume that the formation of $[Cu(NH_3)_4]^{2+}$ in the first step is complete and allow some of it to dissociate into Cu^{2+} and NH_3 until equilibrium has been reached. If we define x as the amount of Cu^{2+} produced by the dissociation reaction, then the stoichiometry of the reaction tells us that the change in the concentration of $[Cu(NH_3)_4]^{2+}$ is $-x$, and the change in the concentration of ammonia is $+4x$, as indicated in the table. The final concentrations of all species (in the bottom row of the table) are the sums of the concentrations after complete reaction and the changes in concentrations.

$$Cu^{2+} + 4\,NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$$

ICE	$[Cu^{2+}]$	$[NH_3]$	$[[Cu(NH_3)_4]^{2+}]$
initial	0.0846	1.00	0
after complete reaction	0	0.66	0.0846
change	$+x$	$+4x$	$-x$
final	x	$0.66 + 4x$	$0.0846 - x$

B Substituting the final concentrations into the expression for the formation constant (K_f) and assuming that $x \ll 0.0846$, which allows us to remove x from the sum and difference,

$$\begin{aligned} K_f &= \frac{[[Cu(NH_3)_4]^{2+}]}{[Cu^{2+}][NH_3]^4} \\ &= \frac{0.0846 - x}{x(0.66 + 4x)^4} \\ &\approx \frac{0.0846}{x(0.66)^4} = 2.1 \times 10^{13} \\ x &= 2.1 \times 10^{-14} \end{aligned}$$

The value of x indicates that our assumption was justified. The equilibrium concentration of $Cu^{2+}(aq)$ in a 1.00 M ammonia solution is therefore 2.1×10^{-14} M.

? Exercise 9.6.1

The ferrocyanide ion ($[Fe(CN)_6]^{4-}$) is very stable, with a K_f of 1×10^{35}. Calculate the concentration of cyanide ion in equilibrium with a 0.65 M solution of $K_4[Fe(CN)_6]$.

Answer

2×10^{-6} M

The Effect of the Formation of Complex Ions on Solubility

What happens to the solubility of a sparingly soluble salt if a ligand that forms a stable complex ion is added to the solution? One such example occurs in conventional black-and-white photography. Recall that black-and-white photographic film contains light-sensitive microcrystals of AgBr, or mixtures of AgBr and other silver halides. AgBr is a sparingly soluble salt, with a K_{sp} of 5.35×10^{-13} at 25°C. When the shutter of the camera opens, the light from the object being photographed strikes some of the crystals on the film and initiates a photochemical reaction that converts AgBr to black Ag metal. Well-formed, stable negative images appear in tones of gray, corresponding to the number of grains of AgBr converted, with the areas exposed to the most light being darkest. To fix the image and prevent more AgBr crystals from being converted to Ag metal during processing of the film, the unreacted AgBr on the film is removed using a complexation reaction to dissolve the sparingly soluble salt.

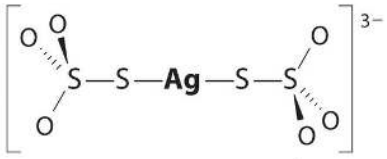
The reaction for the dissolution of silver bromide is as follows:

$$\mathrm{AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)} \tag{9.6.2}$$

with

$$K_{sp} = 5.35 \times 10^{-13} \text{ at } 25°\text{C} \tag{9.6.3}$$

The equilibrium lies far to the left, and the equilibrium concentrations of Ag^+ and Br^- ions are very low (7.31×10^{-7} M). As a result, removing unreacted AgBr from even a single roll of film using pure water would require tens of thousands of liters of water and a great deal of time. Le Chatelier's principle tells us, however, that we can drive the reaction to the right by removing one of the products, which will cause more AgBr to dissolve. Bromide ion is difficult to remove chemically, but silver ion forms a variety of stable two-coordinate complexes with neutral ligands, such as ammonia, or with anionic ligands, such as cyanide or thiosulfate ($S_2O_3^{2-}$). In photographic processing, excess AgBr is dissolved using a concentrated solution of sodium thiosulfate.



thiosulfate complex of Ag^+

The reaction of Ag^+ with thiosulfate is as follows:

$$Ag^+_{(aq)} + 2S_2O^{2-}_{3(aq)} \rightleftharpoons [Ag(S_2O_3)_2]^{3-}_{(aq)} \tag{9.6.4}$$

with

$$K_f = 2.9 \times 10^{13} \tag{9.6.5}$$

The magnitude of the equilibrium constant indicates that almost all Ag^+ ions in solution will be immediately complexed by thiosulfate to form $[Ag(S_2O_3)_2]^{3-}$. We can see the effect of thiosulfate on the solubility of **AgBr** by writing the appropriate reactions and adding them together:

$$\mathrm{AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)} \quad K_{sp} = 5.35 \times 10^{-13}$$
$$\mathrm{Ag^+(aq) + 2S_2O_3^{2-}(aq) \rightleftharpoons [Ag(S_2O_3)_2]^{3-}(aq)} \quad K_f = 2.9 \times 10^{13}$$
$$\mathrm{AgBr(s) + 2S_2O_3^{2-}(aq) \rightleftharpoons [Ag(S_2O_3)_2]^{3-}(aq) + Br^-(aq)} \quad K = K_{sp}K_f = 15$$

Comparing K with K_{sp} shows that the formation of the complex ion increases the solubility of **AgBr** by approximately 3×10^{13}. The dramatic increase in solubility combined with the low cost and the low toxicity explains why sodium thiosulfate is almost universally used for developing black-and-white film. If desired, the silver can be recovered from the thiosulfate solution using any of several methods and recycled.

> *If a complex ion has a large K_f, the formation of a complex ion can dramatically increase the solubility of sparingly soluble salts.*

Example 9.6.2: Common Ion Effect in Complexation

Due to the common ion effect, we might expect a salt such as AgCl to be much less soluble in a concentrated solution of KCl than in water. Such an assumption would be incorrect, however, because it ignores the fact that silver ion tends to form a two-coordinate complex with chloride ions ($AgCl_2^-$). Calculate the solubility of AgCl in each situation:

a. in pure water
b. in 1.0 M KCl solution, ignoring the formation of any complex ions
c. the same solution as in part (b) except taking the formation of complex ions into account, assuming that $AgCl_2^-$ is the only Ag^+ complex that forms in significant concentrations

At 25°C, $K_{sp} = 1.77 \times 10^{-10}$ for AgCl and $K_f = 1.1 \times 10^5$ for $AgCl_2^-$.

Given: K_{sp} of AgCl, K_f of $AgCl_2^-$, and KCl concentration

Asked for: solubility of AgCl in water and in KCl solution with and without the formation of complex ions

Strategy:

A. Write the solubility product expression for AgCl and calculate the concentration of Ag^+ and Cl^- in water.
B. Calculate the concentration of Ag^+ in the KCl solution.
C. Write balanced chemical equations for the dissolution of AgCl and for the formation of the $AgCl_2^-$ complex. Add the two equations and calculate the equilibrium constant for the overall equilibrium.
D. Write the equilibrium constant expression for the overall reaction. Solve for the concentration of the complex ion.

Solution

A. If we let x equal the solubility of AgCl, then at equilibrium

$$[Ag^+] = [Cl^-] = x \text{ M}.$$

Substituting this value into the solubility product expression,

$$\begin{aligned} K_{sp} &= [Ag^+][Cl^-] \\ &= (x)(x) \\ &= x^2 \\ &= 1.77 \times 10^{-10} \\ x &= 1.33 \times 10^{-5} \end{aligned}$$

Thus the solubility of **AgCl** in pure water at 25°C is 1.33×10^{-5} M.

B. If x equals the solubility of AgCl in the KCl solution, then at equilibrium $[Ag^+] = x$ M and $[Cl^-] = (1.0 + x)$ M. Substituting these values into the solubility product expression and assuming that $x \le 1.0$:

$$\begin{aligned} K_{sp} &= [Ag^+][Cl^-] \\ &= (x)(1.0 + x) \\ &\approx x(1.0) \\ &= 1.77 \times 10^{-10} = x \end{aligned}$$

If the common ion effect were the only important factor, we would predict that **AgCl** is approximately five orders of magnitude less soluble in a 1.0 M KCl solution than in water.

C. To account for the effects of the formation of complex ions, we must first write the equilibrium equations for both the dissolution and the formation of complex ions. Adding the equations corresponding to K_{sp} and K_f gives us an equation that describes the dissolution of AgCl in a KCl solution. The equilibrium constant for the reaction is therefore the product of K_{sp} and K_f:

$$\begin{aligned} AgCl(s) &\rightleftharpoons Ag^+(aq) + Cl^-(aq) \quad K_{sp} = 1.77 \times 10^{-10} \\ Ag^+aq) + 2Cl^- &\rightleftharpoons [AgCl_2]^- \quad K_f = 1.1 \times 10^5 \\ AgCl(s) + Cl^- &\rightleftharpoons [AgCl_2]^- \quad K = K_{sp}K_f = 1.9 \times 10^{-5} \end{aligned}$$

D. If we let x equal the solubility of AgCl in the KCl solution, then at equilibrium $[AgCl_2^-] = x$ and $[Cl^-] = 1.0 - x$. Substituting these quantities into the equilibrium constant expression for the net reaction and assuming that $x \le 1.0$,

$$\begin{aligned} K &= \frac{[AgCl_2^-]}{[Cl^-]} \\ &= \frac{x}{1.0 - x} \approx 1.9 \times 10^{-5} \\ &= x \end{aligned}$$

That is, AgCl dissolves in 1.0 M KCl to produce a 1.9×10^{-5} M solution of the $AgCl_2^-$ complex ion. Thus we predict that AgCl has approximately the same solubility in a 1.0 M KCl solution as it does in pure water, which is 10^5 times greater than that

predicted based on the common ion effect. (In fact, the measured solubility of AgCl in 1.0 M KCl is almost a factor of 10 greater than that in pure water, largely due to the formation of other chloride-containing complexes.)

? Exercise 9.6.2

Calculate the solubility of mercury(II) iodide ($\mathbf{HgI_2}$) in each situation:

a. pure water

b. a 3.0 M solution of NaI, assuming $[HgI_4]^{2-}$ is the only Hg-containing species present in significant amounts

$$K_{sp} = 2.9 \times 10^{-29} \text{ for } HgI_2 \text{ and } K_f = 6.8 \times 10^{29} \text{ for } [HgI_4]^{2-}.$$

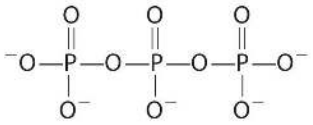
Answer a

1.9×10^{-10} M

Answer b

1.4 M

Complexing agents, molecules or ions that increase the solubility of metal salts by forming soluble metal complexes, are common components of laundry detergents. Long-chain carboxylic acids, the major components of soaps, form insoluble salts with Ca^{2+} and Mg^{2+}, which are present in high concentrations in "hard" water. The precipitation of these salts produces a bathtub ring and gives a gray tinge to clothing.



triphosphate

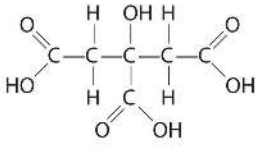
Adding a complexing agent such as pyrophosphate ($O_3POPO_3^{4-}$, or $P_2O_7^{4-}$) or triphosphate ($P_3O_{10}^{5-}$) to detergents prevents the magnesium and calcium salts from precipitating because the equilibrium constant for complex-ion formation is large:

$$\mathbf{Ca^{2+}(aq) + O_3POPO_4^{4-}(aq) \rightleftharpoons [Ca(O_3POPO_3)]^{2-}(aq)}$$

with

$$\mathbf{K_f = 4 \times 10^4}$$

However, phosphates can cause environmental damage by promoting eutrophication, the growth of excessive amounts of algae in a body of water, which can eventually lead to large decreases in levels of dissolved oxygen that kill fish and other aquatic organisms. Consequently, many states in the United States have banned the use of phosphate-containing detergents, and France has banned their use beginning in 2007. "Phosphate-free" detergents contain different kinds of complexing agents, such as derivatives of acetic acid or other carboxylic acids. The development of phosphate substitutes is an area of intense research.



Citric acid,
a hydroxy polycarboxylic acid

Commercial water softeners also use a complexing agent to treat hard water by passing the water over ion-exchange resins, which are complex sodium salts. When water flows over the resin, sodium ion is dissolved, and insoluble salts precipitate onto the resin surface. Water treated in this way has a saltier taste due to the presence of Na^+, but it contains fewer dissolved minerals.

Complexing Agents in MRIs

Another application of complexing agents is found in medicine. Unlike x-rays, magnetic resonance imaging (MRI) can give relatively good images of soft tissues such as internal organs. MRI is based on the magnetic properties of the ^{1}H nucleus of hydrogen atoms in water, which is a major component of soft tissues. Because the properties of water do not depend very much on whether it is inside a cell or in the blood, it is hard to get detailed images of these tissues that have good contrast. To solve this problem, scientists have developed a class of metal complexes known as "MRI contrast agents." Injecting an MRI contrast agent into a patient selectively affects the magnetic properties of water in cells of normal tissues, in tumors, or in blood vessels and allows doctors to "see" each of these separately (Figure **9.6.2**). One of the most important metal ions for this application is Gd^{3+}, which with seven unpaired electrons is highly paramagnetic. Because $Gd^{3+}(aq)$ is quite toxic, it must be administered as a very stable complex that does not dissociate in the body and can be excreted intact by the kidneys. The complexing agents used for gadolinium are ligands such as $DTPA^{5-}$ (diethylene triamine pentaacetic acid), whose fully protonated form is shown in Figure **9.6.2**.

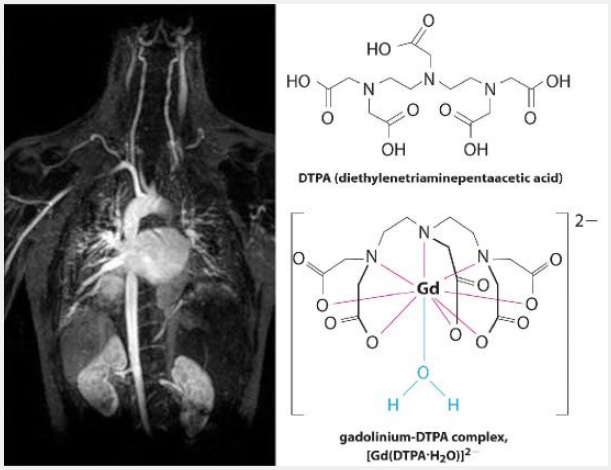


Figure **9.6.2**: An MRI Image of the Heart, Arteries, and Veins. When a patient is injected with a paramagnetic metal cation in the form of a stable complex known as an MRI contrast agent, the magnetic properties of water in cells are altered. Because the different environments in different types of cells respond differently, a physician can obtain detailed images of soft tissues.

Summary

The formation of complex ions can substantially increase the solubility of sparingly soluble salts if the complex ion has a large K_f. A complex ion is a species formed between a central metal ion and one or more surrounding ligands, molecules or ions that contain at least one lone pair of electrons. Small, highly charged metal ions have the greatest tendency to act as Lewis acids and form complex ions. The equilibrium constant for the formation of the complex ion is the formation constant (K_f). The formation of a complex ion by adding a complexing agent increases the solubility of a compound.

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9.7: Chelation

Ligands like chloride, water, and ammonia are said to be monodentate (one-toothed, from the Greek mono, meaning “one,” and the Latin dent-, meaning “tooth”): they are attached to the metal via only a single atom. Ligands can, however, be bidentate (two-toothed, from the Greek di, meaning “two”), tridentate (three-toothed, from the Greek tri, meaning “three”), or, in general, polydentate (many-toothed, from the Greek poly, meaning “many”), indicating that they are attached to the metal at two, three, or several sites, respectively. Ethylenediamine ($H_2NCH_2CH_2NH_2$, often abbreviated as en) and diethylenetriamine ($H_2NCH_2CH_2NHCH_2CH_2NH_2$, often abbreviated as dien) are examples of a bidentate and a tridentate ligand, respectively, because each nitrogen atom has a lone pair that can be shared with a metal ion. When a bidentate ligand such as ethylenediamine binds to a metal such as Ni^{2+}, a five-membered ring is formed. A metal-containing ring like that shown is called a chelate ring (from the Greek chele, meaning “claw”). Correspondingly, a polydentate ligand is a chelating agent, and complexes that contain polydentate ligands are called chelate complexes.



A chelate complex

Experimentally, it is observed that metal complexes of polydentate ligands are significantly more stable than the corresponding complexes of chemically similar monodentate ligands; this increase in stability is called the chelate effect. For example, the complex of Ni^{2+} with three ethylenediamine ligands, $[Ni(en)_3]^{2+}$, should be chemically similar to the Ni^{2+} complex with six ammonia ligands, $[Ni(NH_3)_6]^{2+}$. In fact, the equilibrium constant for the formation of $[Ni(en)_3]^{2+}$ is almost 10 orders of magnitude larger than the equilibrium constant for the formation of $[Ni(NH_3)_6]^{2+}$ (Table E4):

$$[Ni(H_2O)_6]^{2+} + 6NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+} + 6H_2O(l) \quad K_f = 4 \times 10^8 \tag{9.7.1}$$

$$[Ni(H_2O)_6]^{2+} + 3en \rightleftharpoons [Ni(en)_3]^{2+} + 6H_2O(l) \quad K_f = 2 \times 10^{18} \tag{9.7.2}$$

The formation constants are formulated as ligand exchange reactions with aqua ligands being displaced by new ligands (NH_3 or en) in the examples above.

> *Chelate complexes are more stable than the analogous complexes with monodentate ligands.*

The stability of a chelate complex depends on the size of the chelate rings. For ligands with a flexible organic backbone like ethylenediamine, complexes that contain five-membered chelate rings, which have almost no strain, are significantly more stable than complexes with six-membered chelate rings, which are in turn much more stable than complexes with four- or seven-membered rings. For example, the complex of nickel (II) with three ethylenediamine ligands is about 363,000 times more stable than the corresponding nickel (II) complex with trimethylenediamine ($H_2NCH_2CH_2CH_2NH_2$, abbreviated as tn):

$$[Ni(H_2O)_6]^{2+} + 3en \rightleftharpoons [Ni(en)_3]^{2+} + 6H_2O(l) \quad K_f = 6.76 \times 10^{17} \tag{9.7.3}$$

$$[Ni(H_2O)_6]^{2+} + 3tn \rightleftharpoons [Ni(tn)_3]^{2+} + 6H_2O(l) \quad K_f = 1.86 \times 10^{12} \tag{9.7.4}$$

*The above measurements were done in a solution of ionic strength 0.15 at 25° C.

Example 9.7.1

Arrange $[Cr(en)_3]^{3+}$, $[CrCl_6]^{3-}$, $[CrF_6]^{3-}$, and $[Cr(NH_3)_6]^{3+}$ in order of increasing stability.

Given: four Cr(III) complexes

Asked for: relative stabilities

Strategy:

A Determine the relative basicity of the ligands to identify the most stable complexes.

B Decide whether any complexes are further stabilized by a chelate effect and arrange the complexes in order of increasing stability.

Solution

A The metal ion is the same in each case: Cr^{3+}. Consequently, we must focus on the properties of the ligands to determine the stabilities of the complexes. Because the stability of a metal complex increases as the basicity of the ligands increases, we need to determine the relative basicity of the four ligands. Our earlier discussion of acid–base properties suggests that ammonia and ethylenediamine, with nitrogen donor atoms, are the most basic ligands. The fluoride ion is a stronger base (it has a higher charge-to-radius ratio) than chloride, so the order of stability expected due to ligand basicity is

$$[CrCl_6]^{3-} < [CrF_6]^{3-} < [Cr(NH_3)_6]^{3+} \approx [Cr(en)_3]^{3+}.$$

B Because of the chelate effect, we expect ethylenediamine to form a stronger complex with Cr^{3+} than ammonia. Consequently, the likely order of increasing stability is

$$[CrCl_6]^{3-} < [CrF_6]^{3-} < [Cr(NH_3)_6]^{3+} < [Cr(en)_3]^{3+}.$$

? Exercise 9.7.1

Arrange $[Co(NH_3)_6]^{3+}$, $[CoF_6]^{3-}$, and $[Co(en)_3]^{3+}$ in order of decreasing stability.

Answer: $[Co(en)_3]^{3+} > [Co(NH_3)_6]^{3+} > [CoF_6]^{3-}$

The Chelate Effect

The chelate effect can be seen by comparing the reaction of a chelating ligand and a metal ion with the corresponding reaction involving comparable monodentate ligands. For example, comparison of the binding of 2,2'-bipyridine with pyridine or 1,2-diaminoethane (ethylenediamine=en) with ammonia. It has been known for many years that a comparison of this type always shows that the complex resulting from coordination with the chelating ligand is **much more thermodynamically stable**. This can be seen by looking at the values for adding two monodentates compared with adding one bidentate, or adding four monodentates compared to two bidentates, or adding six monodentates compared to three bidentates.

> *The Chelate Effect is that complexes resulting from coordination with the chelating ligand is much more thermodynamically stable than complexes with non-chelating ligands.*

A number of points should be highlighted from the formation constants in Table E4. In Table **9.7.1**, it can be seen that the ΔH° values for the formation steps are almost identical, that is, heat is evolved to about the same extent whether forming a complex involving monodentate ligands or bidentate ligands. What is seen to vary significantly is the ΔS° term which changes from negative (unfavorable) to positive (favorable). Note as well that there is a dramatic increase in the size of the ΔS° term for adding two compared to adding four monodentate ligands. (-5 to -35 $JK^{-1}mol^{-1}$). What does this imply, if we consider ΔS° to give a measure of disorder?

In the case of complex formation of Ni^{2+} with ammonia or 1,2-diaminoethane, by rewriting the equilibria, the following equations are produced.

$$[Ni(H_2O)_6]^{2+} + 6\,NH_3 \overset{\beta_6}{\Leftrightarrow} [Ni(NH_3)_6]^{2+} \quad \textbf{1f}$$

$$[Ni(NH_3)_6]^{2+} \Leftrightarrow [Ni(H_2O)_6]^{2+} + 6\,NH_3 \quad \textbf{1d}$$

$$[Ni(H_2O)_6]^{2+} + 3\,en \overset{\beta_3}{\Leftrightarrow} [Ni(en)_3]^{2+} \quad \textbf{2f}$$

$$[Ni(NH_3)_6]^{2+} + 3\,en \Leftrightarrow [Ni(en)_3]^{2+} + 6NH_3 \quad \textbf{3}$$

Using the equilibrium constant for the reaction (3 above) where the *three* bidentate ligands replace the *six* monodentateligands, we find that at a temperature of 25° C:

$$\Delta G^\circ = -2.303\,RT\,\log_{10} K$$

$$= -2.303\,RT\,(18.28 - 8.61)$$

$$= -54\ \text{kJ mol}^{-1}$$

Based on measurements made over a range of temperatures, it is possible to break down the $\Delta G°$ term into the enthalpy and entropy components.

$$\Delta G° = \Delta H° - T\Delta S°$$

The result is that: $\Delta H° = -29 kJ mol^{-1}$

$$- T\Delta S° = -25 \text{ kJ mol}^{-1}$$
and at 25C (298K)
$$\Delta S° = +88 \text{ J K}^{-1} \text{ mol}^{-1}$$

For many years, these numbers have been **incorrectly recorded** in textbooks. For example, the third edition of "Basic Inorganic Chemistry" by F.A. Cotton, G. Wilkinson and P.L. Gaus, John Wiley & Sons, Inc, 1995, on page 186 gives the values as:

$$\Delta G° = -67 \text{ kJ mol}^{-1}$$
$$\Delta H° = -12 \text{ kJ mol}^{-1}$$
$$-T\Delta S° = -55 \text{ kJ mol}^{-1}$$

The conclusion they drew from these incorrect numbers was that the chelate effect was essentially an entropy effect, since the $T\Delta S°$ contribution was nearly 5 times bigger than $\Delta H°$.

In fact, the breakdown of the $\Delta G°$ into $\Delta H°$ and $T\Delta S°$ shows that the two terms are nearly equal (-29 and -25 kJ mol^{-1}, respectively) with the $\Delta H°$ term a little bigger! The entropy term found is still much larger than for reactions involving a non-chelating ligand substitution at a metal ion. How can we explain this enhanced contribution from entropy? One explanation is to count the number of species on the left and right hand side of the equation above.

It will be seen that on the left-hand-side there are 4 species, whereas on the right-hand-side there are 7 species, that is a net gain of 3 species occurs as the reaction proceeds. This can account for the increase in entropy since it represents an increase in the disorder of the system. An alternative view comes from trying to understand how the reactions might proceed. To form a complex with 6 monodentates requires 6 separate favorable collisions between the metal ion and the ligand molecules. To form the tris-bidentate metal complex requires an initial collision for the first ligand to attach by one arm but remember that the other arm is always going to be nearby and only requires a rotation of the other end to enable the ligand to form the chelate ring.

If you consider dissociation steps, then when a monodentate group is displaced, it is lost into the bulk of the solution. On the other hand, if one end of a bidentate group is displaced the other arm is still attached and it is only a matter of the arm rotating around and it can be reattached again. **Both** conditions favor the formation of the complex with bidentate groups rather than monodentate groups.

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9.8: Bonding in Octahedral Complex Ions- Crystal Field Theory

Learning Objectives

- To understand how crystal field theory explains the electronic structures and colors of metal complexes.

One of the most striking characteristics of transition-metal complexes is the wide range of colors they exhibit. In this section, we describe crystal field theory (CFT), a bonding model that explains many important properties of transition-metal complexes, including their colors, magnetism, structures, stability, and reactivity. The central assumption of CFT is that metal–ligand interactions are purely electrostatic in nature. Even though this assumption is clearly not valid for many complexes, such as those that contain neutral ligands like CO, CFT enables chemists to explain many of the properties of transition-metal complexes with a reasonable degree of accuracy. The Learning Objective of this Module is to understand how crystal field theory explains the electronic structures and colors of metal complexes.

d-Orbital Splittings

CFT focuses on the interaction of the five (n − 1)d orbitals with ligands arranged in a regular array around a transition-metal ion. We will focus on the application of CFT to octahedral complexes, which are by far the most common and the easiest to visualize. Other common structures, such as square planar complexes, can be treated as a distortion of the octahedral model. According to CFT, an octahedral metal complex forms because of the electrostatic interaction of a positively charged metal ion with six negatively charged ligands or with the negative ends of dipoles associated with the six ligands. In addition, the ligands interact with one other electrostatically. As you learned in our discussion of the valence-shell electron-pair repulsion (VSEPR) model, the lowest-energy arrangement of six identical negative charges is an octahedron, which minimizes repulsive interactions between the ligands.

We begin by considering how the energies of the d orbitals of a transition-metal ion are affected by an octahedral arrangement of six negative charges. Recall that the five d orbitals are initially degenerate (have the same energy). If we distribute six negative charges uniformly over the surface of a sphere, the d orbitals remain degenerate, but their energy will be higher due to repulsive electrostatic interactions between the spherical shell of negative charge and electrons in the d orbitals (Figure **9.8.1*a***). Placing the six negative charges at the vertices of an octahedron does not change the average energy of the d orbitals, but it does remove their degeneracy: the five d orbitals split into two groups whose energies depend on their orientations. As shown in Figure **9.8.1*b***, the d_{z^2} and $d_{x^2-y^2}$ orbitals point directly at the six negative charges located on the x, y, and z axes. Consequently, the energy of an electron in these two orbitals (collectively labeled the e_g orbitals) will be greater than it will be for a spherical distribution of negative charge because of increased electrostatic repulsions. In contrast, the other three d orbitals (d_{xy}, d_{xz}, and d_{yz}, collectively called the t_{2g} orbitals) are all oriented at a 45° angle to the coordinate axes, so they point between the six negative charges. The energy of an electron in any of these three orbitals is lower than the energy for a spherical distribution of negative charge.

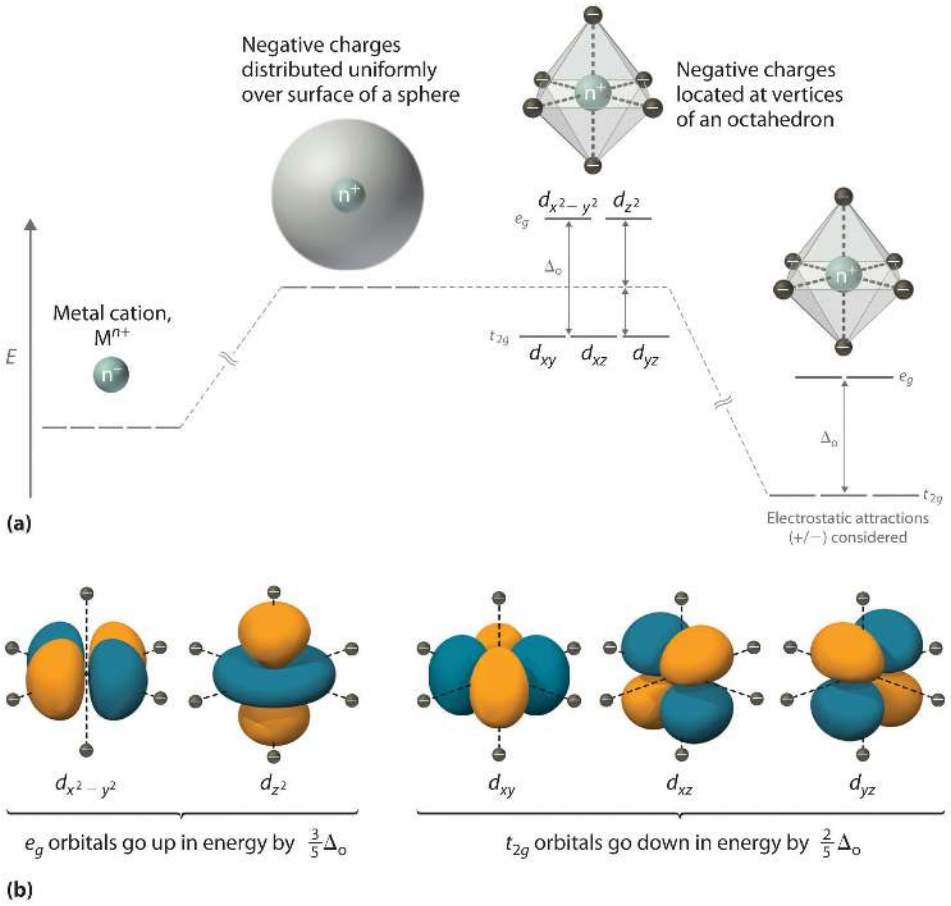


Figure **9.8.1**: An Octahedral Arrangement of Six Negative Charges around a Metal Ion Causes the Five d Orbitals to Split into Two Sets with Different Energies. (a) Distributing a charge of −6 uniformly over a spherical surface surrounding a metal ion causes the energy of all five d orbitals to increase due to electrostatic repulsions, but the five d orbitals remain degenerate. Placing a charge of −1 at each vertex of an octahedron causes the d orbitals to split into two groups with different energies: the $d_{x^2-y^2}$ and d_{z^2} orbitals increase in energy, while the d_{xy}, d_{xz}, and d_{yz} orbitals decrease in energy. The average energy of the five d orbitals is the same as for a spherical distribution of a −6 charge, however. Attractive electrostatic interactions between the negatively charged ligands and the positively charged metal ion (far right) cause all five d orbitals to decrease in energy but does not affect the splittings of the orbitals. (b) The two e_g orbitals (left) point directly at the six negatively charged ligands, which increases their energy compared with a spherical distribution of negative charge. In contrast, the three t_{2g} orbitals (right) point between the negatively charged ligands, which decreases their energy compared with a spherical distribution of charge. (CC BY-SA-NC; anonymous by request)

The difference in energy between the two sets of d orbitals is called the crystal field splitting energy (Δ_o), where the subscript o stands for octahedral. As we shall see, the magnitude of the splitting depends on the charge on the metal ion, the position of the metal in the periodic table, and the nature of the ligands. (Crystal field splitting energy also applies to tetrahedral complexes: Δ_t.) It is important to note that the splitting of the d orbitals in a crystal field does not change the total energy of the five d orbitals: the two e_g orbitals increase in energy by $0.6\Delta_o$, whereas the three t_{2g} orbitals decrease in energy by $0.4\Delta_o$. Thus the total change in energy is

$$2(0.6\Delta_o) + 3(-0.4\Delta_o) = 0. \tag{9.8.1}$$

> *Crystal field splitting does not change the total energy of the d orbitals.*

Thus far, we have considered only the effect of repulsive electrostatic interactions between electrons in the d orbitals and the six negatively charged ligands, which increases the total energy of the system and splits the d orbitals. Interactions between the positively charged metal ion and the ligands results in a net stabilization of the system, which decreases the energy of all five d orbitals without affecting their splitting (as shown at the far right in Figure **9.8.1***a*).

Electronic Structures of Metal Complexes

We can use the d-orbital energy-level diagram in Figure **9.8.1** to predict electronic structures and some of the properties of transition-metal complexes. We start with the Ti^{3+} ion, which contains a single d electron, and proceed across the first row of the transition metals by adding a single electron at a time. We place additional electrons in the lowest-energy orbital available, while keeping their spins parallel as required by Hund's rule. As shown in Figure **9.8.2**, for d^1–d^3 systems—such as $[Ti(H_2O)_6]^{3+}$, $[V(H_2O)_6]^{3+}$, and $[Cr(H_2O)_6]^{3+}$, respectively—the electrons successively occupy the three degenerate t_{2g} orbitals with their spins parallel, giving one, two, and three unpaired electrons, respectively. We can summarize this for the complex $[Cr(H_2O)_6]^{3+}$, for example, by saying that the chromium ion has a d^3 electron configuration or, more succinctly, Cr^{3+} is a d^3 ion.

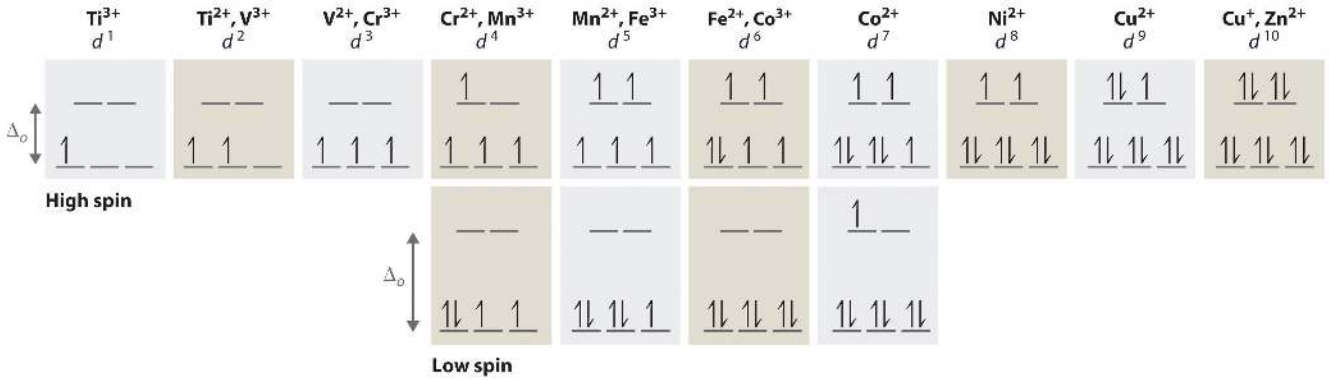


Figure **9.8.2**: The Possible Electron Configurations for Octahedral d^n Transition-Metal Complexes (n = 1–10). Two different configurations are possible for octahedral complexes of metals with d^4, d^5, d^6, and d^7 configurations; the magnitude of Δ_o determines which configuration is observed. (CC BY-SA-NC; anonymous by request)

When we reach the d^4 configuration, there are two possible choices for the fourth electron: it can occupy either one of the empty e_g orbitals or one of the singly occupied t_{2g} orbitals. Recall that placing an electron in an already occupied orbital results in electrostatic repulsions that increase the energy of the system; this increase in energy is called the spin-pairing energy (P). If Δ_o is less than P, then the lowest-energy arrangement has the fourth electron in one of the empty e_g orbitals. Because this arrangement results in four unpaired electrons, it is called a high-spin configuration, and a complex with this electron configuration, such as the $[Cr(H_2O)_6]^{2+}$ ion, is called a high-spin complex. Conversely, if Δ_o is greater than P, then the lowest-energy arrangement has the fourth electron in one of the occupied t_{2g} orbitals. Because this arrangement results in only two unpaired electrons, it is called a low-spin configuration, and a complex with this electron configuration, such as the $[Mn(CN)_6]^{3-}$ ion, is called a low-spin complex. Similarly, metal ions with the d^5, d^6, or d^7 electron configurations can be either high spin or low spin, depending on the magnitude of Δ_o.

In contrast, only one arrangement of d electrons is possible for metal ions with d^8–d^{10} electron configurations. For example, the $[Ni(H_2O)_6]^{2+}$ ion is d^8 with two unpaired electrons, the $[Cu(H_2O)_6]^{2+}$ ion is d^9 with one unpaired electron, and the $[Zn(H_2O)_6]^{2+}$ ion is d^{10} with no unpaired electrons.

> *If Δ_o is less than the spin-pairing energy, a high-spin configuration results. Conversely, if Δ_o is greater, a low-spin configuration forms.*

Factors That Affect the Magnitude of Δ_o

The magnitude of Δ_o dictates whether a complex with four, five, six, or seven d electrons is high spin or low spin, which affects its magnetic properties, structure, and reactivity. Large values of Δ_o (i.e., $\Delta_o > P$) yield a low-spin complex, whereas small values of Δ_o (i.e., $\Delta_o < P$) produce a high-spin complex. As we noted, the magnitude of Δ_o depends on three factors: the charge on the metal ion, the principal quantum number of the metal (and thus its location in the periodic table), and the nature of the ligand. Values of Δ_o for some representative transition-metal complexes are given in Table **9.8.1**.

Table **9.8.1**: Crystal Field Splitting Energies for Some Octahedral (Δ_o)* and Tetrahedral (Δ_t) Transition-Metal Complexes

Octahedral Complexes	Δ_o (cm^{-1})	Octahedral Complexes	Δ_o (cm^{-1})	Tetrahedral Complexes	Δ_t (cm^{-1})
$[Ti(H_2O)_6]^{3+}$	20,300	$[Fe(CN)_6]^{4-}$	32,800	VCl_4	9010
$[V(H_2O)_6]^{2+}$	12,600	$[Fe(CN)_6]^{3-}$	35,000	$[CoCl_4]^{2-}$	3300
$[V(H_2O)_6]^{3+}$	18,900	$[CoF_6]^{3-}$	13,000	$[CoBr_4]^{2-}$	2900
$[CrCl_6]^{3-}$	13,000	$[Co(H_2O)_6]^{2+}$	9300	$[CoI_4]^{2-}$	2700
$[Cr(H_2O)_6]^{2+}$	13,900	$[Co(H_2O)_6]^{3+}$	27,000		
$[Cr(H_2O)_6]^{3+}$	17,400	$[Co(NH_3)_6]^{3+}$	22,900		
$[Cr(NH_3)_6]^{3+}$	21,500	$[Co(CN)_6]^{3-}$	34,800		
$[Cr(CN)_6]^{3-}$	26,600	$[Ni(H_2O)_6]^{2+}$	8500		
$Cr(CO)_6$	34,150	$[Ni(NH_3)_6]^{2+}$	10,800		
$[MnCl_6]^{4-}$	7500	$[RhCl_6]^{3-}$	20,400		
$[Mn(H_2O)_6]^{2+}$	8500	$[Rh(H_2O)_6]^{3+}$	27,000		
$[MnCl_6]^{3-}$	20,000	$[Rh(NH_3)_6]^{3+}$	34,000		
$[Mn(H_2O)_6]^{3+}$	21,000	$[Rh(CN)_6]^{3-}$	45,500		
$[Fe(H_2O)_6]^{2+}$	10,400	$[IrCl_6]^{3-}$	25,000		
$[Fe(H_2O)_6]^{3+}$	14,300	$[Ir(NH_3)_6]^{3+}$	41,000		

*Energies obtained by spectroscopic measurements are often given in units of wave numbers (cm^{-1}); the wave number is the reciprocal of the wavelength of the corresponding electromagnetic radiation expressed in centimeters: 1 cm^{-1} = 11.96 J/mol.

Source of data: Duward F. Shriver, Peter W. Atkins, and Cooper H. Langford, Inorganic Chemistry, 2nd ed. (New York: W. H. Freeman and Company, 1994).

Factor 1: Charge on the Metal Ion

Increasing the charge on a metal ion has two effects: the radius of the metal ion decreases, and negatively charged ligands are more strongly attracted to it. Both factors decrease the metal–ligand distance, which in turn causes the negatively charged ligands to interact more strongly with the d orbitals. Consequently, the magnitude of Δ_o increases as the charge on the metal ion increases. Typically, Δ_o for a tripositive ion is about 50% greater than for the dipositive ion of the same metal; for example, for $[V(H_2O)_6]^{2+}$, Δ_o = 11,800 cm^{-1}; for $[V(H_2O)_6]^{3+}$, Δ_o = 17,850 cm^{-1}.

Factor 2: Principal Quantum Number of the Metal

For a series of complexes of metals from the same group in the periodic table with the same charge and the same ligands, the magnitude of Δ_o increases with increasing principal quantum number: Δ_o (3d) < Δ_o (4d) < Δ_o (5d). The data for hexaammine complexes of the trivalent Group 9 metals illustrate this point:

$$[Co(NH_3)_6]^{3+}: \Delta_o = 22{,}900\ cm^{-1}$$

$$[Rh(NH_3)_6]^{3+}: \Delta_o = 34{,}100\ cm^{-1}$$

$$[Ir(NH_3)_6]^{3+}: \Delta_o = 40{,}000\ cm^{-1}$$

The increase in Δ_o with increasing principal quantum number is due to the larger radius of valence orbitals down a column. In addition, repulsive ligand–ligand interactions are most important for smaller metal ions. Relatively speaking, this results in shorter M–L distances and stronger d orbital–ligand interactions.

Factor 3: The Nature of the Ligands

Experimentally, it is found that the Δ_o observed for a series of complexes of the same metal ion depends strongly on the nature of the ligands. For a series of chemically similar ligands, the magnitude of Δ_o decreases as the size of the donor atom increases. For example, Δ_o values for halide complexes generally decrease in the order $F^- > Cl^- > Br^- > I-$ because smaller, more localized charges, such as we see for F^-, interact more strongly with the d orbitals of the metal ion. In addition, a small neutral ligand with a highly localized lone pair, such as NH_3, results in significantly larger Δ_o values than might be expected. Because the lone pair points directly at the metal ion, the electron density along the M–L axis is greater than for a spherical anion such as F^-. The experimentally observed order of the crystal field splitting energies produced by different ligands is called the spectrochemical series, shown here in order of decreasing Δ_o:

$$\underset{\text{strong-field ligands}}{CO \approx CN^- > NO_2^-} > en > NH_3 > \underset{\text{intermediate-field ligands}}{SCN^- > H_2O > oxalate^{2-} > OH^- > F} > acetate^- > \underset{\text{weak-field ligands}}{Cl^- > Br^- > I^-}$$

The values of Δ_o listed in Table **9.8.1** illustrate the effects of the charge on the metal ion, the principal quantum number of the metal, and the nature of the ligand.

> *The largest Δ_o splittings are found in complexes of metal ions from the third row of the transition metals with charges of at least +3 and ligands with localized lone pairs of electrons.*

Example 9.8.1

For each complex, predict its structure, whether it is high spin or low spin, and the number of unpaired electrons present.

a. $[CoF_6]^{3-}$
b. $[Rh(CO)_2Cl_2]^-$

Given: complexes

Asked for: structure, high spin versus low spin, and the number of unpaired electrons

Strategy:

a. From the number of ligands, determine the coordination number of the compound.
b. Classify the ligands as either strong field or weak field and determine the electron configuration of the metal ion.
c. Predict the relative magnitude of Δ_o and decide whether the compound is high spin or low spin.
d. Place the appropriate number of electrons in the d orbitals and determine the number of unpaired electrons.

Solution

a. A With six ligands, we expect this complex to be octahedral.

B The fluoride ion is a small anion with a concentrated negative charge, but compared with ligands with localized lone pairs of electrons, it is weak field. The charge on the metal ion is +3, giving a d^6 electron configuration.

C Because of the weak-field ligands, we expect a relatively small Δ_o, making the compound high spin.

D In a high-spin octahedral d^6 complex, the first five electrons are placed individually in each of the d orbitals with their spins parallel, and the sixth electron is paired in one of the t_{2g} orbitals, giving four unpaired electrons.

b. A This complex has four ligands, so it is either square planar or tetrahedral.

B C Because rhodium is a second-row transition metal ion with a d^8 electron configuration and CO is a strong-field ligand, the complex is likely to be square planar with a large Δ_o, making it low spin. Because the strongest d-orbital interactions are along the x and y axes, the orbital energies increase in the order $d_{z^2}d_{yz}$, and d_{xz} (these are degenerate); d_{xy}; and $d_{x^2-y^2}$.

D The eight electrons occupy the first four of these orbitals, leaving the $d_{x^2-y^2}$. orbital empty. Thus there are no unpaired electrons.

? Exercise 9.8.1

For each complex, predict its structure, whether it is high spin or low spin, and the number of unpaired electrons present.

a. $[Mn(H_2O)_6]^{2+}$
b. $[PtCl_4]^{2-}$

Answer a

octahedral; high spin; five

Answer b

square planar; low spin; no unpaired electrons

Crystal Field Stabilization Energies

Recall that stable molecules contain more electrons in the lower-energy (bonding) molecular orbitals in a molecular orbital diagram than in the higher-energy (antibonding) molecular orbitals. If the lower-energy set of d orbitals (the t_{2g} orbitals) is selectively populated by electrons, then the stability of the complex increases. For example, the single d electron in a d^1 complex such as $[Ti(H_2O)_6]^{3+}$ is located in one of the t_{2g} orbitals. Consequently, this complex will be more stable than expected on purely electrostatic grounds by $0.4\Delta_o$. The additional stabilization of a metal complex by selective population of the lower-energy d orbitals is called its crystal field stabilization energy (CFSE). The CFSE of a complex can be calculated by multiplying the number of electrons in t_{2g} orbitals by the energy of those orbitals ($-0.4\Delta_o$), multiplying the number of electrons in e_g orbitals by the energy of those orbitals ($+0.6\Delta_o$), and summing the two. Table **9.8.2** gives CFSE values for octahedral complexes with different d electron configurations. The CFSE is highest for low-spin d^6 complexes, which accounts in part for the extraordinarily large number of Co(III) complexes known. The other low-spin configurations also have high CFSEs, as does the d^3 configuration.

Table **9.8.2**: CFSEs for Octahedral Complexes with Different Electron Configurations (in Units of Δo)

	High Spin		CFSE (Δ_o)	Low Spin		CFSE (Δ_o)
	t_{2g}	e_g		t_{2g}	e_g	
d^0			0			
d^1	↑		0.4			
d^2	↑ ↑		0.8			
d^3	↑ ↑ ↑		1.2			
d^4	↑ ↑ ↑	↑	0.6	↑↓ ↑ ↑		1.6
d^5	↑ ↑ ↑	↑ ↑	0.0	↑↓ ↑↓ ↑		2.0
d^6	↑↓ ↑ ↑	↑ ↑	0.4	↑↓ ↑↓ ↑↓		2.4
d^7	↑↓ ↑↓ ↑	↑ ↑	0.8	↑↓ ↑↓ ↑↓	↑	1.8
d^8	↑↓ ↑↓ ↑↓	↑ ↑	1.2			
d^9	↑↓ ↑↓ ↑↓	↑↓ ↑	0.6			
d^{10}	↑↓ ↑↓ ↑↓	↑↓ ↑↓	0.0			

CFSEs are important for two reasons. First, the existence of CFSE nicely accounts for the difference between experimentally measured values for bond energies in metal complexes and values calculated based solely on electrostatic interactions. Second, CFSEs represent relatively large amounts of energy (up to several hundred kilojoules per mole), which has important chemical consequences.

> *Octahedral d^3 and d^8 complexes and low-spin d^6, d^5, d^7, and d^4 complexes exhibit large CFSEs.*

Summary

Crystal field theory, which assumes that metal–ligand interactions are only electrostatic in nature, explains many important properties of transition-metal complexes, including their colors, magnetism, structures, stability, and reactivity. Crystal field theory (CFT) is a bonding model that explains many properties of transition metals that cannot be explained using valence bond theory. In CFT, complex formation is assumed to be due to electrostatic interactions between a central metal ion and a set of negatively charged ligands or ligand dipoles arranged around the metal ion. Depending on the arrangement of the ligands, the d orbitals split into sets of orbitals with different energies. The difference between the energy levels in an octahedral complex is called the crystal field splitting energy (Δ_o), whose magnitude depends on the charge on the metal ion, the position of the metal in the periodic table, and the nature of the ligands. The spin-pairing energy (P) is the increase in energy that occurs when an electron is added to an already occupied orbital. A high-spin configuration occurs when the Δ_o is less than P, which produces complexes with the maximum number of unpaired electrons possible. Conversely, a low-spin configuration occurs when the Δ_o is greater than P, which produces complexes with the minimum number of unpaired electrons possible. Strong-field ligands interact strongly with the d orbitals of the metal ions and give a large Δ_o, whereas weak-field ligands interact more weakly and give a smaller Δ_o. The colors of transition-metal complexes depend on the environment of the metal ion and can be explained by CFT.

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9.9: Bonding in Non-Octahedral Complex Ions- Crystal Field Theory

Learning Objectives

- Understand the d-orbital degeneracies of square planar and tetrahedral metal complexes.

Tetragonal and Square Planar Complexes

If two *trans*- ligands in an octahedral complex are either chemically different from the other four (as in *trans*-$[Co(NH_3)_4Cl_2]^+$), or at a different distance from the metal than the other four, the result is a tetragonally distorted octahedral complex. The electronic structures of such complexes are best viewed as the result of distorting an octahedral complex. Consider, for example, an octahedral complex such as $[Co(NH_3)_6]^{3+}$: two *trans*- NH_3 molecules are slowly removed from the metal along the ±z axes, as shown in the top half of Figure **9.9.1**. As the two axial Co–N distances increase simultaneously, the d-orbitals that interact most strongly with the two axial ligands decrease in energy due to a decrease in electrostatic repulsions between the electrons in these orbitals and the negative ends of the ligand dipoles. The affected d orbitals are those with a component along the ±z axes—d_{z^2}, d_{xz}, and d_{yz}. These orbitals are not affected equally, however: because the d_{z^2} orbital points directly at the two ligands being removed, its energy will decrease much more rapidly than the degenerate energies of the d_{xz} and d_{yz}, as shown in the bottom half of Figure **9.9.1**. In addition, the effective positive charge on the metal increases somewhat as the axial ligands are removed, increasing the attraction between the four remaining ligands and the metal. This increases the extent of their interactions with the other two d orbitals and increases their energies. Again, the two d orbitals are not affected equally: because the $d_{x^2-y^2}$ orbital points directly at the four in-plane ligands, its energy increases to a greater extent than the energy of the d_{xy} orbital, which points between the in-plane ligands. If the two axial ligands are moved infinitely far away from the metal, a square planar complex is formed. The energy of the d_{xy} orbital actually surpasses that of the d_{z^2} orbital in the process. The largest orbital splitting in a square planar complex, between the $d_{x^2-y^2}$ and d_{xy} energy levels, is identical in magnitude to Δ_o.

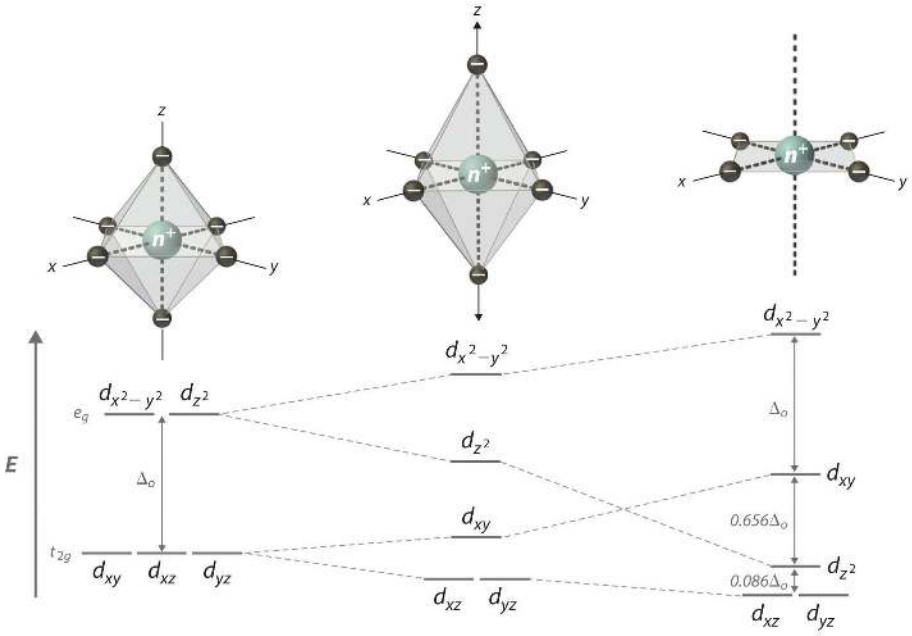


Figure **9.9.1** d-Orbital Splittings for Tetragonal and Square Planar Complexes. (CC BY-SA-NC; anonymous by request)

Moving the two axial ligands away from the metal ion along the z axis initially generates an elongated octahedral complex (the center compound of Figure **9.9.1**) and eventually produces a square planar complex (right). As shown below the structures, an axial elongation causes the d_{z^2} d_{xz} and d_{yz} orbitals to decrease in energy and the $d_{x^2-y^2}$ and d_{xy} orbitals to increase in energy. The change in energy is not the same for all five d orbitals. The d_{z^2} orbital has a smaller xy component than does the d_{xy} orbital, so it reaches a lower energy level; thus, the order of these orbitals is reversed.

Tetrahedral Complexes

In a tetrahedral arrangement of four ligands around a metal ion, none of the ligands lies on any of the three coordinate axes (illustrated in part (a) in Figure **9.9.2**); consequently, none of the five d orbitals points directly at the ligands. Nonetheless, the d_{xy}, d_{xz}, and d_{yz} orbitals interact more strongly with the ligands than do $d_{x^2-y^2}$ and d_{z^2}; this again results in a splitting of the five d orbitals into two groups. The splitting of the energies of the orbitals in a tetrahedral complex (Δ_t) is much smaller than that for an octahedral complex (Δ_o), however, for two reasons: first, the d orbitals interact less strongly with the ligands in a tetrahedral arrangement; second, there are only four negatively-charged regions rather than six, which decreases the electrostatic interactions by one-third if all other factors are equal. It can be shown that for complexes of the same metal ion with the same charge, the same ligands, and the same M–L distance, $\Delta_t = \frac{4}{9}\Delta_o$. The relationship between the splitting of the five d orbitals in octahedral and tetrahedral crystal fields imposed by the same ligands is shown schematically in part (b) in Figure **9.9.2**.

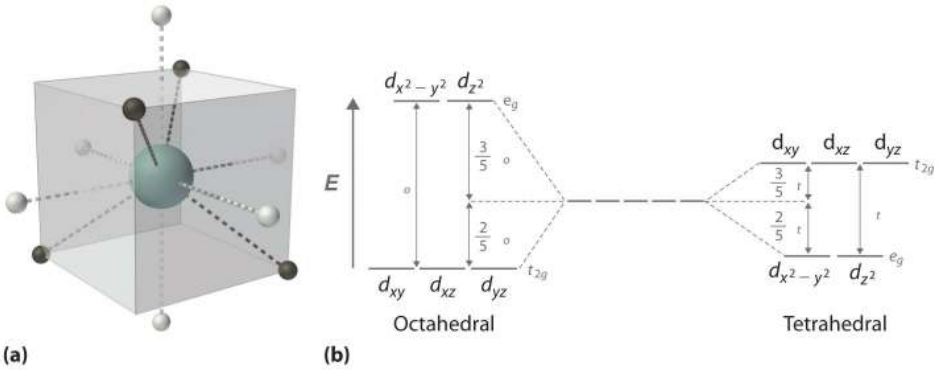


Figure **9.9.2**: d-Orbital Splittings for a Tetrahedral Complex. (a) In a tetrahedral complex, none of the five d orbitals points directly at or between the ligands. (b) Because the d_{xy}, d_{xz}, and d_{yz}orbitals (the t_{2g} orbitals) interact more strongly with the ligands than do the $d_{x^2-y^2}$ and d_{z^2} orbitals (the e_g orbitals), the order of orbital energies in a tetrahedral complex is the opposite of the order in an octahedral complex. (CC BY-SA-NC; anonymous by request)

> *$\Delta_t < \Delta_o$ because of weaker d-orbital–ligand interactions and decreased electrostatic interactions.*

Example 9.9.1: Predicting Structure

For each complex, predict its structure, whether it is high spin or low spin, and the number of unpaired electrons present.

1. $[Cu(NH_3)_4]^{2+}$
2. $[Ni(CN)_4]^{2-}$

Solution

Because Δ_o is so large for the second- and third-row transition metals, all four-coordinate complexes of these metals are square planar due to the much higher crystal field stabilization energy (CFSE) for square planar versus tetrahedral structures. The only exception is for d^{10} metal ions such as Cd^{2+}, which have zero CFSE and are therefore tetrahedral as predicted by the VSEPR model. Four-coordinate complexes of the first-row transition metals can be either square planar or tetrahedral; the former is favored by strong-field ligands, whereas the latter is favored by weak-field ligands. For example, the $[Ni(CN)_4]^{2-}$ ion is square planar, while the $[NiCl_4]^{2-}$ ion is tetrahedral.

1.

The copper in this complex is a d^9 ion and it has a coordination number of 4. So it is probably either square planar or tetrahedral. To estimate which, we need to fill in the CFT splitting diagrams for each with 9 electrons and ask which has a lower energy. Comparing the square planer (Figure **9.9.1**) splitting diagram with tetrahedral (Figure **9.9.2**), suggests that 9 electrons will have a net lower total energy for square planar (since the $d_{x^2-y^2}$ orbital is high in energy, the others are lower).

For the square planar structure, neither high nor low spin states are possible (only one state) with a single unpaired electron.

2.

The nickle in this complex is a d^8 ion and it has a coordination number of 4. So it is probably either square planar or tetrahedral. To estimate which, we need to fill in the CFT splitting diagrams for each with 8 electrons and ask which has a lower energy. Comparing the square planer (Figure **9.9.1**) splitting diagram with tetrahedral (Figure **9.9.2**), suggests that 8 electrons will have a net lower total energy for square planar (since the $d_{x^2-y^2}$ orbital is high in energy, the others are lower).

For the square planar structure, it is a low spin complex since a high spin requires a lot of energy to promote to the $d_{x^2-y^2}$ orbital. Hence, there are no unpaired electrons

? Exercise 9.9.1

What are the geometries of the following two complexes?

1. $[AlCl_4]^-$
2. $[Ag(NH_3)_2]^+$

Answer 1

tetrahedral

Answer 2

linear

Summary

Distorting an octahedral complex by moving opposite ligands away from the metal produces a tetragonal or square planar arrangement, in which interactions with equatorial ligands become stronger. Because none of the d orbitals points directly at the ligands in a tetrahedral complex, these complexes have smaller values of the crystal field splitting energy Δ_t. In tetrahedral molecular geometry, a central atom is located at the center of four substituents, which form the corners of a tetrahedron. Tetrahedral geometry is common for complexes where the metal has d^0 or d^{10} electron configuration. The CFT diagram for tetrahedral complexes has $d_{x^2-y^2}$ and d_{z^2} orbitals equally low in energy because they are between the ligand axis and experience little repulsion. In square planar molecular geometry, a central atom is surrounded by constituent atoms, which form the corners of a square on the same plane. The square planar geometry is prevalent for transition metal complexes with d^8 configuration. The CFT diagram for square planar complexes can be derived from octahedral complexes yet the $d_{x^2-y^2}$ level is the most destabilized and is left unfilled.

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9.10: Magnetic Behavior of Atoms, Molecules, and Materials

Learning Objectives

- To understand the difference between Ferromagnetism, paramagnetism and diamagnetism
- To identify if a chemical will be paramagnetic or diamagnetic when exposed to an external magnetic field

The magnetic moment of a system measures the strength and the direction of its magnetism. The term itself usually refers to the magnetic dipole moment. Anything that is magnetic, like a bar magnet or a loop of electric current, has a magnetic moment. A magnetic moment is a vector quantity, with a magnitude and a direction. An electron has an electron magnetic dipole moment, generated by the electron's intrinsic spin property, making it an electric charge in motion. There are many different magnetic behavior including paramagnetism, diamagnetism, and ferromagnetism.

An interesting characteristic of transition metals is their ability to form magnets. Metal complexes that have unpaired electrons are magnetic. Since the last electrons reside in the d orbitals, this magnetism must be due to having unpaired d electrons. The spin of a single electron is denoted by the quantum number m_s as +(1/2) or –(1/2). This spin is negated when the electron is paired with another, but creates a weak magnetic field when the electron is unpaired. More unpaired electrons increase the paramagnetic effects. The electron configuration of a transition metal (d-block) changes in a coordination compound; this is due to the repulsive forces between electrons in the ligands and electrons in the compound. Depending on the strength of the ligand, the compound may be paramagnetic or diamagnetic.

Ferromagnetism (Permanent Magnet)

Ferromagnetism is the basic mechanism by which certain materials (such as iron) form **permanent magnets**. This means the compound shows permanent magnetic properties rather than exhibiting them only in the presence of an external magnetic field (Figure 9.10.1). In a ferromagnetic element, electrons of atoms are grouped into domains in which each domain has the same charge. In the presence of a magnetic field, these domains line up so that charges are parallel throughout the entire compound. Whether a compound can be ferromagnetic or not depends on its number of unpaired electrons and on its atomic size.

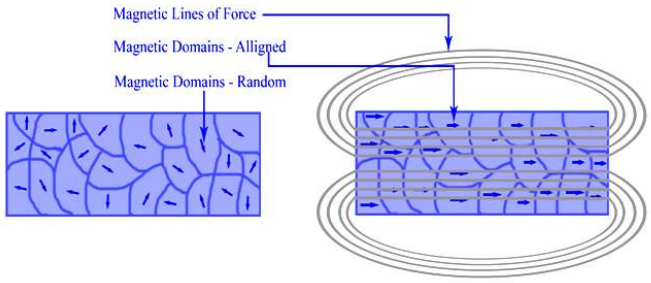


Figure 9.10.1: Ferromagnetism (a) nonmagnatized material and (2) Magnetized material with corresponding magnetic fields shown.

Ferromagnetism, the permanent magnetism associated with nickel, cobalt, and iron, is a common occurrence in everyday life. Examples of the knowledge and application of ferromagnetism include Aristotle's discussion in 625 BC, the use of the compass in 1187, and the modern-day refrigerator. Einstein demonstrated that electricity and magnetism are inextricably linked in his theory of special relativity.

Paramagnetism (Attracted to Magnetic Field)

Paramagnetism refers to the magnetic state of an atom with one or more unpaired electrons. The unpaired electrons are attracted by a magnetic field due to the electrons' magnetic dipole moments. Hund's Rule states that electrons must occupy every orbital singly before any orbital is doubly occupied. This may leave the atom with many unpaired electrons. Because unpaired electrons can spin in either direction, they display magnetic moments in any direction. This capability allows paramagnetic atoms to be attracted to magnetic fields. Diatomic oxygen, O_2 is a good example of paramagnetism (described via molecular orbital theory). The following video shows liquid oxygen attracted into a magnetic field created by a strong magnet:



Video 9.10.1: Paramagnetism of Liquid Oxygen

Diamagnetism (Repelled by Magnetic Field)

As shown in the video, molecular oxygen (O_2) is paramagnetic and is attracted to the magnet. In contrast, molecular nitrogen (N_2) has no unpaired electrons and is diamagnetic; it is unaffected by the magnet. Diamagnetic substances are characterized by paired electrons, e.g., no unpaired electrons. According to the Pauli Exclusion Principle which states that no two electrons may occupy the same quantum state at the same time, the electron spins are oriented in opposite directions. This causes the magnetic fields of the electrons to cancel out; thus there is no net magnetic moment, and the atom cannot be attracted into a magnetic field. In fact, diamagnetic substances are weakly ***repelled*** by a magnetic field as demonstrated with the pyrolytic carbon sheet in Figure 9.10.2.

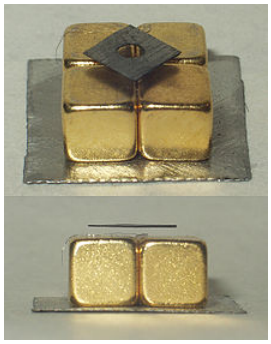


Figure 9.10.2: Levitating pyrolytic carbon: A small (~6 mm) piece of pyrolytic graphite levitating over a permanent neodymium magnet array (5 mm cubes on a piece of steel). Note that the poles of the magnets are aligned vertically and alternate (two with north facing up, and two with south facing up, diagonally). (Public Domain; Splarka via Wikipedia).

How to Tell if a Substance is Paramagnetic or Diamagnetic

The magnetic properties of a substance can be determined by examining its electron configuration: If it has unpaired electrons, then the substance is paramagnetic and if all electrons are paired, the substance is then diamagnetic. This process can be broken into three steps:

1. Write down the electron configuration
2. Draw the valence orbitals
3. Identify if unpaired electrons exist
4. Determine whether the substance is paramagnetic or diamagnetic

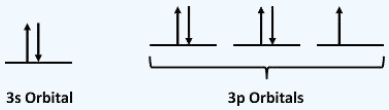
Example 9.10.1: Chlorine Atoms

Step 1: Find the electron configuration

For Cl atoms, the electron configuration is $3s^2 3p^5$

Step 2: Draw the valence orbitals

Ignore the core electrons and focus on the valence electrons only.



Step 3: Look for unpaired electrons

There is one unpaired electron.

Step 4: Determine whether the substance is paramagnetic or diamagnetic

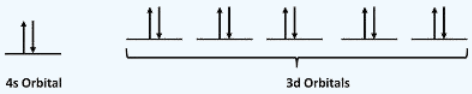
Since there is an unpaired electron, **Cl** atoms are paramagnetic (albeit, weakly).

Example 9.10.2: Zinc Atoms

Step 1: Find the electron configuration

For Zn atoms, the electron configuration is $4s^2 3d^{10}$

Step 2: Draw the valence orbitals



Step 3: Look for unpaired electrons

There are no unpaired electrons.

Step 4: Determine whether the substance is paramagnetic or diamagnetic

Because there are no unpaired electrons, **Zn** atoms are diamagnetic.

Exercise 9.10.1

a. How many unpaired electrons are found in oxygen atoms ?
b. How many unpaired electrons are found in bromine atoms?
c. Indicate whether boron atoms are paramagnetic or diamagnetic.
d. Indicate whether $\mathbf{F^-}$ ions are paramagnetic or diamagnetic.
e. Indicate whether $\mathbf{Fe^{2+}}$ ions are paramagnetic or diamagnetic.

Answer a

The O atom has $2s^2 2p^4$ as the electron configuration. Therefore, O has 2 unpaired electrons.

Answer b

The Br atom has $4s^2 3d^{10} 4p^5$ as the electron configuration. Therefore, Br has 1 unpaired electron.

Answer c

The B atom has $2s^2 2p^1$ as the electron configuration. Because it has one unpaired electron, it is paramagnetic.

Answer d

The $\mathbf{F^-}$ ion has $2s^2 2p^6$ as the electron configuration. Because it has no unpaired electrons, it is diamagnetic.

Answer e

The Fe^{2+} ion has $3d^6$ as the electron configuration. Because it has 4 unpaired electrons, it is paramagnetic.

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9.11: Magnetic Behavior of Complex Ions

Learning Objectives

- Discuss the correlation between the electronic structure of a coordination complex and its magnetic properties

Experimental evidence of magnetic measurements supports the theory of high- and low-spin complexes. Remember that molecules such as O_2 that contain unpaired electrons are paramagnetic. Paramagnetic substances are attracted to magnetic fields. Many transition metal complexes have unpaired electrons and hence are paramagnetic. Molecules such as N_2 and ions such as Na^+ and $[Fe(CN)_6]^{4-}$ that contain no unpaired electrons are **diamagnetic**. Diamagnetic substances have a slight tendency to be **repelled** by magnetic fields.

When an electron in an atom or ion is unpaired, the magnetic moment due to its spin makes the entire atom or ion **paramagnetic**. The size of the magnetic moment of a system containing unpaired electrons is related directly to the number of such electrons: the greater the number of unpaired electrons, the larger the magnetic moment. Magnetic susceptibility measures the force experienced by a substance in a magnetic field. When we compare the weight of a sample to the weight measured in a magnetic field (Figure 9.11.1), paramagnetic samples that are attracted to the magnet will appear heavier because of the force exerted by the magnetic field. We can calculate the number of unpaired electrons based on the increase in weight.

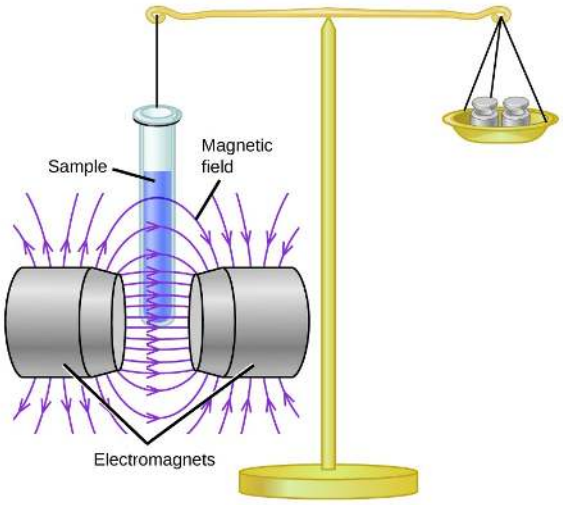


Figure 9.11.1: A Gouy balance compares the mass of a sample in the presence of a magnetic field with the mass with the electromagnet turned off to determine the number of unpaired electrons in a sample. (CC BY-SA 3.0; OpenStax).

From this experiment, the measured magnetic moment of low-spin d^6 $[Fe(CN)_6]4-$ ion confirms that iron is diamagnetic, whereas the high-spin d^6 $[Fe(H_2O)_6]^{2+}$ complex has four unpaired electrons with a magnetic moment that confirms this arrangement. Therefore, the observed magnetic moment is used to determine the number of unpaired electrons present.

Magnetic Properties of Coordination Compounds

An interesting characteristic of transition metals is their ability to form magnets. Metal complexes that have unpaired electrons are magnetic. Since the last electrons reside in the d orbitals, this magnetism must be due to having unpaired d electrons. Considering only monometallic complexes, unpaired electrons arise because the complex has an odd number of electrons or because electron pairing is destabilized. For example, the Ti(III) ion has one d electron and must be (weakly) paramagnetic, regardless of the geometry or the nature of the ligands. However, the Ti(II) ion with two d-electrons, sometimes forms complexes with two unpaired electrons and sometimes forms complexes with no unpaired electrons.

As an example, Fe prefers to exist as Fe^{3+} and is known to have a coordination number of six. Since the configuration of Fe^{3+} has five d electrons, we would expect to see five unpaired spins in complexes with Fe. This is true for $[FeF_6]^{3-}$; however, $[Fe(CN)_6]^{3-}$ only has one unpaired electron, making it a weaker magnet. This trend can be explained based on the properties of the ligands.

Based off the spectrochemical series, we expect CN^- ligands to have a stronger electric field than that of F^- ligands, so the energy differences in the d-orbitals should be greater for the cyanide complex.

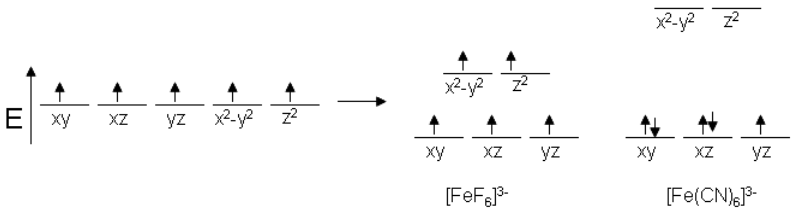


Figure **9.11.2**: Crystal field theory splitting diagram. Example of influence of ligand electronic properties on d orbital splitting. This shows the comparison of low-spin versus high-spin electrons.

For this to make sense, there must be some sort of energy benefit to having paired spins for our cyanide complex (the spin pairing energy). That is, the energy level difference must be more than the repulsive energy of pairing electrons together. Since systems strive to achieve the lowest energy possible, the electrons will pair up before they will move to the higher orbitals. This is referred to as low spin, and an electron moving up before pairing is known as high spin.

Exercise 9.11.1

Which ligand is most likely to form a high-spin complexes when bound to transition metals: **en**, F^- , or CN^-?

Answer

F^- are more likely to form high spin complexes, since is a weak-field ligand on the spectrochemical series.

Tetrahedral complexes have naturally weaker splitting because none of the ligands lie within the plane of the orbitals. As a result, they have either have too many or too few d electrons to warrant consideration about high or low spin configurations. Square planar compounds, on the other hand, stem solely from transition metals with eight d electrons. For example, $[Ni(CN)_4]^{2-}$, $[Pt(NH_3)_3Cl]^+$, and $[PtCl_4]^{2-}$ are all diamagnetic. Since this encompasses the full spectrum of ligand strength, we can conclude that square planar compounds are always low spin and therefore are weakly magnetic.

Example 9.11.2

Which one of the following coordination compounds would you expect to be paramagnetic?

a. $[Zn(NH_3)_4]Cl_2$
b. $K[FeCl_4]$ (low spin, tetrahedral)
c. $[Cd(H_2O)_6]SO_4$

Solution

Let's consider each compound individually. Since each compound has only one complex ion, we only need to consider how the d electrons are distributed in the ligand field of that ion. We can ignore the other parts (the counter ions) of the compound.

a. The zinc ion in $[Zn(NH_3)_4]Cl_2$ has a +2 oxidation state, so it is a d^{10} ion since the zinc atom loses two 4s electrons and no 3d electrons to form the ion. We do not need to fill ion the electrons in the corresponding tetrahedral d-orbital diagram, since we know they will all be paired up. This is a diamagnetic compound.
b. The iron ion in $K[FeCl_4]$ (low spin, tetrahedral) has a 3+ oxidation state so it is a d^5 ion since the iron atom loses two 4s electrons and one 3d electron. Adding 5 electrons to the tetrahedral d-orbital diagram identifies that one electron will be unpaired. This compound will be paramagnetic (but weakly since only on electron is unpaired).
c. The cadmium ion in $[Cd(H_2O)_6]SO_4$ has a +2 oxidation state, so it is a d^{10} ion since the cadmium atom loses two 5s electrons and no 4d electrons to form the ion. We do not need to fill ion the electrons in the corresponding octahedral d-orbital diagram, since we know they will all be paired up. This is a diamagnetic compound.

Exercise 9.11.2

Predict the number of unpaired electrons for each of the following complex ions

a. $[Fe(CN)_6]^{4-}$
b. $[Ru(NH_3)_6]^{3+}$
c. $[Cr(NH_3)_6]^{2+}$
d. $[EuCl_6]^{4-}$

Answer a

Fe^{2+} is $3d^6$ ion and has 0 unpaired electron in low spin complexes

Answer b

Ru^{3+} is $4d^5$ ion and has 1 unpaired electron in low spin complexes

Answer c

Cr^{2+} is $4d^4$ ion and has 4 and 2 unpaired electrons in high spin and low spin complexes, respectively, depending on spin pairing energy

Answer d

Eu^{2+} is $4f^7$ ion and has 7 unpaired electrons in high spin complexes

In bi- and polymetallic complexes, in which the individual centers have an odd number of electrons or electrons are high-spin, the situation is more complicated. If there is interaction between the two (or more) metal centers, the electrons may couple, resulting in a weak magnet, or they may enhance each other. When there is no interaction, the two (or more) individual metal centers behave as if in two separate molecules.

Summary

- Unpaired electrons exist when the complex has an odd number of electrons or because electron pairing is destabilized.
- The more unpaired electrons, the stronger the magnetic property.
- Tetrahedral complexes have weaker splitting because none of the ligands lie within the plane of the orbitals.
- Square planar compounds are always low-spin and therefore are weakly magnetic.
- In bi- and polymetallic complexes, the electrons may couple through the ligands, resulting in a weak magnet, or they may enhance each other.

Contributors and Attributions

- Source: Boundless. "Magnetic Properties." *Boundless Chemistry* Boundless, 26 May. 2016. Retrieved 4 May. 2017 from www.boundless.com/chemistry/...ties-616-6882/.

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9.12: Optical Properties of Coordination Compounds (Color)

The human eye perceives a mixture of all the colors, in the proportions present in sunlight, as white light. Complementary colors, those located across from each other on a color wheel, are also used in color vision. The eye perceives a mixture of two complementary colors, in the proper proportions, as white light. Likewise, when a color is missing from white light, the eye sees its complement. For example, when red photons are absorbed from white light, the eyes see the color green. When violet photons are removed from white light, the eyes see lemon yellow (Figure **9.12.1**).

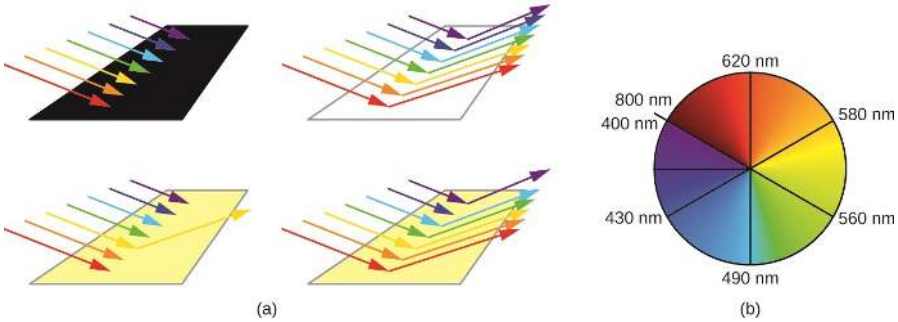


Figure **9.12.1**: (a) An object is black if it absorbs all colors of light. If it reflects all colors of light, it is white. An object has a color if it absorbs all colors except one, such as this yellow strip. The strip also appears yellow if it absorbs the complementary color from white light (in this case, indigo). (b) Complementary colors are located directly across from one another on the color wheel. (CC BY 4.0; OpenStax)

The blue color of the $\mathbf{[Cu(NH_3)_4]^{2+}}$ ion results because this ion absorbs orange and red light, leaving the complementary colors of blue and green (Figure **9.12.2**). If white light (ordinary sunlight, for example) passes through $\mathbf{[Cu(NH_3)_4]SO_4}$ solution, some wavelengths in the light are absorbed by the solution. The $\mathbf{[Cu(NH_3)_4]^{2+}}$ ions in solution absorb light in the red region of the spectrum. The light which passes through the solution and out the other side will have all the colors in it except for the red. We see this mixture of wavelengths as pale blue (cyan). The diagram gives an impression of what happens if you pass white light through a $\mathbf{[Cu(NH_3)_4]SO_4}$ solution.

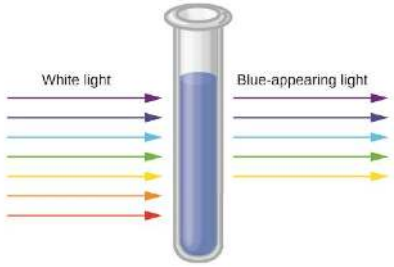


Figure **9.12.2**: A solution of $[Cu(NH_3)_4]^{2+}$ ions absorbs red and orange light, so the transmitted light appears as the complementary color, blue. (CC BY 4.0; OpenStax)

Working out what color you will see is not easy if you try to do it by imagining "mixing up" the remaining colors. You would not have thought that all the other colors apart from some red would look cyan, for example. Sometimes what you actually see is quite unexpected. Mixing different wavelengths of light doesn't give you the same result as mixing paints or other pigments. You can, however, sometimes get some estimate of the color you would see using the idea of complementary colors.

Recall that the color we observe when we look at an object or a compound is due to light that is transmitted or reflected, not light that is absorbed, and that reflected or transmitted light is complementary in color to the light that is absorbed. Thus a green compound absorbs light in the red portion of the visible spectrum and vice versa, as indicated by the complementary color wheel.



Figure **9.12.3**: The partially filled d orbitals of the stable ions $Cr^{3+}(aq)$, $Fe^{3+}(aq)$, and $Co^{2+}(aq)$ (left, center and right, respectively) give rise to various colors. (credit: Sahar Atwa)

The striking colors exhibited by transition-metal complexes are caused by excitation of an electron from a lower-energy d orbital to a higher-energy d orbital, which is called a **d–d transition** (Figure **9.12.4**). For a photon to effect such a transition, its energy must be equal to the difference in energy between the two d orbitals, which depends on the magnitude of Δ_o.

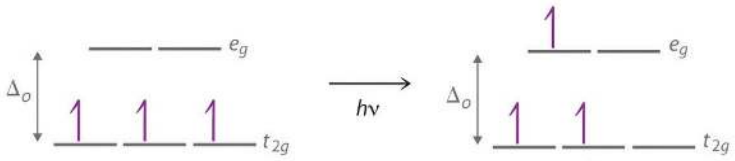


Figure **9.12.4**: In a d–d transition of an octahedral complex, an electron in one of the t_{2g} orbitals of an octahedral complex such as the $[Cr(H_2O)_6]^{3+}$ ion absorbs a photon of light with energy equal to Δ_o, which causes the electron to move to an empty or singly occupied e_g orbital.

Example 9.12.1: Colors of Complexes

The octahedral complex $[Ti(H_2O)_6]^{3+}$ has a single *d* electron. To excite this electron from the ground state t_{2g} orbital to the e_g orbital, this complex absorbs light from 450 to 600 nm. The maximum absorbance corresponds to Δ_o and occurs at 499 nm. Calculate the value of Δ_o in Joules and predict what color the solution will appear.

Solution

We can convert wavelength to frequency:

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

$$= \frac{3.00 \times 10^8\, m/s}{(499\ \cancel{nm}) \times \left(\frac{1\, m}{10^9\ \cancel{nm}}\right)}$$

$$= 6.01 \times 10^{14} s^{-1} = 6.01 \times 10^{14}\, Hz$$

And then using Planck's equation that related the frequency of light to energy

$$E = h\nu$$

so

$$E = (6.63 \times 10^{-34} \text{J·s}) \times (6.01 \times 10^{14}\, Hz)$$

$$= 3.99 \times 10^{-19}\, J$$

Because the complex absorbs 600 nm (orange) through 450 (blue), the indigo, violet, and red wavelengths will be transmitted, and the complex will appear purple.

Note: This is the energy for one transition (i.e., in one complex). If you want to calculate the energy in J/mol, then you have to multiply this by Avogadro's number (N_A).

Exercise 9.12.1

A complex that appears green, absorbs photons of what wavelengths?

Answer

red, 620–800 nm

Color Depends on Oxidation State

Small changes in the relative energies of the orbitals that electrons are transitioning between can lead to drastic shifts in the color of light absorbed. Therefore, the colors of coordination compounds depend on many factors. As shown in Figure **9.12.4**, different aqueous metal ions can have different colors. In addition, different oxidation states of one metal can produce different colors, as shown for the vanadium complexes in the link below.



Watch this video of the reduction of vanadium complexes to observe the colorful effect of changing oxidation states.

Color Depends on Ligand Field

The specific ligands coordinated to the metal center also influence the color of coordination complexes. Because the energy of a photon of light is inversely proportional to its wavelength, the color of a complex depends on the magnitude of Δ_o, which depends on the structure of the complex. For example, the complex $[Cr(NH_3)_6]^{3+}$ has strong-field ligands and a relatively large Δ_o. Consequently, it absorbs relatively high-energy photons, corresponding to blue-violet light, which gives it a yellow color. A related complex with weak-field ligands, the $[Cr(H_2O)_6]^{3+}$ ion, absorbs lower-energy photons corresponding to the yellow-green portion of the visible spectrum, giving it a deep violet color. For example, the iron(II) complex $[Fe(H_2O)_6]SO_4$ appears blue-green because the high-spin complex absorbs photons in the red wavelengths (Figure **9.12.5**). In contrast, the low-spin iron(II) complex $K_4[Fe(CN)_6]$ appears pale yellow because it absorbs higher-energy violet photons.



Figure **9.12.5**: Both (a) hexaaquairon(II) sulfate and (b) potassium hexacyanoferrate(II) contain d^6 iron(II) octahedral metal centers, but they absorb photons in different ranges of the visible spectrum. (CC BY 4.0; OpenStax)

In general, strong-field ligands cause a large split in the energies of *d* orbitals of the central metal atom (large Δ_{oct}). Transition metal coordination compounds with these ligands are yellow, orange, or red because they absorb higher-energy violet or blue light. On the other hand, coordination compounds of transition metals with weak-field ligands are often blue-green, blue, or indigo because they absorb lower-energy yellow, orange, or red light.

> *Strong-field ligands cause a large split in the energies of d orbitals of the central metal atom and transition metal coordination compounds with these ligands are typically yellow, orange, or red because they absorb higher-energy violet or blue light. Coordination compounds of transition metals with weak-field ligands are often blue-green, blue, or indigo because they absorb lower-energy yellow, orange, or red light.*

Example **9.12.2**: Matching Colors to Ligand Fields

Identify the color (either blue, green, yellow, or orange) for the following complex ions formed with Co^{3+}:

a. $[Co(CN)_6]^{-2}_3$

b. $[Co(NH_3)_6]^{3+}_3$
c. $[CoF_6]^{-4}_3$
d. $[Co(H_2O)_6]^{3+}$

Solution

Each of these complex ions has the same metal with the same oxidation state, so the ligand field is the relevant factors. Each of the complex ions also has an octahedral ligand field, so we only need to compare the strength of the ligands in determining Δ_o, which is determined by the spectrochemical series.

The ligands for each complex ions are: (a) CN^-, (b) NH_3, (c) F^- and (d) H_2O, which are ranked in increasing Δ_o magnitude:

$$F^- < H_2O < NH_3 < CN^- \tag{9.12.1}$$

The relationship between the Δ_o and the energy of the photons are absorbed in the d-d transition of Co^{3+} is given by equating Planck's equation to the crystal field splitting parameter:

$$E = h\nu = \frac{hc}{\lambda} = \Delta_o \tag{9.12.2}$$

Now, we need to get a relative correlation between observed color (to the eye) and the wavelength of the light that is absorbed. From the complementary color wheel in Figure **9.12.1** we get the following relationships (arranged from highest energy absorbed to lowest):

- 400-nm Violet light absorbed → Green-yellow observed
- 430-nm Blue light absorbed → Orange observed
- 450-nm Blue light absorbed → Yellow observed
- 490-nm Blue-green light absorbed → Red observed
- 570-nm Yellow-green light absorbed → Violet observed
- 580-nm Yellow light absorbed → Dark blue observed
- 600-nm Orange light absorbed → Blue observed
- 650-nm Red light absorbed → Green observed

Of the four possible colors given in the problem (blue, green, yellow, and orange), the corresponding colors that are absorbed are (600 nm, 650 nm, 450 nm, and 430, respectively). From Equation 9.12.2, the smaller λ of absorbed light corresponds to the higher energy photons, so we would correlate the four wavelengths of absorbing photons in terms of increasing energy to observed color:

$$\underbrace{650\,nm}_{green} < \underbrace{600\,nm}_{blue} < \underbrace{450\,nm}_{yellow} < \underbrace{430\,nm}_{orange} \tag{9.12.3}$$

Now, just correlate the ranking in Equation 9.12.3 to the ranking in Equation 9.12.1:

$$\underbrace{F^-}_{green} < \underbrace{H_2O}_{blue} < \underbrace{NH_3}_{yellow} < \underbrace{CN^-}_{orange}$$

and more specifically in terms of the original question

$$\underbrace{[CoF_6]^{-4}_3}_{green} < \underbrace{[Co(H_2O)_6]^{3+}}_{blue} < \underbrace{[Co(NH_3)_6]^{3+}_3}_{yellow} < \underbrace{[Co(CN)_6]^{-2}_3}_{orange}$$

? Exercise 9.12.1

If a complex ion $[M(NH_3)_6]^{2+}$ is red in solution, which of the following ligands, after a ligand exchange reaction to substitute for the ammine ligands, may shift the solution to be orange? More than one answer is possible.

$$Cl^-, CN^-, CO, F^- H_2O, I^-, en, NO_2^-, OH^-, SCN^-$$

Answer

Shifting from red to orange is an increase in Δ_o, so those ligands that are stronger field ligands than NH_3 in the list (deterimined via the spectrochemical series) are CN^-, CO, en, and NO_2^-.

A coordination compound of the Cu^+ ion has a d^{10} configuration, and all the e_g orbitals are filled. To excite an electron to a higher level, such as the 4*p* orbital, photons of very high energy are necessary. This energy corresponds to very short wavelengths in the ultraviolet region of the spectrum. No visible light is absorbed, so the eye sees no change, and the compound appears white or colorless. A solution containing $[Cu(CN)_2]^-$, for example, is colorless. On the other hand, octahedral Cu^{2+} complexes have a vacancy in the e_g orbitals, and electrons can be excited to this level. The wavelength (energy) of the light absorbed corresponds to the visible part of the spectrum, and Cu^{2+} complexes are almost always colored—blue,

blue-green violet, or yellow (Figure **9.12.6**). Although CFT successfully describes many properties of coordination complexes, molecular orbital explanations (beyond the introductory scope provided here) are required to understand fully the behavior of coordination complexes.



Figure **9.12.6**: (a) Copper(I) complexes with d^{10} configurations such as CuI tend to be colorless, whereas (b) d^9 copper(II) complexes such as $Cu(NO_3)_2{\cdot}5H_2O$ are brightly colored. (CC BY 4.0; OpenStax)

Gems

A ruby is a pink to blood-red colored gemstone that consist of trace amounts of chromium in the mineral corundum $\boldsymbol{Al_2O_3}$. In contrast, emeralds are colored green by trace amounts of chromium within a $Be_3Al_2Si_6O_{18}$ matrix. We can now understand why emeralds and rubies have such different colors, even though both contain Cr^{3+} in an octahedral environment provided by six oxide ions. Although the chemical identity of the six ligands is the same in both cases, the Cr–O distances are different because the compositions of the host lattices are different (Al_2O_3 in rubies and $Be_3Al_2Si_6O_{18}$ in emeralds). In ruby, the Cr–O distances are relatively short because of the constraints of the host lattice, which increases the d orbital–ligand interactions and makes Δ_o relatively large. Consequently, rubies absorb green light and the transmitted or reflected light is red, which gives the gem its characteristic color. In emerald, the Cr–O distances are longer due to relatively large $[Si_6O_{18}]^{12-}$ silicate rings; this results in decreased d orbital–ligand interactions and a smaller Δ_o. Consequently, emeralds absorb light of a longer wavelength (red), which gives the gem its characteristic green color. It is clear that the environment of the transition-metal ion, which is determined by the host lattice, dramatically affects the spectroscopic properties of a metal ion.



Gem-quality crystals of ruby and emerald. The colors of both minerals are due to the presence of small amounts of Cr^{3+} impurities in octahedral sites in an otherwise colorless metal oxide lattice.

The absorbance spectrum of a ruby is shown Figure **9.12.7;**. The number and positions of the peaks in the spectrum is determined by the electronic structure of the compound, which in this case depends upon the identity of the metal and the identities, number, and geometry of the surrounding ions. Crystal field theory may be used to predict the electronic structure and thus the absorbance spectrum. If white light is shown on the gem, the absorbance spectrum indicates which wavelengths of light are removed. In this case, there are strong bands centered at 414 and 561 nm. These wavelengths correspond with blue and yellow-green light, respectively. For the most part, these colors are not present in the light reaching ones eyes. An alternative way to express this concept is to recognize that the spectrum of light reaching the eye is the product of the spectrum of the incident light (white light) and the **transmittance spectrum**. For this ruby, the transmittance spectrum has a peak at 481 nm and a broad plateau past 620 nm. (Note that there is significant attenuation of the light across the entire spectrum.) Thus only light with wavelengths near 481 nm (cyan) and greater than 620 nm (red) reach the eye.

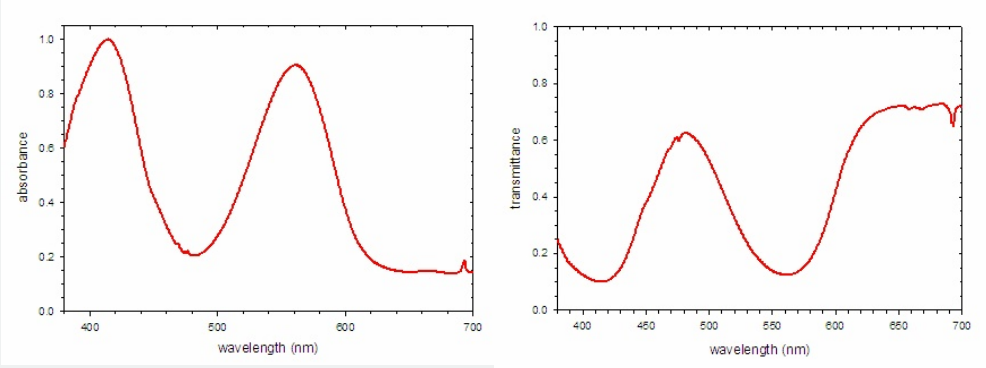
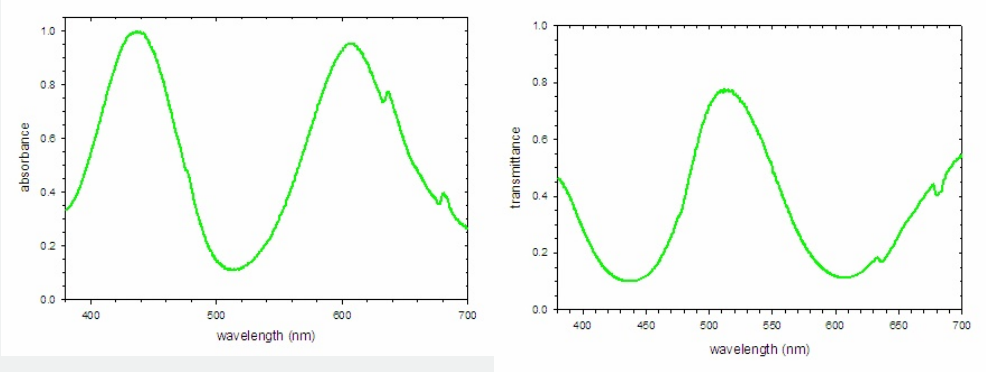


Figure **9.12.7**: (left) Absorbance spectrum of a ruby from Chanthaburi, Thailand. (right) corresponding Transmittance spectrum of a ruby from Chanthaburi, Thailand. Data obtained from the Caltech Mineral Spectroscopy Server

A similar analysis of the spectrum of an emerald is possible. The absorbance spectrum (Figure **9.12.8**;) shows strong bands at 438 and 606 nm, which remove blue and orange light, respectively. The light that is not absorbed is shown by the transmittance spectrum, which indicates the dominant band of light reaching the eye is centered at 512 nm (green light) with smaller contributions from the far blue and red portions of the spectrum. This combination of wavelengths produces a deep green color.



(left) Absorbance spectrum of an emerald from Malyshevo, Ural, Russia. (right) Corresponding transmittance spectrum of the emerald from Malyshevo, Ural, Russia. Data obtained from the Caltech Mineral Spectroscopy Server

Summary

When atoms or molecules absorb light at the proper frequency, their electrons are excited to higher-energy orbitals. For many main group atoms and molecules, the absorbed photons are in the ultraviolet range of the electromagnetic spectrum, which cannot be detected by the human eye. For coordination compounds, the energy difference between the *d* orbitals often allows photons in the visible range to be absorbed.

Contributors and Attributions

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- Prof. David Blauch (Davidson College)

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CHAPTER OVERVIEW

10: Bioinorganic Chemistry

Introduction to Bioinorganic Chemistry

What is bioinorganic chemistry? To answer this question, we should probably define what the other fields of chemistry are first...

You probably know that "**biochemistry**" is the study of the chemistry of biology - or life. The term "**organic chemistry**" literally means the *chemistry of life*. Organic chemistry is the study of carbon-based molecules because the first molecules that were isolated from living organisms contained carbon. On the other hand, the first minerals and other non-living things seemed to be made of other elements. For quite some time scientists naively assumed that all living things were made of carbon-based molecules, while non-living things did not contain carbon. "Organic chemistry" was the study of the carbon-based molecules of life, while "**inorganic chemistry**" was the study of "non-living" and "non-carbon" molecules.

Do these these historic definitions still hold true? To answer that question, let's look at one of the most important reactions in *your* life, shown below.

$$O_2 + 4e^- + 4H^+ \rightleftharpoons H_2O \tag{10.1}$$

Is this reaction *carbon-based*? Is it *living*? Well, take a deep breath! When you breath, you inhale mostly nitrogen gas (N_2), but also some oxygen gas (O_2). The oxygen gas that you inhale is critical for energy production in every one of your cells. During aerobic metabolism, O_2 accepts 4 electrons and 4 hydrogen ions to become two molecules of water. This reaction provides the driving force for phosphorylation of ATP that is required to fuel countless other essential reactions that keep you alive. This reaction is responsible for all aerobic life. And, it's *inorganic*! This simple example shows how the historic names of organic and inorganic chemistry should not be taken literally.

There are additional inorganic components required for this reaction too! For example, most of the proteins of the electron transport chain (the proteins that catalyze reduction of oxygen in the mitochondria of your cells) require metal cofactors and metal active sites. Please watch the video below to see some examples. Articles about the individual proteins from the video are provided below.



Links to articles about proteins discussed in this video:

- Cytochrome C Oxidase
- Ribozyme (has not been written yet!)
- Hemocyanin (has not been written yet!)
- Urease (has not been written yet!)

Sources

1. Franz, Katherine J., The Periodic Table of Life, Core Concepts in Chemistry, a free course on iTunes U from Duke University.

10.1: A Molecular Depot- Human Serum Albumin Carries Essential Cu and Zn in Serum
10.2: Iron acquisition in bacteria- Siderophores
10.3: Fe Wars- Lactoferrin
10.4: Iron Storage- Ferritin
10.5: Antioxidant- Cu/Zn Superoxide dismutase (SOD1)
10.6: Keep Cu Safe- Intracellular Copper Chaperones
10.7: Cytochrome C
10.8: Cytochrome Oxidase
10.9: Potassium Channels
10.10: Chemotherapy- Pt anticancer agents

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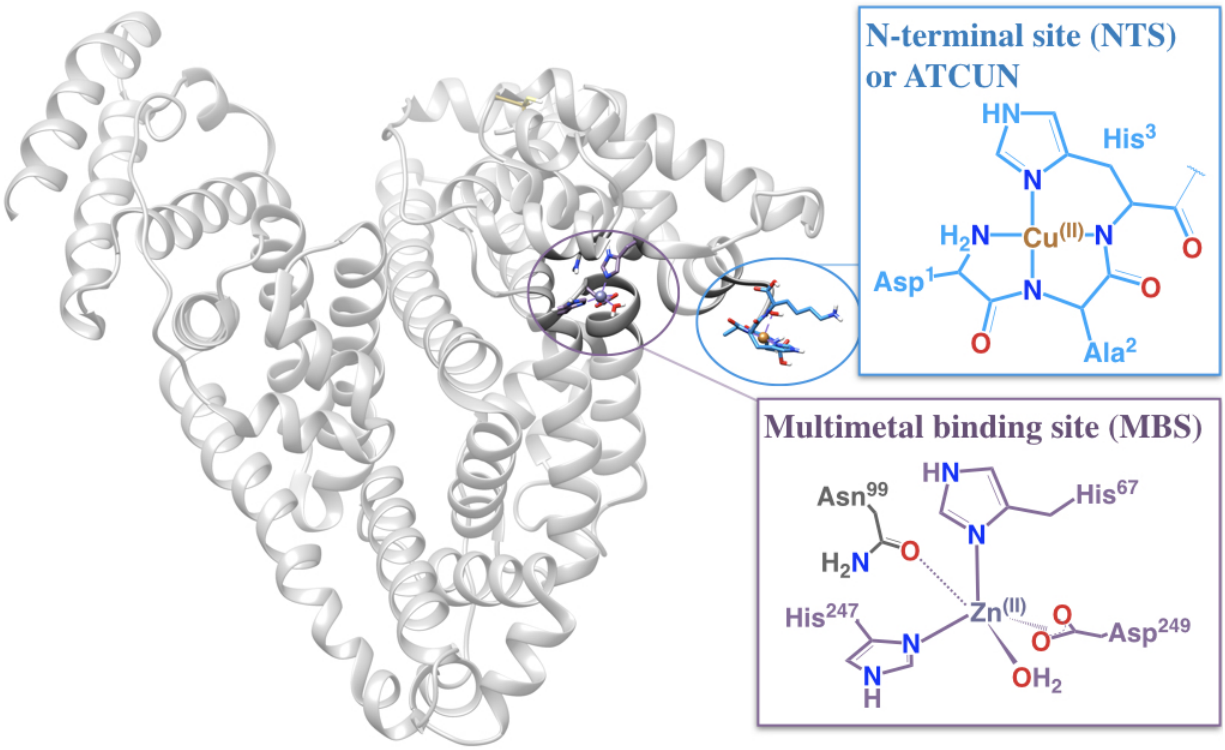
10.1: A Molecular Depot- Human Serum Albumin Carries Essential Cu and Zn in Serum

Human Serum Albumin

Human serum albumin (HSA) is a 66.5 kD protein found in human blood plasma and cerebrospinal fluid. In fact, it is the most abundant protein in human blood, constituting over half of plasma protein with a concentration of 0.6 mM under normal physiological conditions.[1]

HSA is a heart-shaped molecule comprised of three homologous domains (referred to as I, II, and III). Each domain contains two helical subdomains (referred to as A and B) connected by a random coil.[2] The structural arrangement of HSA engenders it's extraordinary ligand binding capacity. Various classes of ligands, including fatty acids (ie. myristate), drugs (ie. ibuprofen or warfarin), hormones (ie. thyroxine), and metal ions are bound and transported by albumin.[3-5] Thus, HSA is commonly referred to as a "molecular depot."

Metal binding to HSA has been extensively explored in various contexts. For example, HSA is an important transporter of essential metal ions, like Cu(II) and Zn(II), but it can also bind toxic metals, such as Ni(II) and Cd(II). Furthermore, HSA-metal binding has been exploited in the development of anticancer drugs due to its ability to bind soft Pt(IV) and Au(I).[6] For a comprehensive review of metal ion interactions with HSA, see reference 6. In this lesson, we will focus on only the interactions between HSA and two metals which are key components in many biological processes: copper and zinc (see figure below).



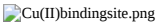
This is a ribbon diagram of human serum albumin with both Cu(II) and Zn(II) bound in their high-affinity binding sites. This structure was created by merging the protein crystal structure of HSA bound to Zn(II) at pH 9.0 (PDB 5IJF) and the small molecule crystal structure of the DAKH model peptide bound to Cu(II) (CCDC-809109). You can print or download a 3D model of this image on the Bioinorganic 3D Shapeways workshop.

Copper

Copper is an essential metal ion involved in a variety of metabolic processes, including mitochondrial respiration, melanin synthesis, cross-linking of collagen, quenching of reactive oxygen species, neurotransmitter development, and more.[7] Its utility in these various systems is oftentimes attributed to its unique ability to cycle between the Cu(I) and Cu(II) oxidation states. Thus, it can act as an electron donor or acceptor as redox cycling occurs.

As copper is absorbed by our digestive system, it enters the bloodstream bound by copper carrying proteins such as ceruloplasmin or HSA. The majority of serum copper (70-95%) is bound to ceruloplasmin; however, this copper is not readily exchangeable. HSA, on the other hand, is capable of exchanging copper with cellular copper acquisition proteins, such as the human copper transporter, Ctr1. Once the exchange occurs, Ctr1 can transport Cu(I) across the plasma membrane, for its involvement in intracellular metabolic processes, like the ones mentioned above.

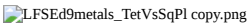
Cu(II) binding to HSA involves the well-characterized ATCUN (amino terminal copper and nickel) binding site, made up of its first three amino acids, Asp-Ala-His. (Figure below) Characteristic of this site are four donor atoms coming from a free -NH_2 terminus, a Histidine in the third position (XXH), and two contributing peptide backbone nitrogens. In aqueous environments, the far coordination sphere also includes an axial water molecule as a fifth ligand, which is oftentimes ignored due to its lability and rather long distance from the Cu center. This water molecule is usually undetectable by spectroscopic techniques other than crystallography. The multidentate characteristic of this binding site contributes to highly stable complexes with Cu(II).



The HSA's Cu(II) binding "ATCUN" site from crystal structure CCDC-809109: Made of the first three amino acids DAH, this site coordinates Cu(II) and Ni(II) in a square-planar 4-N coordination geometry. Axial coordination of a labile H_2O molecule is shown, however is often not considered as part of the stable coordination geometry.

According to Ligand Field Theory (LFT), all of the backbone nitrogen donor atoms at the Cu(II) binding site are classified as sigma donors, which means they are capable of sigma bonding with the metal. The N-terminal amine, and backbone amides are also pi donors, which means they are capable of forming pi bonds with the metal. Pi donors are weak field ligands and favor small Δ. The deporotonated amides are especially strong bases that stabilize the bonding interaction despite that they are weak field ligands. The imidazole nitrogen is both a sigma donor and a pi acceptor, due to its double bonded pi system. This means that the imidazole donor is capable of accepting electrons from the metal ion into its pi* orbitals. Pi-acceptors are strong field ligands and favor large Δ. Therefore, the ATCUN site contains both pi-donor that are strong bases and a pi-acceptor. The presence of both types of ligands helps in making this complex more stable.

LFT predicts that the N-ligands are coordinated around the Cu(II) center with square planar geometry. With four ligands (ignoring the axial H_2O), geometry is typically square planar or tetrahedral. A d^9 metal, like Cu(II) prefers square planar arrangements due to LFSE. A comparison of tetrahedral and square planar splitting diagrams for d^9 metals is shown below.

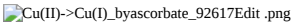


Comparison of LFSE for d^9 metals with 4 coordinating ligands. In the case of d^9, the square planar arrangement, with a more negative LFSE is more energetically favorable.

Shown above is a comparison of the d-orbital splitting diagrams of two possible geometries for 4 donor groups around a metal center, as we see in the ATCUN site of HSA. From LFSE calculations, it is clear that in this case, the square planar arrangement is more energetically favorable. (LFSE calculations are shown with an energy scale relative to Δ_o.) Because Cu(II) is a d^9 metal and will always have one unpaired electron, it does not have distinct high or low spin states. However, it should be noted that all square planar complexes favor low spin, because of the large Δ that is a consequence of square planar geometry.

In the presence of ascorbate, a biological reductant, HSA can facilitate Cu reduction from Cu(II)-->Cu(I) oxidation state (Figure below). The precise location of HSA's Cu(I) binding site is currently unknown, but details of its coordination environment have been elucidated through X-ray absorption spectroscopy.[15] This protein's bidentate Cu(I) binding site is comprised of two Histidine residues, oriented 180° apart approximately 1.89 Å from the Cu center. Although two-coordinate geometry are not usually observed for other first-row transition metal ions, it a common geometry observed when Cu(I) is bound to polypeptides. Since Cu(I) is a d^{10}

metal with no LFSE, it can be oriented in any coordination geometry. Because Cu(I) has a relatively low charge, two ligands can apparently be enough to satisfy it electrostatically.



Reduction of Cu(II) bound to HSA: Scheme of Cu(II) reduction to Cu(I) in the presence of electron donor, Vitamin C (ascorbic acid or ascorbate). The Cu(II) complex at the NTS has Jahn-Teller distorted square planar geometry, and the Cu(I) complex has linear geometry. The Cu(II) complex has a measurable d-d transition, while the Cu(I) complex does not.

In the reaction shown in the figure above, Cu(II) gains an electron via the weak reducing agent, Vitamin C. UV-vis spectroscopic techniques are oftentimes employed to monitor Cu(II)-->Cu(I) reduction such as this. This is possible because as a d^9 metal, Cu(II) has a d-d transition which absorbs radiation in the UV-vis range. This transition yields a measurable signal. Cu(I), on the other hand, does not have any d-d transitions because all d orbitals are filled, and it is therefore spectroscopically silent. During experimentation, Cu(I) presence is measured by the disappearance of a signal given by Cu(II)'s d-d transitions.

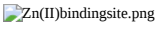
In terms of kinetics, Cu(II) exchanges ligands faster than Cu(I), but Cu(I) is still labile. Both oxidation states allow for little or no LFSE, and both oxidation states have d electrons occupying antibonding molecular orbitals. Both of these factors contribute to increased ligand exchange rate.

Zinc

Zinc is the second-most abundant transition metal in living systems (iron is the most abundant but does not bind significantly to HSA; rather Fe binds tightly to transferrin in serum).[11] Because Zn(II) is effectively a Lewis acid, it serves as a cofactor in many enzymatic reactions. For example, Zn(II) is found at the active site of carbonic anhydrase, which regulates CO_2 balance in blood and other tissues.[12] Moreover, Zn(II) provides structure to some proteins, as in the case of "zinc fingers." Zinc fingers are part of transcription factors, which recognize and bind a specific DNA sequence during DNA transcription and replication. Zn also functions in the brain, playing a role in synaptic plasticity and learning. However, it has also been recognized as a neurotoxin in high concentrations; thus, Zn homeostasis is important in sustaining life.[11]

HSA is involved in Zn homeostasis, and is the primary Zn transport protein in the human circulatory system.[8] In many cases, HSA acts as a "zinc buffer," controlling the amount of free Zn(II) that is available for cellular uptake.[10] Interestingly, HSA-Zn binding and HSA-fatty acid binding is interdependent. Upon fatty acid binding, HSA undergoes a conformational change which disturbs the preformed Zn(II) binding site. Therefore, researchers suggest that HSA might facilitate the interplay between extracellular Zn speciation and energy metabolism.[14]

Zn(II) binds to HSA at what is referred to as the multi-metal binding site, or MBS. This site gets its name for its ability to coordinate a variety of metals including Cu(II), Ni(II), Zn(II) and Cd(II). Thorough spectroscopic investigation of Zn(II) binding to the MBS indicates that the first ligand shell includes two imidazole N's of His 67 and 247, two carbonyl oxygens of Asn 99 and Asp 249 and a third oxygen from a coordinating water molecule at pH 7.4.[9] However, crystal structure data collected at pH 9.0 and representing HSA with a bound Zn ion does not show coordination of Asn 99. (Figure below, pdb.5IJF) Differences in pH are known to result in conformational changes to HSA and could explain the discrepancy in coordinating atoms observed in the crystal structure and in spectroscopic data.



Structure of Zn(II) bound to HSA from PDB 5IJF: Close up of HSA's Zn(II) binding site at pH 9.0, located at the interface of domains I and II. Other spectroscopic data (collected at pH close to 7) indicates coordination through His 67, His 247, Asp 249, Asn 99, and H_2O. In PDB entry 51JF, above, binding is similar, though not involving Asn 99.

The HSAB character of Zn(II) and its coordinating ligands can explain this site's metal preference. Imidazole nitrogens are borderline bases, and carbonyl groups are hard bases. Zn(II) is typically considered a borderline acid, so it makes sense for these ligands to prefer Zn(II) over a softer acids such as Cu(I) or Cd(II).

Because Zn(II) is a d^{10} metal, it has zero LFSE. Therefore, LFSE is not a contributing factor when determining the geometry of this binding site. Instead, geometry is determined by the most sterically favorable arrangement of ligands. In the case of 4 coordinate

ligand arrangements, tetrahedral geometry, with bond angles of 109.5°, is more sterically favorable than square planar geometry, with bond angles of 90°. It is worth noting that steric factors may also include the structural constraints of the protein itself due to folding or otherwise. Another consequence of zero LFSE is increased lability or rate of ligand exchange, which is essential considering the biological implications of HSA-Zn binding.

As mentioned previously, metal binding to HSA is not only relevant for normal physiological processes, but also in pharmaceuticals. HSA is a target for a variety of metallodrugs, including some for the treatment of cancer.[13] Such metal binding occurs at the Cys-34 residue, which is the only Cysteine out of 35 in the protein that is not involved in disulfide bridging.[6] Therefore it provides a S-donor that can attract metallodrugs, especially those containing soft metals like Au(I) and Pt(II). Unlike the other metal binding sites, this one is not stabilized by the chelate effect, and binds metals via a single metal-sulfur bond.

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Contributed by

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10.1: A Molecular Depot- Human Serum Albumin Carries Essential Cu and Zn in Serum is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

10.2: Iron acquisition in bacteria- Siderophores

Siderophores

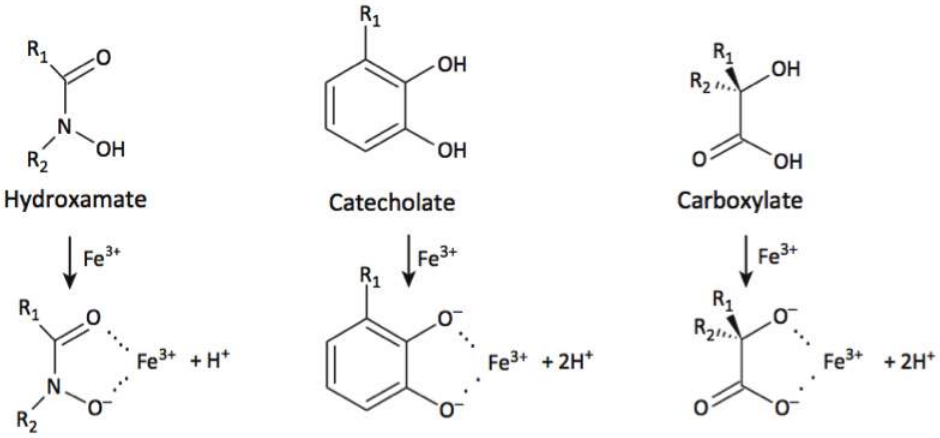
This is a video introduction to siderophores: the small molecules produced and secreted by bacteria to acquire precious iron from their environment.



Most all living organisms require iron for crucial processes that allow for the life and growth of cells. Animals receive this nutrient from diet, but plants and single-celled organisms must utilize different strategies.[1] There are two main mechanisms by which cells acquire iron. The simpler of the two, is iron diffusion across cellular membranes.[2] This mechanism is more difficult, despite the prominence of iron in the atmosphere. This is due to the aerobic nature of the environment, which causes iron to be present in the highly insoluble form, $Fe(OH)_3$. The insolubility means there is a low Fe(III) concentration (10^{-18} M) of available iron; too low to provide sustenance to microorganisms, which require a minimum concentration of 10^{-8} M to live and grow.[3, 4] To circumvent the lacking bioavailability of iron, these organisms synthesize and secrete siderophores. Siderophores are low molecular weight compounds that chelate iron and transport it into cells under low iron environments.[5] Siderophores have the highest specificity and affinity for Fe(III), but are capable of forming complexes with other metallic ions, like Fe^{2+}, Zn^{2+}, Ga^{3+}, and Cr^{3+}.[2]

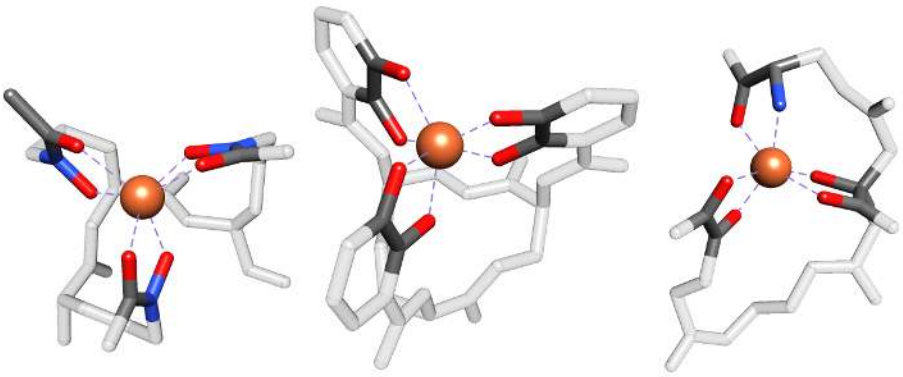
Siderophores are an incredibly diverse group of biocompounds, with hundreds of different types categorized. The most common siderophores fall into three main categories: hydroxamates, catecholates, and carboxylates.[2] The functional groups of these structures that are the main component in iron chelation are shown below, in Figure 1.

Figure 1[2]: Functional groups of siderophores and the complexes that form upon binding to Fe(III). R-groups represent the variable groups.



These bidentate functional groups interact with iron through two negatively-charged oxygen atoms, but this is not a steadfast rule. Some distortions can occur and other atoms like nitrogen or sulfur can be substituted as one of the interacting atoms (although this has a tendency to reduce Fe(III) affinity).[6] The functional groups act as bidentate ligands, but naturally occurring siderophores can arrange multiples of these groups through the variable R-groups into a higher chelating structure. Hexadentate and tetradentate structures are the most common. Hexadentate siderophores tend to bind to Fe(III) more so than tetradentate or bidentate siderophores, due to the chelate effect. The resulting hexadentate complexes are also more stable and less labile, which makes sense, since one iron-bound ligand–instead of two or three–increases the entropy.[3] Examples of hexadentate siderophores are in Figure 2.

Figure 2: Examples of the three types of siderophores in a hexadentate formation. The colored portions highlight the iron and siderophore functional groups. The light gray represents the variable groups. (A) A ferrichrome ligand, a type of hydroxamate from an Esherichia coli cell.[7] (B) An enterobactin ligand, a type of catecholate from a Bacillus subtilis cell.[8] (C) A staphyloferrin ligand, a type of carboxylate from a Staphylococci.[9]

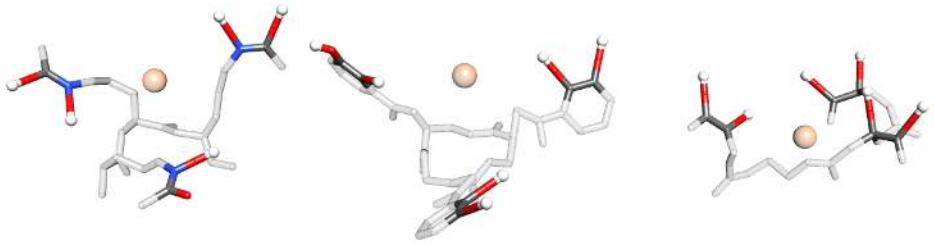


Fe(III) is typically found in an environment with an aqueous solution, meaning the naturally-occurring complex is the octahedral $Fe(H_2O)_6^{3+}$. Siderophores surround this complex, usually in a hexadentate manner that results in octahedral geometry. Typically, the water is replaced completely by siderophore in an entropically-favorable way. In this new complex, Fe(III) is in a d^5 electron configuration. As previously mentioned, siderophores donate multiple oxygen atoms to form a complex with iron. The donation of oxygen atoms means these ligands are σ and π donors, which are weak field ligands and support a high spin configuration. The combination of the complex's geometry and the metal center's high spin configuration means that there is no ligand field stabilization energy.

Without bound Fe(III), siderophore are not rigid compounds (Figure 3). The metal-ligand bond is what stabilizes their structure. Complex stability and the siderophores' high affinity for iron comes from the aforementioned ligand denticity as well as the multiple hard acid and hard base interactions. Fe(III) is a hard acid and the oxygen atoms on the siderophore are all hard bases.[10] The affinity for iron increases with higher negative charges on siderophores.[6] More negatively-charged siderophores are harder bases, which form tighter interaction to Fe(III). As shown in Figure 1, catecholates and carboxylates usually have two negatively-charged oxygen atoms per functional group, while hydroxamates have one. This alludes to the idea that the former groups have higher iron affinity.

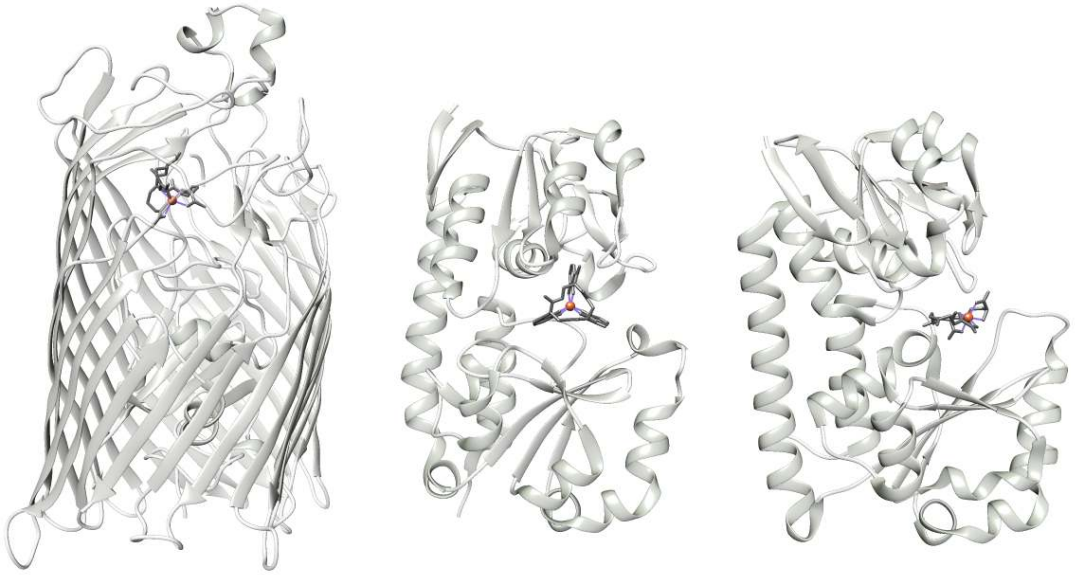
Fe(III)-siderophore complexation is sensitive to pH values. Free iron and protons (hydrogen atoms) compete for the unbound siderophores.[11] In low pH environments, there is a high concentration of solvated hydrogen atoms, resulting in higher competition for the siderophores (Figure 3). A low pKa value relates to a strong acid that is able to donate protons. In Figure 1 above, both the catecholate and carboxylate groups donate two hydrogen atoms (protons), as opposed to the hydroxamate group, which donates one. The former two will have lower pKa, and thus a higher negative charge density, which means a higher iron affinity.[6]

Figure 3[7, 8, 9]: Siderophores unbound to Fe(III). The octahedral geometry is not held without the metal. Here, hydrogens have bound to the siderophores, replacing the Fe(III) bonds.



Once the Fe(III)-siderophore complex has formed, it is introduced into the cells by complex, energy-dependent transportation mechanisms.[12] The introduction usually begins when the complex binds to a receptor protein on the cellular outer membrane, which have high affinity for the complexes. The binding changes the protein conformationally as the Fe(III)-siderophore complex is shuttled through and released into the periplasm. Once there, it binds to another high affinity proton and then taken directly or passed through a chain of transport proteins until it reaches its final destination.[13] Examples of some membrane-bound transport proteins are in Figure 4.

Figure 4: Examples of the three types of siderophores in a hexadentate formation. The dark gray and colored portions highlight the Fe(III)-siderophore complexes. The light gray represents the membrane proteins. **(A)** An FhuA protein bound to a ferrichrome ligand.[7, 12] **(B)** An FeuA protein bound to an enterobactin ligand.[8, 14] **(C)** A SirA protein bound to a staphylococci ligand.[9, 15]



The function of a siderophore is to bring insoluble iron from the environment into the cell. All siderophore perform this task uniformly. However, there are multiple mechanisms for iron release into the cell. There are two common mechanisms utilized by the majority siderophores. The first involves a reduction of Fe(III) to Fe(II), which results in a lowered iron affinity and looser bond to the siderophore. This is energetically favorable as it does not degrade the siderophore in any way, so it can be reused in iron

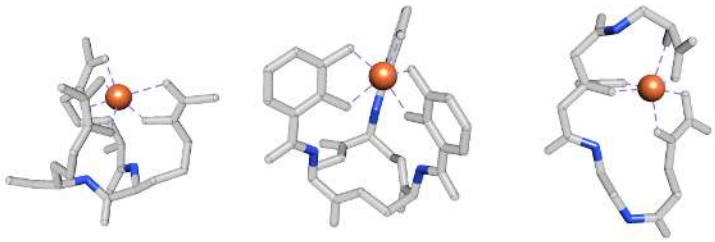
acquisition.[16] Less frequently, the backbone of a siderophore undergoes a hydrolysis reaction. These have a tendency to yield a siderophore product that is useless for re-secretion into the environment.[16, 17]

Reduction to Fe(II) produces a weaker bond to the siderophore and, overall, a less stable complex. Stability constants for the reduced iron form are on average 20 orders of magnitude lower. Contributing to this, is the fact that Fe(II) is a softer acid, which has weaker interactions with the strongly basic oxygen-donor groups. What's more, it's not as effective at outcompeting solvated hydrogens to bind these groups. This weaker metal-ligand interaction means Fe(II) is more labile and likely to dissociate.[3]

The stability of the Fe(III)-siderophore complexes make it difficult for reduction to occur, but various facilitators help the reaction along. There are certain chelators and reductive enzymes that directly catalyze the reduction reaction, but the surrounding environment plays multiple roles as well.[6] Hydrophobic regions and low pH mediums stimulate reduction. In acidic conditions, H^+ ions can partially dechelate the iron-siderophore complex. This reduced ligand denticity results in a less stable complex, which makes reduction more likely.[3]

Reduced denticity is the main theory behind the second release mechanism. Here chelation is decreased through hydrolysis of the siderophore backbone instead of through protonation of the donor groups. This reaction effectively breaks the siderophore, but significantly decreases iron affinity. The disposal of a siderophore is not energetically favorable, which is one reason this mechanism is not as popular of a strategy. What's more, siderophore hydrolysis requires a siderophore with hydrolyzable groups embedded into its backbone (Figure 5), which leaves a limited selection of siderophores.[3]

Figure 5[7, 8, 9]: Hydrolyzable portions of siderophore backbones shown in blue.



Although siderophores are bacterial structures, they're helpful to humans using the above chemistry to chelate iron and either acquire the metal or sequester it away. Medicinally, siderophores act as sneaky antibiotics through a "Trojan-Horse" strategy. These drugs kill toxic bacterial cells by covalently linking an antibiotic agent to the backbone of a siderophore. The modified siderophore still binds to Fe(III) and the bacterial cell–which is unable to sense the new cytotoxic agent–allows the complex inside.[10] Siderophores also help with iron excess diseases (hemochromatosis, iron poisoning) and malaria by chelating Fe(III). In the case of the former, this helps remove iron buildup; in the latter, Fe(III) is sequestered away from cells inside the parasite (which leads to death).[5]

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10.2: Iron acquisition in bacteria- Siderophores is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

10.3: Fe Wars- Lactoferrin

Iron Wars

Wars can be started over metals like gold or silver, but the human body wages an internal war against pathogens on a daily basis over a seemingly insignificant metal: iron (see figure 1). While largely known for its rusting abilities, iron is also the catalyst for numerous metabolic processes, a binding agent in molecules like hemoglobin, and is even speculated to be a contributing ion to the early formation of macromolecules that eventually led to life forms.[1] However, humans aren't the only organisms that need this ion as a nutrient source; bacterial species depend on ions like iron to survive.[1] As a result of this mutual need, iron wars break out between bacteria and the human body, and each side has used scientific methods to more efficiently acquire this resource.

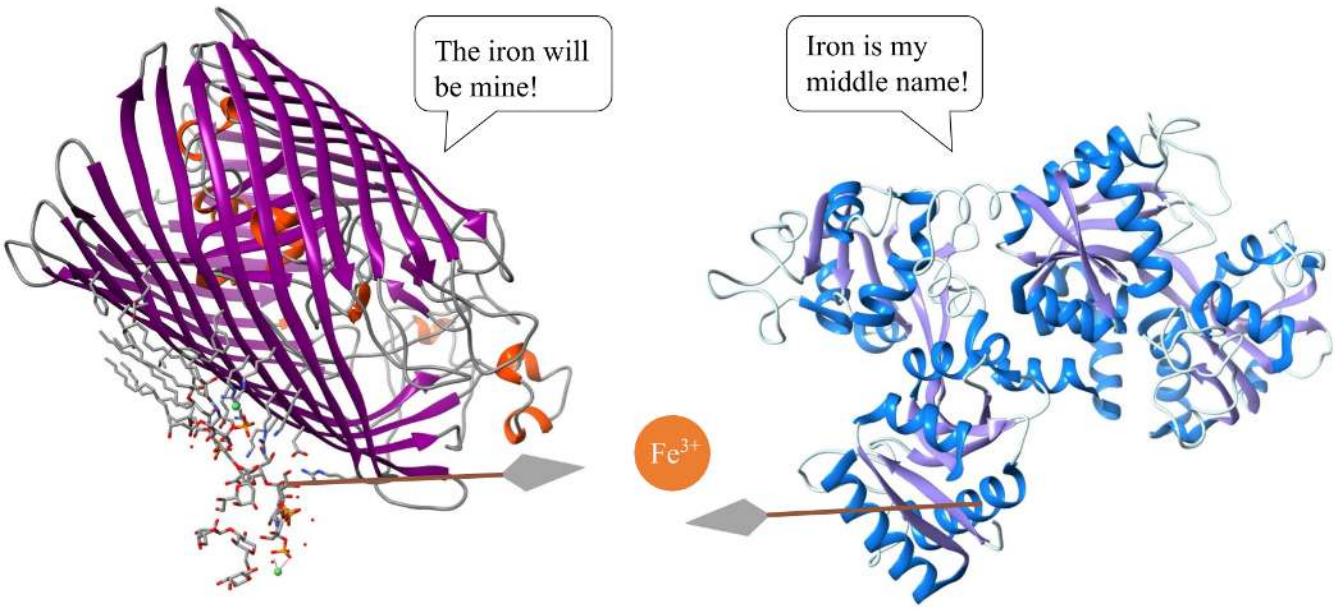


Figure 1: Cartoon depicting the "iron wars" between human and bacterial iron-sequestering proteins. Right: *E. Faecalis* siderophore, ferric hydroxamate. Left: human protein, lactoferrin.

Enter to the scene lactoferrin, a iron-chelating protein that has an extremely high binding affinity for iron (III).[2] Lactoferrin is a member of the transferrin family, a group of proteins that bind specifically to iron and perform various functions in the body (see figure 2).[2] Transferrin, while in some cases able to prevent bacterial infection, is used more efficiently as an iron transport protein. Transferrin has a lower binding affinity to iron than lactoferrin does, and a slight dip below biological pH can trigger the protein to release its ion.[3] On the other hand, lactoferrin binds to iron with a much higher affinity, and the ion is not known to be released until pH drops to around 2-3.[4] A pH of this acidity can be found in the body in places such as inflammation sites, cellular vesicles, or the stomach.[4] The ability for lactoferrin to retain iron in a pH far below the biological level of 7.4 makes lactoferrin a more effective tool in the war over iron than transferrin, but less effective as an iron source for the body itself.

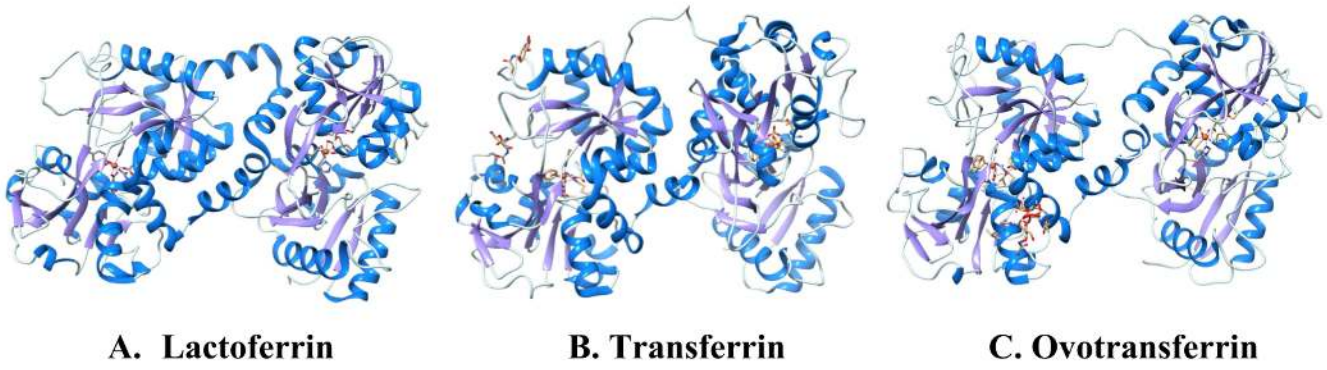


Figure 2: Comparison of the structures of three iron chelating proteins in the transferrin family: Lactoferrin, transferrin, and ovotransferrin. All transferrin proteins bind with high affinity to iron (III) ions, but lactoferrin has the highest binding affinity ($K_D \sim 10^{-20}$ M compared with $K_D \sim 10^{-9}$ M for transferrin). [6,10]

In addition to its antibacterial defenses, lactoferrin performs other functions in the body. The overall structure includes a unique cationic region on its N-terminal (See figure 3).[2] This basic region has been found to bind to lipopolysaccharides and glycosaminoglycans.[2] This binding feature allows lactoferrin to more directly attack bacteria because lipopolysaccharides and glycosaminoglycans are commonly found in the cell membrane of bacteria, and lactoferrin has been found to bind to the surfaces of bacteria and prevent iron uptake.[2] Additionally, this cationic region can bind to DNA, and thus serves as a defense against viruses by binding to viral DNA and preventing its spread through the body.[2] Recent research has taken particular interest in using lactoferrin as an oral cancer treatment, because when it is digested in the stomach, it is broken down to the peptide lactoferricin and absorbed into the bloodstream.[2] Lactoferricin has been found to prevent cellular growth by inhibiting the function of proteins involved in cellular reproduction.[5]

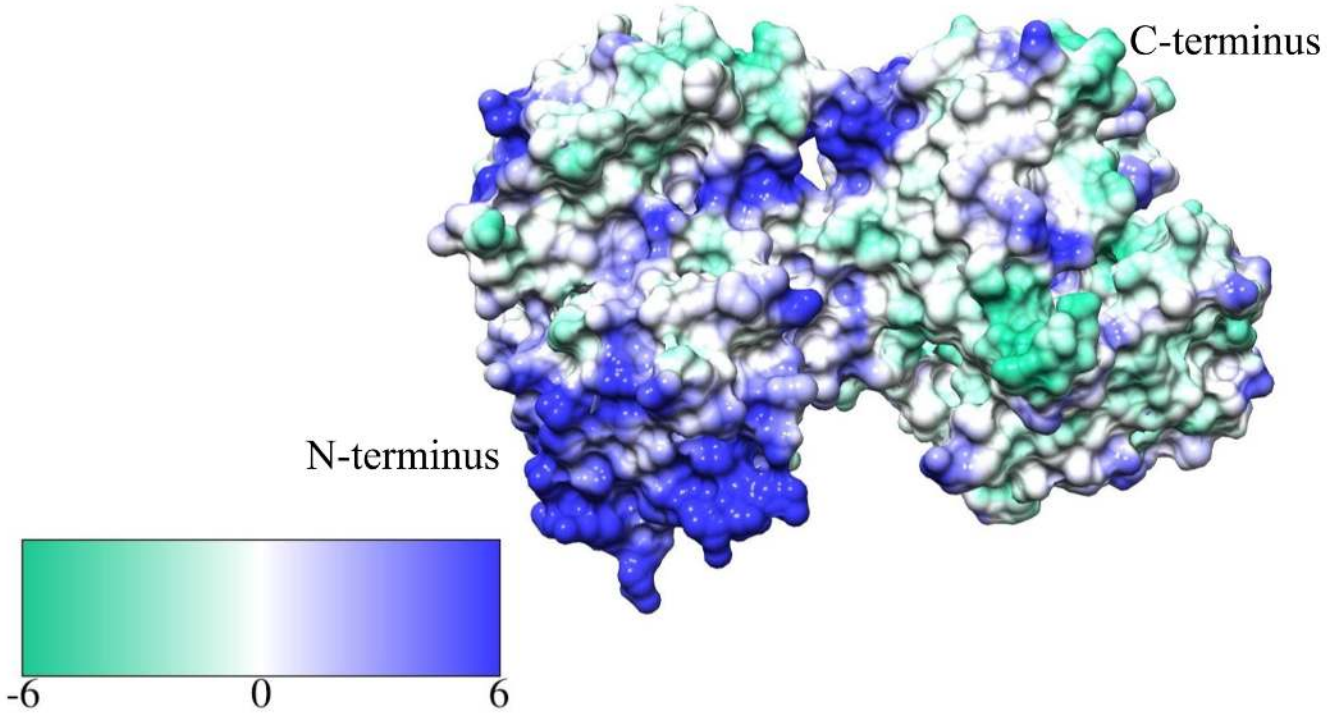


Figure 3: The cationic region of lactoferrin is highlighted in blue. This site on the N-terminus provides lactoferrin with unique properties that aid in its antimicrobial defense system.[2,5] It is able to bind directly to the surfaces of bacteria, the free DNA of viruses, and even inhibit overproduction of cancer cells.[2,5]

The structure of lactoferrin is essential for its high binding affinity. Lactoferrin has two hemispheres; the N-terminal, and the C-terminal, which are connected by an alpha helix (see figure 4a).[2] Each terminal is divided into two lobes, with a “cleft” between them where the metal binding site is located.[6] The amino acids found at the binding site are the same in all transferrin proteins, and consists of two phenolate oxygens from two tyrosines, a histidine, an aspartic acid, and a carbonate ion bound to an arginine (see figure 4b).[2,4]

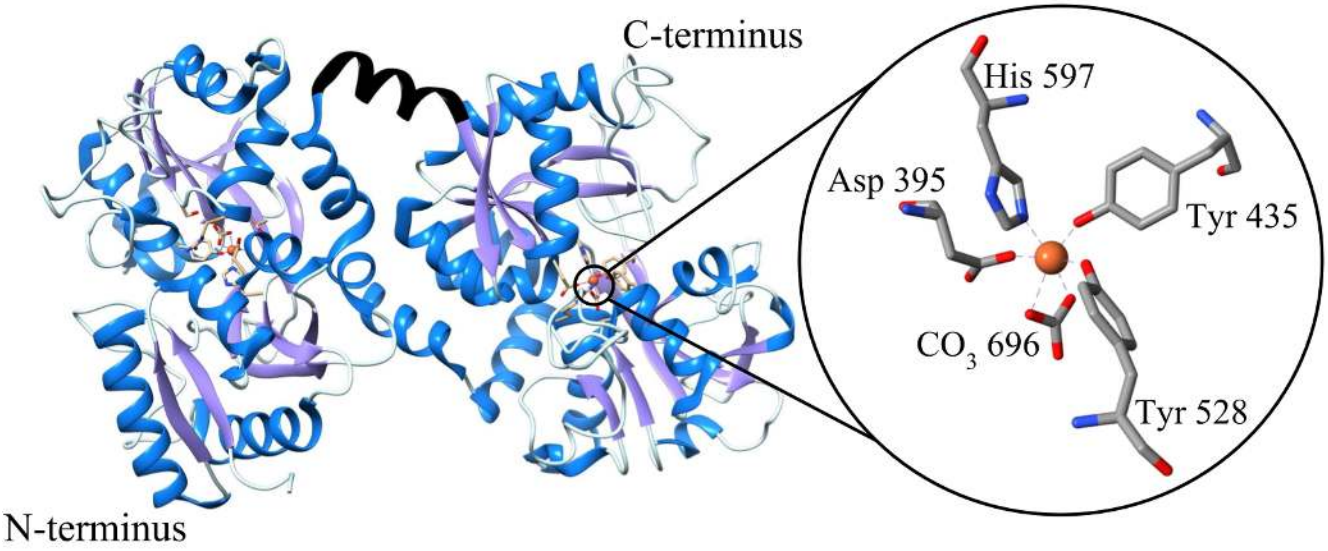


Figure 4 a-b: a) Molecule lactoferrin pictured, the alpha helix connecting N-terminal to C-terminal is pictured in black. In other transferrin proteins, this connection is a flexible beta sheet. It is predicted that this rigid helix contributes to the conformational changes experienced by lactoferrin that allow it to retain iron ions at a lower pH.[6] b) The active binding site of lactoferrin on the C-terminus, but identical amino acids are on the N-terminal. Consists of four amino acids, and a carbonate ion with an iron (III) ion in the center.

It is predicted that the carbonate is the first to bind to the iron ion, followed by the tyrosine groups.[6] Then lactoferrin undergoes a conformational change, wherein the N-terminus closes like a hinge, to lock the iron into place.[6] The resulting structure brings the iron closer to the histidine and the aspartic acid found at the binding site, and the resulting complex displays an octahedral coordination geometry (see figure 5).[6] This final structure is very stable and allows the lactoferrin protein to retain the iron ions in a pH as low as 2-3.[2]

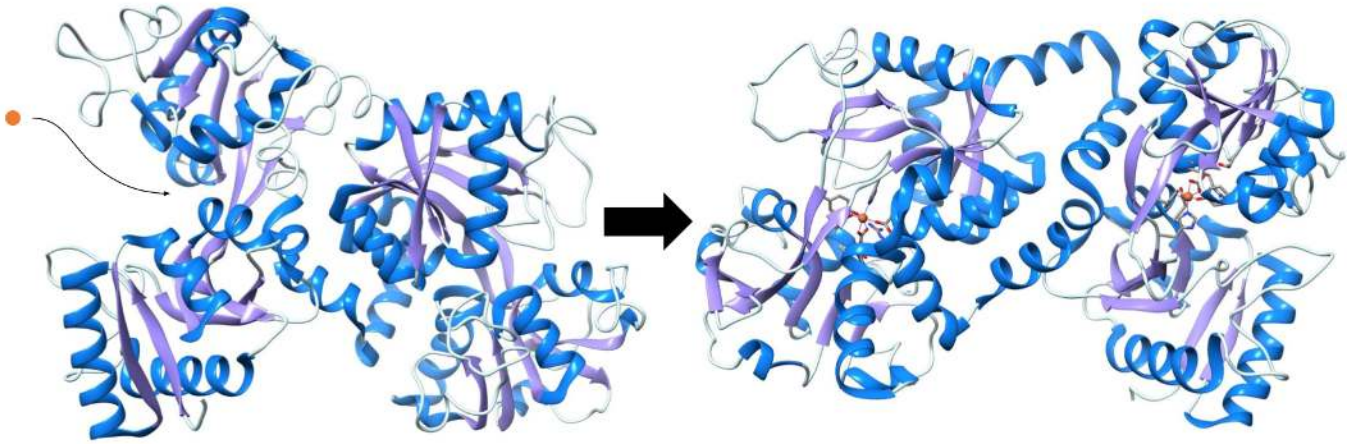


Figure 5: The apo-form of lactoferrin (left) undergoes a conformational change upon binding to iron (III) on the N-terminal side. The lobe closes like a hinge around the binding site, which locks the iron into place and creates an extremely stable complex.

Lactoferrin has high specificity for iron (III) ions. This is likely due to the combination of several different factors, some of which contribute to general stability of the metal complex, and some that lead to the iron (III) preference.

The chelate effect is a thermodynamic factor that contributes to general metal complex stability, because it explains that stability increases as entropy increases. That is to say that as the number of individual molecules in a system increases, so does the stability of a complex. For example, when an ion (M^{n+}) is not bound to a system or protein in the body, it is likely bound to six water molecules, since this complex is more stable than a charged ion, and there is plenty of water in the body. So, when that ion binds to a single complex with multiple binding atoms, the chelate effect contributes to high stability of the metal-protein complex, because the number of free molecules goes from two to seven (see figure 6). For this reason, it is entropically favorable for iron to form a bond with lactoferrin because it replaces six individual molecules with a multidentate ligand.

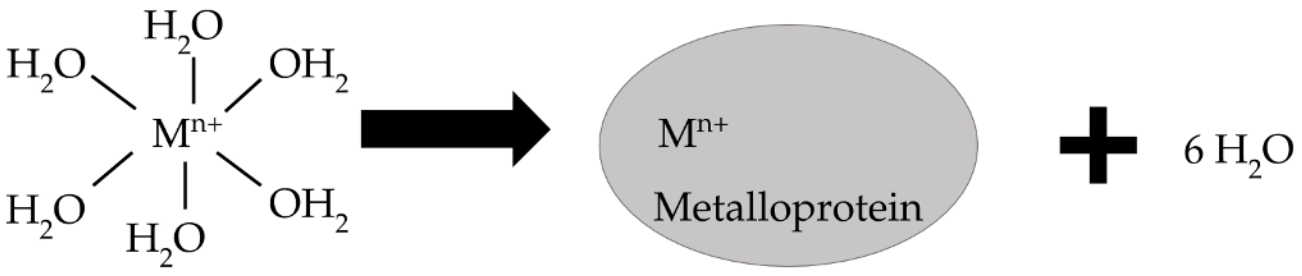


Figure 6: When an iron (III) is “free” in the human body, it usually forms bonds to water molecules. The chelate effect explains that increasing the number of free individual molecules is a favorable reaction, so when that ion binds to a protein with multiple binding atoms, it forms a single metal-protein complex and six free water molecules. Thus, the total number of molecules in a system goes from two to seven, which increases the entropy, or chaos.

The chelate effect is a thermodynamic explanation for the stability of the formation of a metalloprotein complex. Hard soft acid-base (HSAB) theory contributes to the iron selectivity of lactoferrin. HSAB theory is a thermodynamic concept that can predict the stability of metal-ligand interactions. Metals are acids, ligands are bases, and generally hard acids interact with hard bases, and soft acids interact with soft bases. Factors such as charge density and characteristics of an interaction (electrostatic vs covalent) contribute to whether a metal or ligand is considered hard or soft. All of the amino acids found in the binding site, with the exception of histidine, prefer hard acids. Since like binds with like, and iron (III) is a hard acid, the site is favorable for iron. However, several other metals are hard acids as well, including magnesium (II), chromium (III), and calcium (II). These other metals are also known to be able to bind to lactoferrin, but are not nearly as common as iron (III), and don’t usually remain bound lower than a pH of 4-5.[7]

Once lactoferrin has bound to the metal ion, the iron(III)-protein complex that forms is extremely stable, as it is with all transferrin proteins. An important factor in this stability is the geometry of the binding site. The d-orbitals of metals have a large influence on geometry. When a metal binds to a ligand, it can form bonding and antibonding orbitals for electrons to occupy. The difference between the orbitals can influence electron spin and configuration (see figure 7). The energy difference between these d-orbitals can be called the field splitting ($\triangle_O$). When $\triangle_O$ is small, the system is said to have a weak field and the electrons are high spin, which means they will occupy the higher energy orbitals before pairing up. On the other hand, when $\triangle_O$ is large, the system has a strong field and are low spin, so they will pair up before occupying a higher orbital.

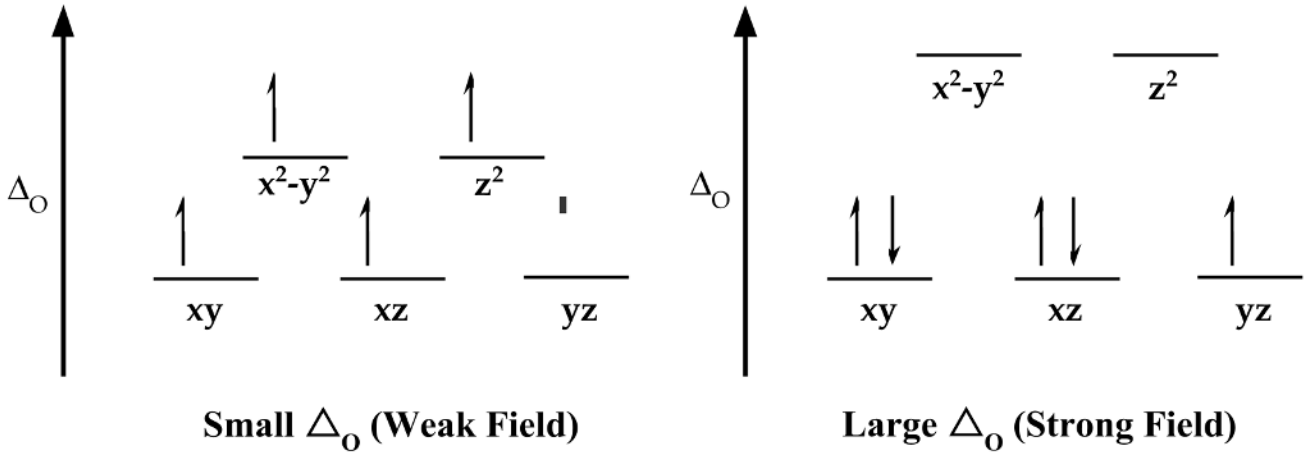


Figure 7: The difference between d-orbitals in metal ions is $\triangle_o$, which influences their electron spin. If $\triangle_o$ is small, then it requires less energy for the electrons to move up into a higher energy orbital than it does to pair up, but when $\triangle_o$ is large, the jump into the next orbital would be too high. Note that this only impacts d_4-d_7 electrons.

Some of the factors that contribute to $\triangle_O$ include the formal charge of the ion, the location of the ion on the periodic table, and the types of ligands in the system. All of the donor atoms in the binding site of lactoferrin (except histidine) are sigma and pi donors. Sigma and pi donors are typically involved in weak field interactions, which is a smaller distance between d-orbitals ($\triangle_O$). In addition, iron (III) has a location in the fourth row of the periodic table, and $\triangle_O$ decreases going up the periodic table. These factors indicate that iron (III) in lactoferrin has a weak field. Since Iron (III) is a d^5 electron, a weak field means that iron's d-electrons will occupy the higher energy orbitals, and won't pair up.

Ligand field stabilization energy (LFSE) can suggest the preferred geometry of an ion. The LFSE is calculated using the equation LFSE = -0.4x + 0.6y, where x is equal to the number of electrons in lower energy orbitals, and y is equal to the number of electrons in higher energy orbitals. Iron (III) has a LFSE of zero, which means there is no other ligand position that would provide a lower LFSE, and so iron is able to form stable bonds in any geometry configuration. Usually d^5 metal ions form an octahedral complex when bound to six ligands (See figure 8). However, in the case of lactoferrin, the carbonate ion causes a slight change in the geometry which results in a distorted octahedral configuration.

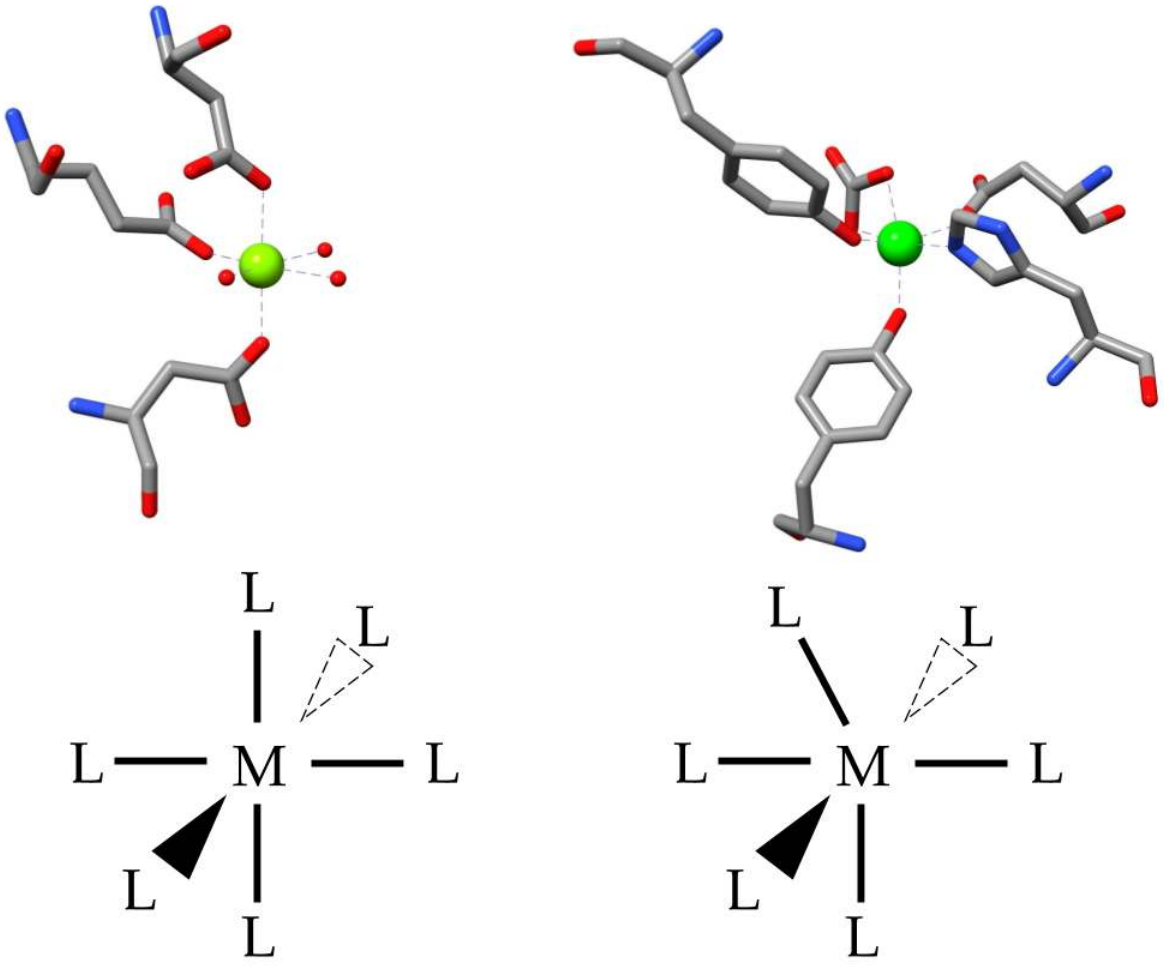


Figure 8: Comparison of the molecular geometries of a standard octahedron and the distorted octahedron of lactoferrin. The carbonate ion found in the binding site of lactoferrin causes the ligand position to shift.

Understanding this concept of crystal field theory provides some insight to how scientists are able to "see" when iron is bound to lactoferrin. The size of $\triangle_O$ can be indicative of whether an ion will undergo a d-d transition or a charge transfer transition. When light waves hit a metal ion and the electrons are excited into a higher d-orbital, the ion is undergoing a d-d transition. Charge transfer, on the other hand, can occur with an exchange of electrons from either the metal to the ligand (MLCT) or from the ligand to the metal (LMCT). In the case of lactoferrin, the majority of the ligands are pi-donors, which is indicative of a ligand to metal charge transfer because the ligand has remaining pi-electrons in its orbitals. The lightwaves excite these electrons into a higher binding orbital of the metal, which produce vibrant colors and strong spectroscopic bands.

Research found the extinction coefficient for the system to be rather large, around 2,500 M^{-1} at a wavelength of 464 nm, which is highly indicative of a charge transfer transition. In addition, the light absorption for lactoferrin is found to be λ=465 nm, which corresponds to the wavelength of blue light. Since colors appear in color as the opposite of the wavelength they absorb (see figure 9), lactoferrin appears as a red-orange color, which is in conjunction with observations initially made of lactoferrin describing it as a red substance found in milk.[2,8]

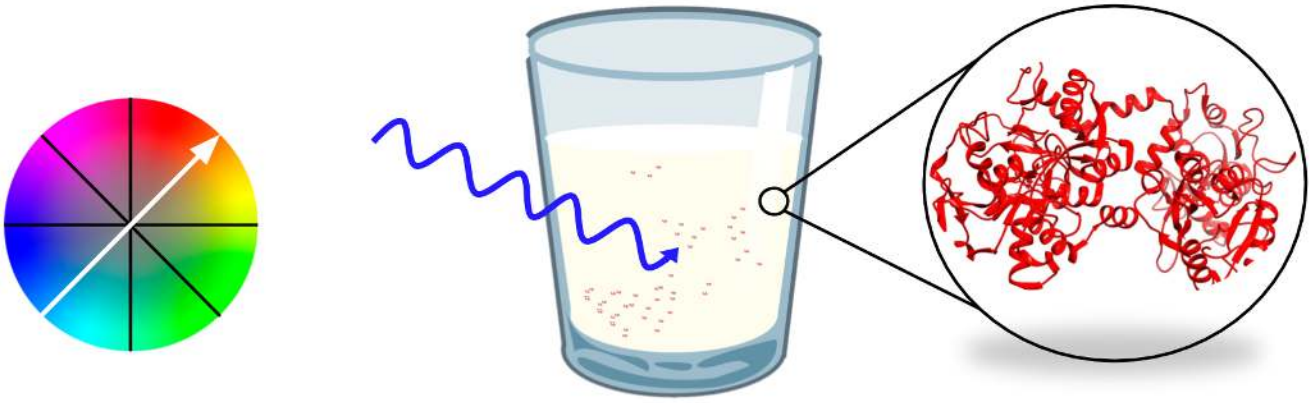


Figure 9: When using spectroscopy, light waves are used to excite electrons in molecular orbitals, and the resulting visible wavelength is the opposite color on a color wheel. In the case of lactoferrin, a wavelength of 465 nm is used to excite the electrons which corresponds to an aqua blue light, and the resulting visible color is red.

Lactoferrin's ability to sequester iron from its environment makes it useful as a defense protein in the innate immune system. After both lobes have taken up an iron ion, it can take a pH as low as 2-3 to remove it. Since bacteria are often not this acidic, but still require iron to perform biological functions, lactoferrin essentially starves bacteria from their nutrition source. Most bacteria are defeated by this tactic, with some notable exceptions.

Some bacteria, such as enterococci, have developed tactics to fight against iron sequestering proteins, including lactoferrin.[9] These tactics include the use of siderophores, ferric reduction, and proteases that can cleave lactoferrin. Siderophores are essentially bacteria's version of lactoferrin, and are also able to bind to iron (III) with high affinity by using the chelate effect the same way lactoferrin does. The method of iron reduction, on the other hand, utilizes HSAB theory, and changes the hard acid iron (III) into an intermediate, which would make the ion less stable in its environment. Finally, proteases that can cleave proteins like lactoferrin are able to change the binding site, which ultimately impacts the ligands bound to the iron. This would cause a change in the geometry of the binding site and cause the iron to "pop out" of place.[9]

While bacteria use these defenses to regain some iron ions, these methods might shed some light on how the human body regains iron ions from lactoferrin. To date, this remains elusive, and it is unclear exactly how the body removes ferric iron from lactoferrin. Unlike transferrin, which has a role that involves sequestering iron ions as well as transporting them for further use,[10] lactoferrin exists almost exclusively in secreted fluids, and is not known to be used for any other reasons than lowering iron concentration. Since transferrin needs to be able to both obtain and release iron fairly easily, it makes sense that iron ions are released around a pH of 5.5, and even a slight dip in pH has been known to trigger the release mechanism.[6,3, 10] However, since lactoferrin is used far more efficiently as an antibacterial agent, then its ability to remain bound to iron in a much lower pH is better at preventing bacteria from obtaining the iron, but makes it a poor source of iron for the body. It is known that lactoferrin can be a source of iron for infants under six months,[11] and it is speculated that lactoferrin must undergo a conformational change to release bound ions. However, further research is needed to understand what this change entails.[6] Since lactoferrin is largely found in secreted fluids, it could be a possibility that it is not intended to release iron ions, since the body is disposing of the protein.

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10.4: Iron Storage- Ferritin

Iron is necessary for life. It is an essential nutrient and living organisms use it frequently and in large amounts. Iron is necessary in the active sites of enzymes that play roles in respiration, electron transfer reactions, energy metabolism, DNA synthesis, and gene regulation.[1] Iron is also necessary for oxygen transport and oxygen storage in the proteins hemoglobin and myoglobin.[2]

Despite the importance of iron for life, excess iron can be toxic.[3] Unregulated free iron can catalyze the production of harmful reactive oxygen species (ROS) and free radicals, most commonly via Fenton chemistry. The Fenton reaction (below) is the reaction between iron(II) ions and hydrogen peroxide to produce the extremely reactive and harmful hydroxyl radical (**$^{\bullet}$OH**).[1]

$$\mathbf{Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH}$$

ROS are strong oxidizing agents and can cause permanent cell damage, organ failure, and death.[4] Furthermore, iron ions have notoriously low solubility. The issues of solubility particularly apply to iron(III) ions which have a solubility of 10^{-18} M at physiological conditions.[1] In environments where oxygen is present, like the bloodstream, iron can form insoluble aggregates, similar to rust.[5,6] For example, dying red blood cells produce ~0.54 mmol of iron per day. If that iron is left free in its aerobic environment, it will react with oxygen and form insoluble rust-like compounds. It's been estimated that a human would have to drink 10^{13} liters of water every day to avoid "rusty" kidneys.[1] Additionally, pathogens need iron to replicate and to survive. Thus, excess iron in an organism could be used both to nourish the organism itself and to nourish infection and disease-causing organisms.[4] Due to the biological necessity of iron, the storage and collection of excess iron in a nontoxic form is vital.

The cell's answer to these obstacles is ferritin. Ferritin is the universal iron storage protein found throughout nature—both in prokaryotic and eukaryotic organisms.[4,7] It is found in plants, animals, and bacteria and is necessary for all living things. In fact, deletion of the ferritin gene is lethal.[8] Ferritin functions both intracellularly and extracellularly.[5] Intracellularly, human ferritin is found in the cytoplasm of the cell.[3,4] Extracellularly, human ferritin has been found in serum. It is currently unknown where this extracellular ferritin comes from and how it leaves the cell, but its concentration in blood is used as a common clinical test for iron levels.[5] The measurement of serum ferritin is considered as one of the most specific and sensitive blood tests for diagnosing iron deficiency.[5]

Ferritin solves the previously discussed obstacles of excess iron in the body. Considering the poor solubility of Fe^{3+} ions, human ferritin is actually rather soluble and gathers excess iron ions without creating insoluble clusters of iron in the body.[6] The transport protein transferrin brings excess iron ions to ferritin as Fe^{2+}. The ferritin protein surrounds the collected iron ions to prevent the Fe^{3+} ions from aggregating in the cytoplasm of the cell or in the bloodstream and to protect them against reaction with any other species present, thus avoiding the production of ROS.[6] Any other ligands in the cell that might bind to iron are blocked out and the iron is stored in a stable form.[2] Ferritin stores excess iron until iron is needed for one of the many processes in which it plays a part. Iron stored in ferritin can comprise almost 10% of total iron in the body.[2]

Structurally, ferritin is a hollow cage and the sequestered iron is stored as an iron(III) mineral within the protein shell (Figure 1).[2,3]

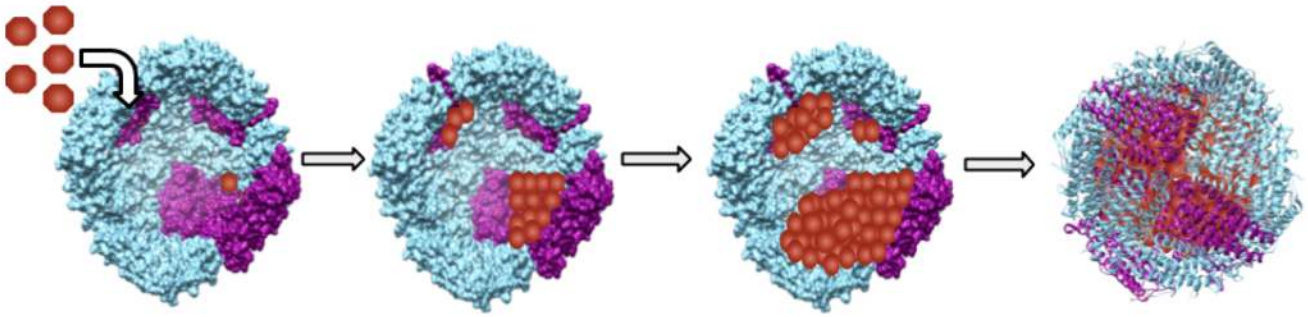


Figure 1. A cartoon diagram of sequestration of iron, which has been crystallized and is stored as an iron/oxy mineral in the hollow cage of ferritin. From left to right, the diagram depicts the cross section of the ferritin protein cage and the growing nucleation in the hollow center of ferritin. Each red shape represents some crystalline, mineral combination of iron, oxygen, and hydrogen (FeOOHcore). Nucleation begins on the purple surfaces of ferritin, which will be discussed in detail later, but is otherwise random. The final image in the diagram on the far right is the spherical ribbon structure of full iron-containing ferritin protein with the cartoon depiction of iron/oxy mineral (red shapes) within the center. While this diagram depicts ferritin being filled to capacity with iron, in reality, ferritin can be filled as much or as little with iron, as needed. Thus, this figure can also be interpreted as different ferritin proteins in environments of different iron concentrations and so storing different amounts of iron. N.B. This diagram is not biologically or chemically representative of the process of iron storage, but is included to provide the reader with a visual of the storage of iron/oxy mineral within the hollow cage of ferritin. The actual process of storage is discussed later.

Ferritin is made of subunits. Each subunit has four polypeptide α-helices or spirals.[2] Structures of ferritin differ based on the organism which produces it. Most ferritin is made of 24 of these subunits.[6] Human ferritin is a 24-subunit, 480 kDa, 12 nm globular protein with a hollow center cavity (cavity diameter of 8 nm).[2] One 24-subunit ferritin protein can store up to 4500 iron ions in its hollow center.[2] Ferritin is a very good space-saving model for the cell because of its high iron to protein ratio (4500 iron ions/8 nm cavity).[2,9] This iron to protein ratio is 200 times that of hemoglobin.[9] Up to 24% of ferritin's weight could be stored iron ions. Meanwhile, bacterial ferritin can be either a 12- or 24-subunit globular protein.[6] However, it is thought that the 12-subunit ferritin's may play an additional role in protecting DNA from oxidative damage, while the 24-subunit bacterial ferritin may control bacterial iron metabolism.[3]

The subunits of human ferritin are classified as the heavy subunit or "H-chain" and the light subunit or "L-chain" (Figure 2).[6] The two subunits, however, are not extremely different in molecular weight or amino acid sequence. The H-chain is made of 178 amino acids with a molecular weight of 21 kDa and the L-chain is made 171 amino acids and weighs 18 kDa.[4] The two types of subunits have ~53% protein sequence identity.[4] The designations of heavy and light are actually a modern recasting of designations that originally reflected the organs from which the two forms were isolated, "H" for heart and "L" for liver.[8]

The two types of subunits combine in different ratios to form the 24-subunit protein shell in humans (Figure 2).[6] This ratio is dependent on the tissue where the ferritin is synthesized.[6] The H subunit is responsible for catalyzing the oxidation of iron(II).[8] The L subunit hosts the site of nucleation and storage of iron.[8] The ratio of H:L will be higher in tissues where iron oxidation activity is high and iron detoxification is needed, such as the heart or the brain.[1,4] Tissues, like those in the spleen, are used more for storage and will have a lower H:L ratio. The human liver produces ferritin that is 50% H and 50% L.

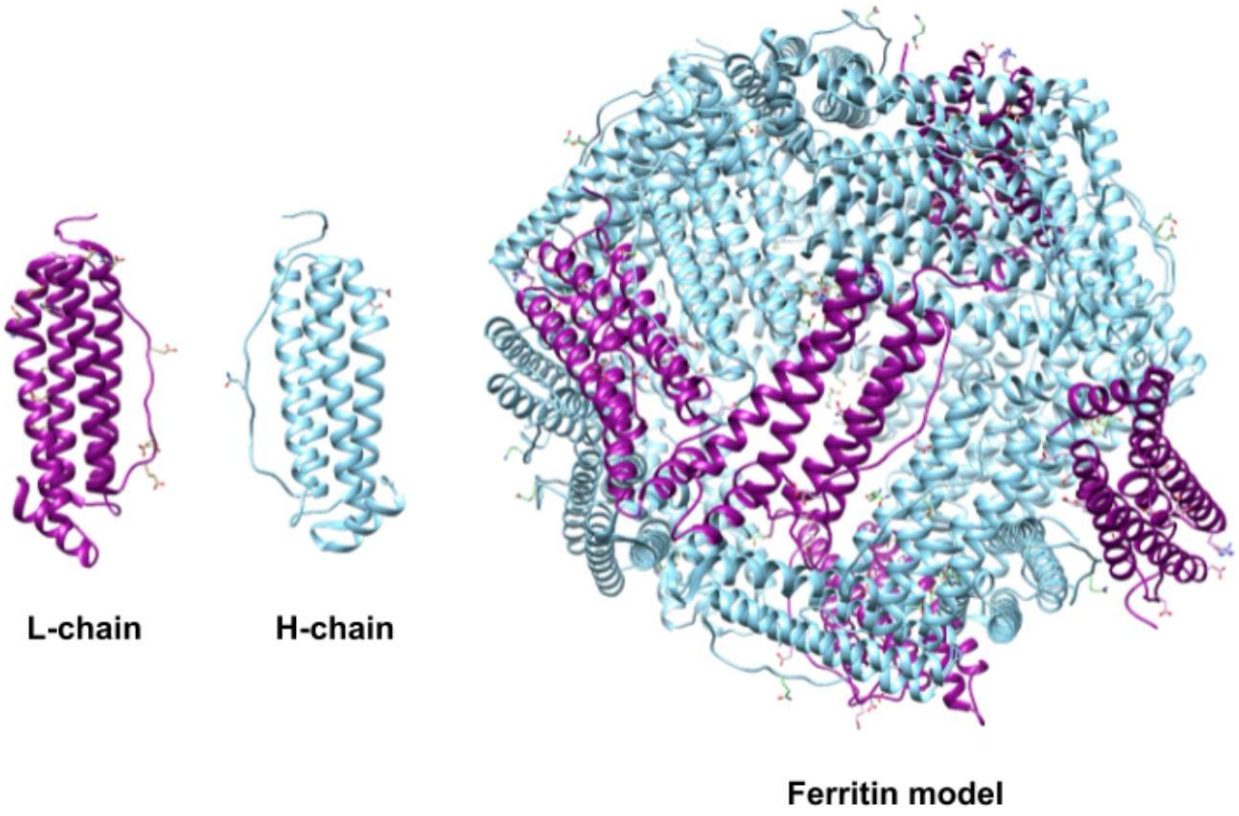


Figure 2. Light (L) (PDB 2FFX) and heavy (H) (PDB 2FHA) human ferritin subunit chains combine to form the human ferritin shell in specific ratios. The H:L ratio is dependent on the tissue where the protein is synthesized. The model seen here was created from the crystal structures of individual subunits, not a biologically obtained structure. However, it is approximately 30% L-type subunit and 70% H-type subunit and would be of a similar ratio to the ferritin found in the brain.[1]

In bacterial ferritin, the H-chain is the only subunit present in the either 12- or 24-subunit shell.[2] Amphibious or fish ferritin can be made up of two to three different types of subunits ("H-","L-", and middle "M-chains").[7] The H and M subunits share similar functions of oxidizing iron.[12] This report will focus on the H and L subunits of human ferritin.

While iron storage has been determined as an important function, it is unknown if this is the only or even primary function of ferritin.[6] Other proposed functions fall mainly under the umbrella of ferritin's role as an antioxidant. It has been proposed that the main role of ferritin could be in reducing oxidative stress and preventing harmful production of ROS from reactions between iron and oxygen or hydrogen peroxide. The exact mechanism of how ferritin works as an antioxidant is unclear, but its characteristic functions can all contribute.[6] For example, the ability to remove O_2 or ROS through reaction with Fe^{2+} and to remove excess Fe^{2+} from the environment both directly reduce oxidative stress; however, if ferritin is produced by the cell for this purpose has yet to be determined.[6]

Entrance: Ferritin's Selectivity for Iron

Fe^{2+} ions are brought to ferritin for storage by the transport protein transferrin. The ions are believed to enter through one of the eight symmetric 3-fold channels or one of the six symmetric 4-fold channels formed by the subunits in the ferritin structure highlighted in Figure 3.[6]

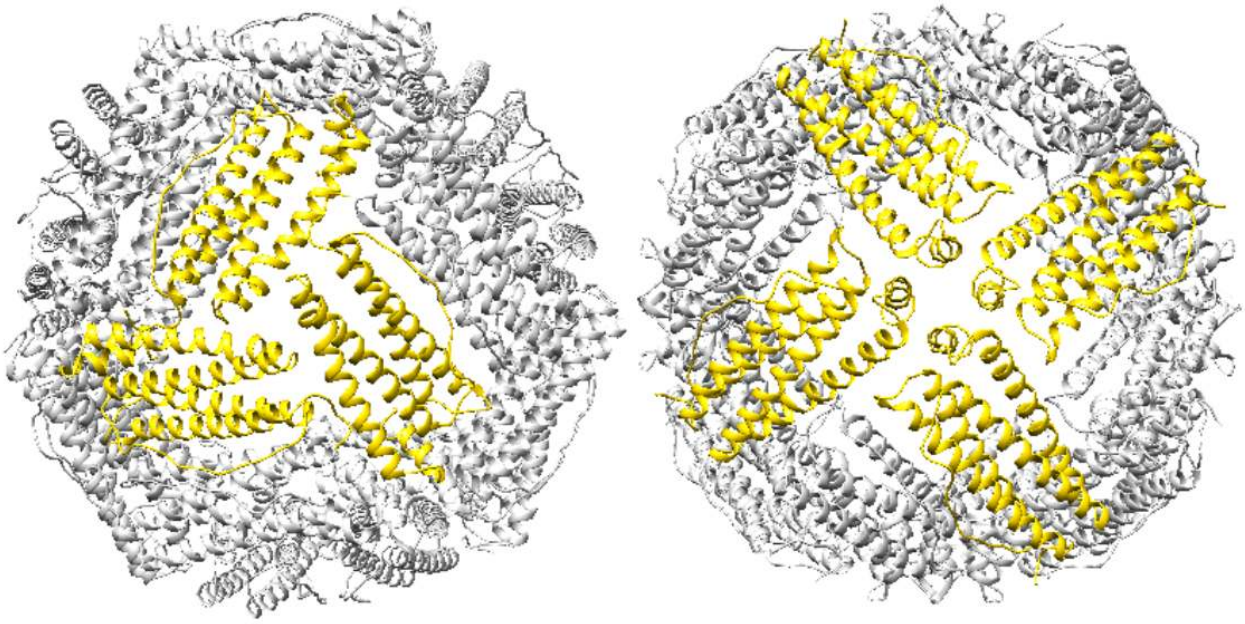


Figure 3. Symmetric channels of entry and exit in Ferritin (PDB: 1FHA). The 3-fold channel on the left appears eight times in the 24 subunit ferritin protein. The 3-fold channel is formed by three subunits. The 4-fold channel on the right appears six times in the 24 subunit ferritin protein. The 4-fold channel is formed by four subunits.

The 3-fold channels are lined with the polar side chains aspartate and glutamate and make the channel hydrophilic.[2] The hydrophilicity of the channel allows for the transport of water, metal cations, and hydrophilic molecules of an appropriate size into and and out of the ferritin center.[4] Most studies indicate that the 3-fold channel is the main channel for Fe^{2+} ions both into and out of the cell.[1,3]

The 4-fold channels are lined with the non-polar side chain leucine and make the channel hydrophobic. It is widely thought that the 4-fold channels are involved with the diffusion of oxygen and hydrogen peroxide into and out of the ferritin center.[1]

Iron(II) ions are oxidized at the “ferroxidase site” on the H-chain subunits (Figure 4). After conversion to Fe^{3+}, the iron is stored as a crystalline iron/oxy mineral.[2] The mineral accumulates on the L-chain (Figure 5).[8]

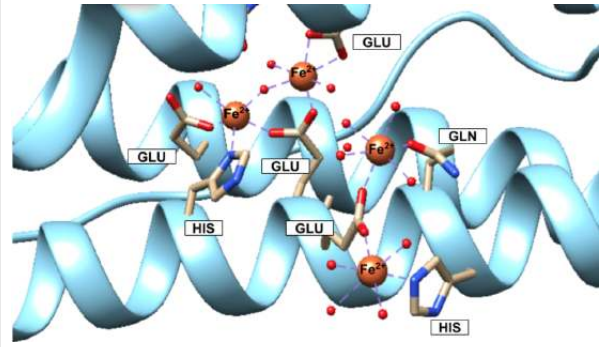


Figure 4. Human Ferritin H-chain (PDB 4YKH). Fe^{2+} ions are both shown traveling on their way to the ferroxidase site and at the ferroxidase site, to be covered in detail later. Fe^{2+} ions can be seen binding to water molecules, oxidizing agents and residues glutamic acid (Glu or GLU), glutamine (Gln or GLN), and histidine (His or HIS). The smaller red balls connecting to the Fe^{2+} ions via a purple dashed line are the oxidizing agents—oxygen molecules, hydrogen peroxide, or water molecules.

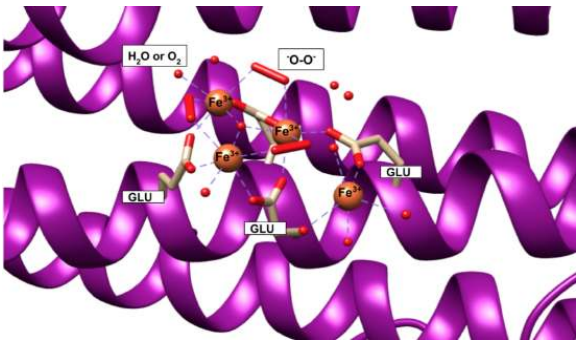


Figure 5. Human Ferritin L-chain (PDB 5LG8). Fe^{3+} ions can be seen binding to water and oxygen molecules (small red balls), peroxo groups (long red cylinders), and residues of glutamic acid (Glu or GLU) from the L-chain. Fe^{3+} is stored as an iron/oxy mineral on the L-chain. This is the beginning of nucleation within the ferritin cavity.

Figures 4 and 5 show iron(II) at the ferroxidase site and iron/oxy mineral at the nucleation site, according to the available crystal structures. The structure of the entire iron mineral core, however, is actually inconsistent throughout the whole mineral and differs even between identical ferritin shells.

Traditionally, it was believed that the iron(III)/oxy mineral that makes up the core was similar to ferrihydrite and ideally structured as 20% tetrahedral and 80% octahedral; however, as more evidence has become available this model has been replaced by a "polyphasic" or heterogeneous model of the iron core that is thought to be more accurate.[2,4] According to the polyphasic model, the mineral structure is heterogeneous in its chemical content and geometric structure.[4] X-ray absorption fine structure (EXAFS) studies concluded that the iron core of ferritin was made of iron ions that are surrounded by six or seven oxygen atoms, surrounded by another shell of iron ions.[2] This inconsistency leads to the conclusion that the mineral is a heterogeneous, hydrated iron(III)/oxy.[3] In other words, the iron core itself is not packed regularly or in a pattern within ferritin.[6]

The composition of the protein shell does not affect the composition of the iron/oxy mineral, however.[6] In fact, two ferritin proteins that are identical in protein makeup (with same H:L ratio) are likely to have a different make-up of their iron cores. The H:L ratio is suspected to affect the geometry of the crystal, due to their inherently different properties. Because the H-chain hosts the ferroxidase site and L-chain hosts the nucleation site, the rate at which the iron is accumulated and the mineral core is formed varies as the ratio does.[6] Studies on the crystal structure of the mineral core have found some cores to be more highly ordered and crystalline and other less ordered and more amorphous; these observations are thought to be the result of, or at least correlate to, different H:L ratios.[6]

Selectivity of iron(II) by ferritin can be explained through hard-soft acid base (HSAB) theory. HSAB theory characterizes metal ions and ligands as either hard, soft, or borderline acids and bases based on the Lewis definition. Characterization, however, should be noted to be a gradient scale for all ions and ligands.HSAB theory states that similarly characterized acids and bases will be more likely to bind with one another; that is, a hard acid will be more likely to bind to a hard base over a soft or borderline base and vice versa. Borderline acids or bases prefer to bind to borderline bases or acids, respectively; however, borderline is more intermediate in character and more flexible in binding. It isn't uncommon for a borderline acid or base to be more slightly more hard or soft in character.

Ferritin binds an Fe^{2+} ion for oxidation. Fe^{2+} is categorized as a borderline acid. The binding sites on the H-chain are glutamic acid (Glu), histidine (His), and glutamine (Gln) residues (Figure 4).[6] Glu and Gln are categorized as hard bases, while His is categorized as borderline base. The oxidizing agents—oxygen molecules, hydrogen peroxide, or water molecules all have hard character. Fe^{2+} as a borderline acid binds well with the binding site of mixed hard and borderline character. HSAB theory supports the selection of Fe^{2+} as the metal ion for the ligand. The selection of Fe^{2+} in ferritin is further supported by experimental work where metals like zinc (which also exists in the body) were also shown to have binding abilities to ferritin.[5] But, zinc, although it is also borderline, has softer character than Fe^{2+} and so would not be as stable or favorable with the hard Glu and Gln ligands.[10]

Because of the initial selection of Fe^{2+} by the H-chain and the crystalline nature of the iron(III) core, the binding of Fe^{3+} by the protein is not as key. However, Fe^{3+} is characterized as a hard acid and the Glu residues on the L-chain and the oxide species in the mineral are also hard, so binding remains preferable.

Selectivity of Fe^{2+} is further supported by the chelate effect. The chelate effect is an entropic effect where a ligand has multiple donor groups for a metal ion. The entropy increases favorably when a chelator is used to bind because there is one molecule binding to the metal ion through multiple donor atoms, rather than multiple individual ligands. The Fe^{2+} binding site of ferritin is a chelator. At the ferroxidase site on the H-chain subunit, the binding site of the Fe^{2+} ions are shown in Figure 6.

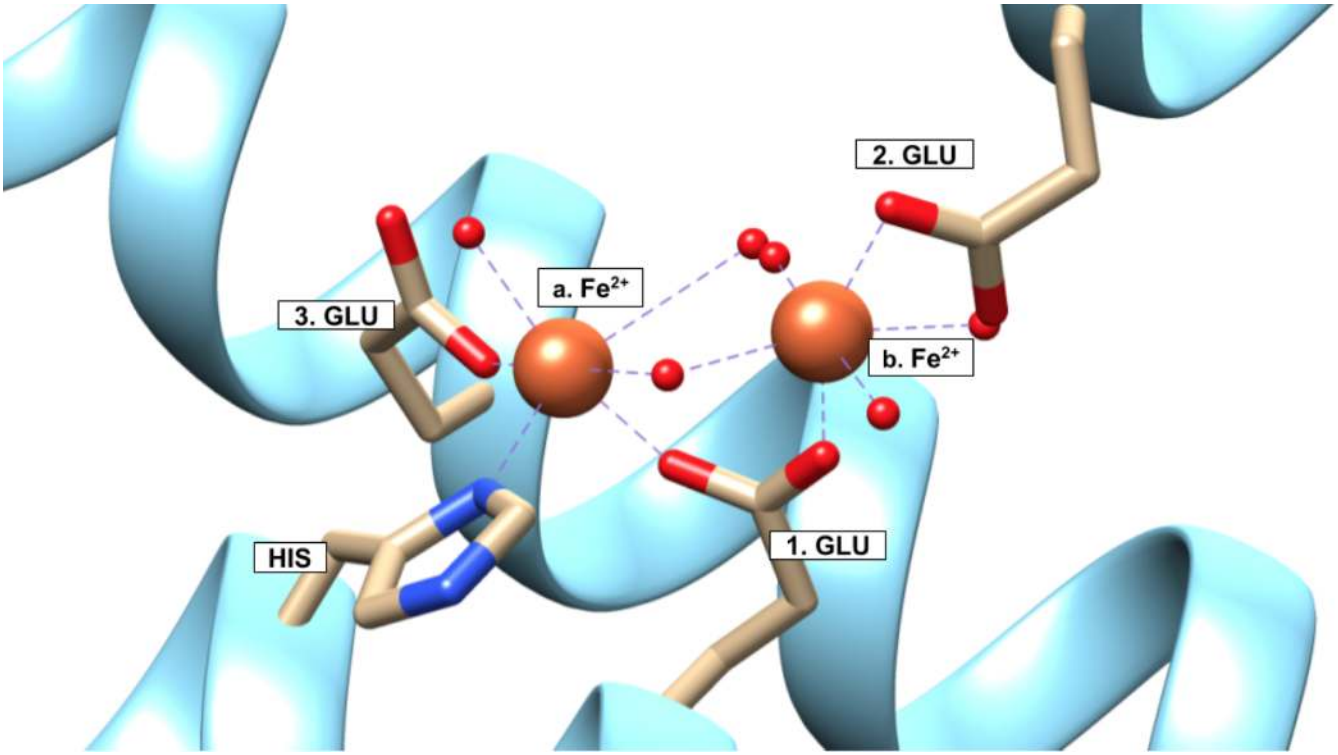


Figure 6. The ferritin protein acts as multidentate chelator for Fe^{2+} at the ferroxidase site. All residues are a part of the same protein. Ferritin binds to a. Fe^{2+} on the left through three different donor atoms, 1. Glu, 3. Glu, and His. Ferritin binds to b. Fe^{2+} on the right through two different donor atoms, 1. Glu and 2. Glu.

According to the crystal structure in Figure 6, the Fe^{2+} binds to a His residue and three different Glu residues all from the same protein. Ferritin can thus be considered a multidentate chelator for Fe^{2+}. The ability for ferritin to perform as a chelator serves ferritin well. Because ferritin stores iron at such high volumes (up to 4500 iron ions), ferritin needs to be able to bind a lot of iron favorably. Based on the increase in entropy from binding, the chelate effect lets ferritin bind iron favorably. That ferritin can bind more than one metal ion to the same molecule creates an even greater increase in entropy and favorability.

Binding at the Ferroxidase Site

The human H-chain has two binding sites for iron(II) called site A and site B. Both sites are occupied by an iron ion, but site A has shown a higher affinity for iron(II).[11] The mechanism for binding at the ferroxidase site is currently unknown. At the present moment, there are two common proposals: the stepwise mechanism and pairwise mechanism.[1] The stepwise mechanism is shown in Figure 7. The mechanism proposes that the two binding sites are occupied one iron at a time.

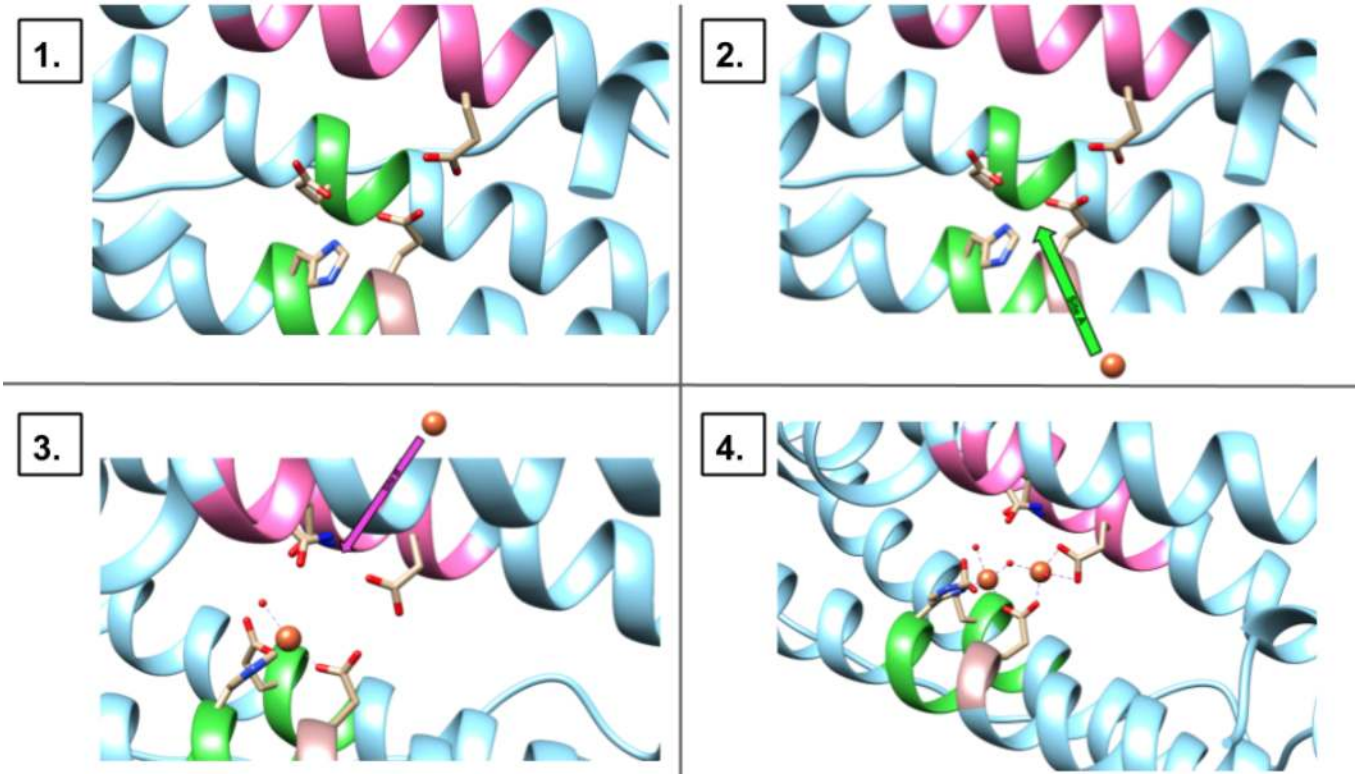


Figure 7. The proposed stepwise binding mechanism states that because site A in green has a higher affinity for Fe (orange spheres) it will be bound before site B in pink is bound by Fe ion. 1. The empty binding site on the H-chain subunit of human ferritin. Site A is in green and on the bottom helix and site B is in pink on the top helix. 2. One Fe^{2+} ion binds to site A. The green arrow denotes where the Fe ion will bind. 3. After site A is bound by iron, a second Fe^{2+} ion binds to site B. The pink arrow denotes where the second Fe^{2+} ion will bind. 4. The di-iron binding site has two iron ions bound. One is bound at site A and one is bound at site B. An oxidizing agent (small red sphere) binds the two metal ions together.

First, one Fe^{2+} binds to site A, then, a second Fe^{2+} will bind to site B. The pairwise mechanism shown in Figure 8 proposes that two Fe^{2+} ions enter site A and site B, in a concerted fashion.

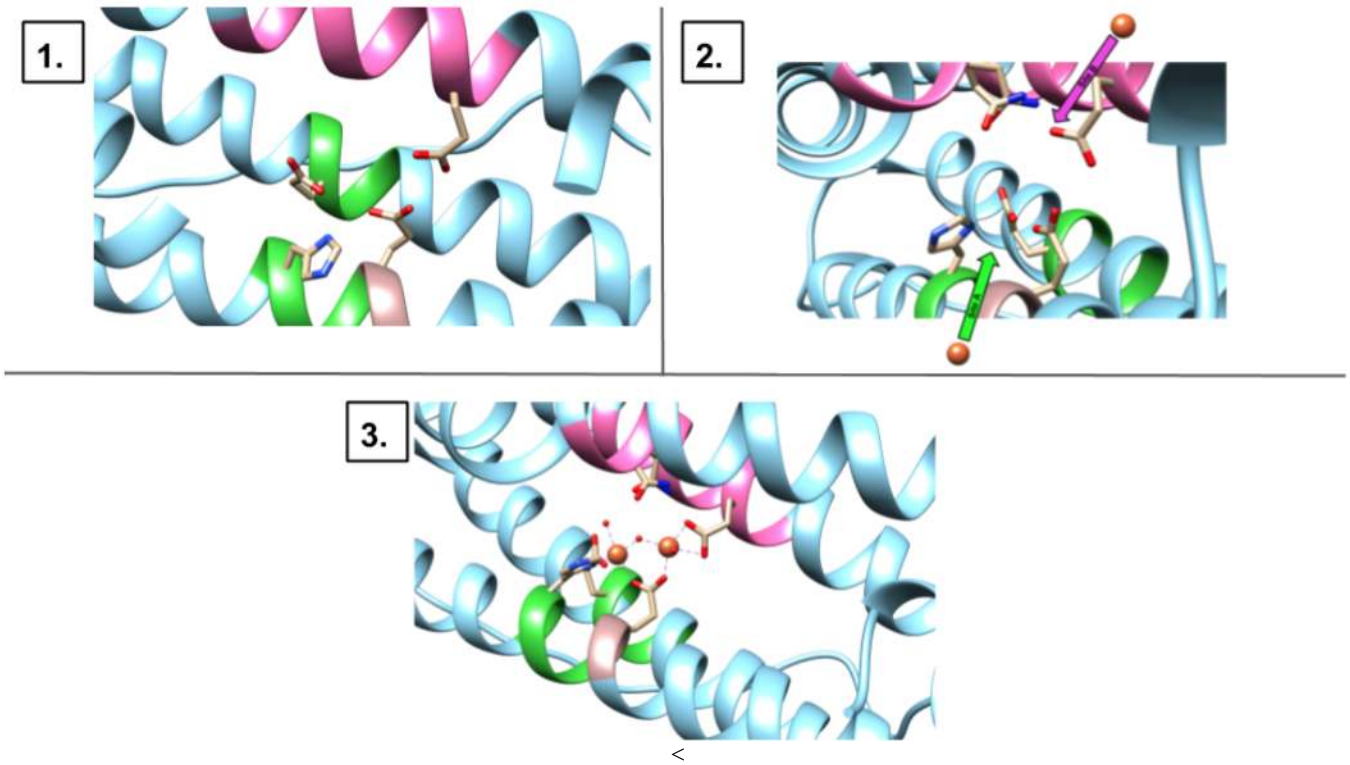


Figure 8. The proposed pairwise binding mechanism states that two Fe^{2+} ions (orange spheres) bind simultaneously to sites A and B. 1. The empty binding site on the H-chain subunit of human ferritin. Site A is in green and on the bottom helix and site B is in pink on the top helix. 2. Two Fe^{2+} ions bind to sites A and B. The green arrow denotes where the Fe^{2+} ion will bind on site A. The pink arrow denotes where the second Fe^{2+} ion will bind on site B. 3. The di-iron binding site has two iron ions bound. One is bound at site A and one is bound at site B. An oxidizing agent (small red sphere) binds the two metal ions together.

There has been evidence, however, that one site, site A, can be occupied by one Fe^{2+} while site B remains unoccupied. This result supports the stepwise mechanism (Figure 7) for binding at the ferroxidase site on the H-chain.[1]

After the iron ions bind to ferritin, a single molecule of some oxidizing agent binds to both ions. The binding of both ions by one molecule is referred to as bridging because the iron ions at sites A and B are bridged by the oxidizing agent.

Redox and Iron Mineralization

Iron(II) is oxidized at the ferroxidase site on the H-chain (sites A and B) by some oxidizing agent, most probably O_2 and H_2O_2.[1] Three reactions/models for Fe^{2+} oxidation and mineralization have been observed. There is a ferroxidation reaction or protein catalysis model (Reactions **1 and 1a-1c**), a mineralization reaction or crystal growth model (Reaction **2**), and a detoxification reaction of Fe^{2+} + H_2O_2 (Reaction **3**).[1] The ferroxidation reaction occurs at the ferroxidase site on the H-chain of ferritin. The ferroxidation reaction for the protein catalysis model of ferritin oxidation can be written as:

$2\ Fe^{2+} + O_2 + 4\ H_2O \rightarrow [Fe^{3+}\text{-O-O-}Fe^{3+}]^{2+}$ (**1a.**)

$[Fe^{3+}\text{-O-O-}Fe^{3+}]^{2+} \rightarrow [Fe_2O\text{-}(OH)_2]^{2+}$ (**1b.**)

$[Fe_2O(OH)_2]^{2+} \rightarrow 2FeOOH_{core} + H_2O_2 + 4\ H^+$ (**1c.**)

Net: $2Fe^{2+} + O_2 + 4\ H_2O \rightarrow 2FeOOH_{core} + H_2O_2 + 4\ H^+$ (**1.**).[1]

The net mineralization reaction for the crystal growth model of ferritin oxidation is written as:

$4\ Fe^{2+} + O_2 + 6\ H_2O \rightarrow 4\ FeOOH_{core} + 8\ H^+$ (**2.**).[1]

The most recently identified of the oxidation and mineralization reactions, the Fe^{2+} + H_2O_2 detoxification reaction is written as:

$2\ Fe^{2+} + H_2O_2 + 2\ H_2O \rightarrow 2\ FeOOH_{core} + 4\ H^+$ (**3.**).[1]

The ferroxidation reaction involves the ferritin molecule most directly. Reaction **1** occurs on the H-chain at the ferroxidase site and has been the reaction focused on up to this point. The two schemes for this reaction that are most frequently proposed are a 2-electron oxidation scheme or a two successive 1-electron oxidation scheme.

The first intermediate produced in reaction **1a** ($[Fe^{3+}\text{-O-O-}Fe^{3+}]^{2+}$) is a μ-peroxo di-iron(III) complex (μ = number of metal ions bridged by a ligand, and μ_2 is often shortened to just "μ"). Raman and Mössbauer spectroscopy, stopped-flow kinetics, and EXAFS have confirmed the existence of the complex. The complex is formed within the first 25-100 ms of the reaction and decays within 150 ms.[1] The μ-peroxo di-iron(III) complex intermediate has been the focus of various studies for its blue coloring and appearance not only in human ferritin, but also other eukaryotic, archaeal, and bacterial ferritin.[12] The blue intermediate from human H-chain ferritin has a UV-vis absorbance of 650 nm and an extinction coefficient measured at 850-1000 $M^{-1}\ cm^{-1}$ per the dimer of $[Fe^{3+}\text{-O-O-}Fe^{3+}]^{2+}$.[1,12] The extinction coefficient (ε < 1000) suggests that this complex is absorbing d-d transitions.

The second intermediate is produced in reaction **1b** ($[Fe_2O\text{-}(OH)_2]^{2+}$) from the decay of the first intermediate is a μ-oxo(hydroxo)-bridged di-iron(III) intermediate.[1] A distance of 3.00 Å has been observed between the two iron ions.[11] Less data is available on this intermediate. While studies have provided strong evidence of the decay of the blue intermediate, the decay product is still in debate and the possibility of a variety of products has been noted.[1]

Oxidation of iron ions for storage in ferritin also proceeds through reactions **2** and **3**. Studies suggest that the primary method and reaction of oxidizing iron for storage in ferritin depends on the flux of iron into ferritin at that time. For example, at a low flux of ≤ 50 Fe^{2+}/ferritin, the iron is oxidized mainly by reaction **1** at the ferroxidase site.[1] However, as more H_2O_2 is produced as a byproduct of reaction **1**, the detoxification reaction (**3**) takes over as the primary reaction. Iron flux of about 100-500 Fe^{2+}/ferritin will cause this switch.[1] Once the iron flux reaches ~800 Fe^{2+}/ferritin, reaction **2** becomes dominant.

Reaction **2** is based on the crystal growth model of ferritin oxidation. At high iron(II) flux into ferritin and after a minimum of 200 Fe^{2+}/ferritin have already formed an iron/oxy mineral core in the center of ferritin, the crystal growth model appears to begin.[1] In this model, iron(II) ions are entering at high rates. Rather than oxidizing every new iron(II) ion at the ferroxidase site or by the detoxification reaction, the iron(II) ions can be oxidized directly by the already-forming iron/oxy mineral core and can be deposited directly onto the mineral.[1] As can be seen in reaction **2**, stoichiometrically, iron(II) ions can be oxidized and directly deposited onto the mineral at 4 Fe^{2+}/O_2, while reaction **1** catalyzed by ferritin can only oxidize 2 Fe^{2+}/O_2.

It has not been determined if both Fe^{2+} ions are required to be bound at the ferroxidase site in order for oxidation to take place. However, unlike binding where there is evidence of a single Fe^{2+} ion being bound at site A, oxidation has never been observed without both Fe^{2+} ions, one at site A and one at site B and bridged by the oxidizing agent, present.[1]

As previously mentioned, nucleation starts on the L-chain subunit of ferritin. However, it is important to note that the majority of the actual iron/oxy mineral formed by the reactions above and held in the center of ferritin does not actually bind to the protein.[8] Instead, the solid mineral core is stabilized by the protein surrounding it.[8]

Metal Center Geometries

The ligands for the ferroxidase site are His and Glu residues as well as a variety of oxygen-containing oxidants, such as O_2 or H_2O_2 molecules.[1,7] Ligand Field Theory (LFT) helps to predict the geometry of metal-ligand complexes. Complexes are classified as high spin or low spin based on the energy field splitting or Δ_o between the non-bonding t_{2g} and the antibonding e_g. High spin complexes will prefer to keep electrons unpaired in the t_{2g}, but low spin complexes will prefer to pair electrons in the t_{2g}. The ligands of LFT encourage strong fields (low spin, large Δ_o) or weak fields (high spin, small Δ_o) based on their categorization as a σ donor, π donor, or π acceptor.

The iron binding sites of ferritin, however, are not simple metal-ligand complexes. As discussed above, when binding to the ferroxidase, two ions of iron(II) bind to the site and are bridged by the oxidizing agent, most commonly O_2. The bridging ligand makes this one binding site and one complex, not two separate single metal or mononuclear complexes. The ferroxidase site is considered to have a di-iron center and to be a dinuclear binding site or dinuclear complex.[1] Because there are two metals in the metal center, molecular orbital interactions in dinuclear complexes are different than those in the one metal center. This difference

is especially noticed in bridged metal complexes, as is present in ferritin, because the orbitals of the two metal ions can overlap.[13] Due to this overlap, electron filling and pairing does not always occur as one would expect with a single metal center.

These dinuclear bridged complexes with iron(II) and iron(III) are not unique to ferritin, but have been seen in methane monooxygenase (MMO), ribonucleotide reductase (RNR), and fatty acid desaturase.[8,12] Comparisons with these other proteins with ferritin have been attempted, but iron's special role as a substrate in ferritin rather than an enzyme cofactor in the others sets it apart and makes ferritin more difficult to discern.[12] Furthermore, the comparisons with these other proteins is not completely correct based on the lability of the di-iron complexes in ferritin. The di-iron(II) binding site complex and the di-iron(III) intermediates of oxidation are labile as they react, degrade, and move toward the center of ferritin. In contrast, the di-iron complexes of MMO are stable cofactors.

For ease, ferritin's ferroxidase binding site will be analyzed according to LFT without consideration of the overlapping of molecular orbitals. Note though that the following analysis does not entirely capture the complexity of the metal-ligand-metal interactions.

According to LFT, His residue is a π acceptor and a weak field ligand. This ligand increases Δ_o and encourages low spin complexes. All oxygen ligands, including water, OH^-, O^{2-}, and Glu residues are π donors and weak field ligands, which decrease Δ_o and encourage high spin complexes. A close-up of the binding sites at the ferroxidase site, such as in Figure 7, shows that the majority of the ligands for both a. Fe^{2+} and b. Fe^{2+} are water or the like and Glu residues, the high spin complex-favoring ligands. Fe^{2+} is a $3d^6$ transition metal with a charge of +2 and thus can be high or low spin. However, when bound to H_2O, Fe^{2+} is high spin with an electron filling diagram shown in Figure 9.

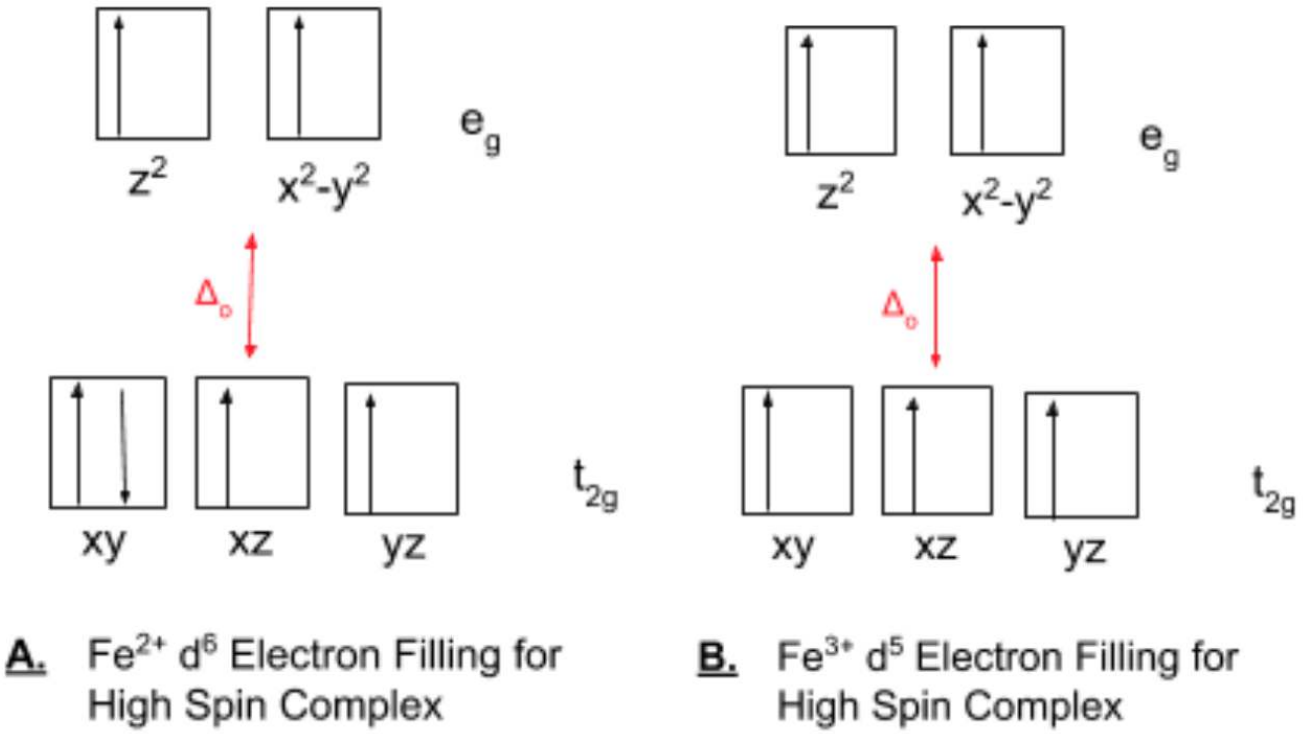


Figure 9. A. LFSE splitting diagram for a high spin single Fe^{2+} metal center. Electrons occupy e_g before pairing up. Δ_o is small. B. LFSE splitting diagram for a high spin single Fe^{3+}. Electrons occupy e_g before pairing up. Δ_o is small.

The complex is thus, overall, high spin and has been described in the literature as initially binding in a high-spin state with octahedral geometry shown in Figure 10.[11,14]

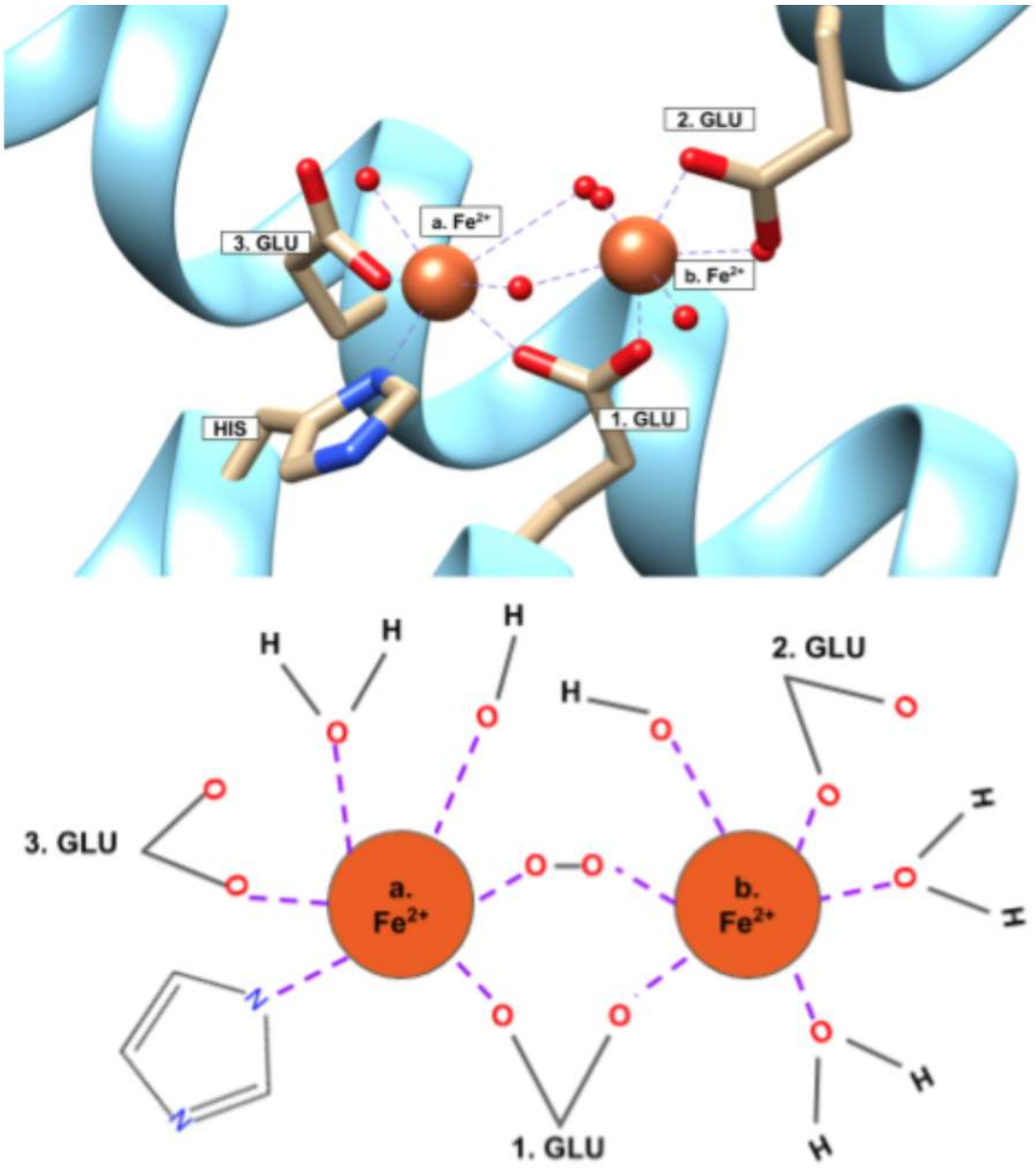


Figure 10. The octahedral geometry can be seen in the crystal structure and in the cartoon diagram extracted from the crystal structure to show the six ligand coordination more clearly. Adapted from Bou-Abdallah, et al.

The ligands for the iron oxide mineral are primarily H_2O, OH^-, or O^{2-}. These use the oxygen as the donor atom. These are all high spin ligands that contribute to the weak field. These ligands will favor a smaller Δ_o and keeping electrons unpaired. Fe^{3+} is a $3d^5$ transition metal with a +3 charge and is more likely to be low spin based on recorded, however, known values of Δ_o for Fe^{3+} and literature on the Fe^{3+} intermediates categorize these Fe^{3+}-O-Fe^{3+} groups as high spin (see electron filling diagram in Figure 9 for a single metal center high spin diagram). $\Delta_o$will thus be smaller and weak field ligands such as the oxygen ligands will be favored.

To highlight the complexity of the dinuclear metal-ligand complex, studies on the magnetic susceptibility (the ratio of magnetic moment per unit volume to the applied magnetizing field intensity) of the Fe^{3+}-O-Fe^{3+} groups suggest that the high spin iron complexes have about one unpaired electron per group.[14] This calculation is clearly in conflict with the molecular orbital diagram in Figure 9, yet the complex is still known to be on average octahedral and high spin.[14] The calculation magnetic moment itself has been a controversial pursuit among scientists.[9]

Iron Release

When cells require iron, for enzyme synthesis, after blood loss, or during embryonic development, the iron stored in ferritin must be released rapidly, on demand, and under control.[8] Although, as with many aspects of ferritin function, the mechanism of iron release to the cell from ferritin is unknown. What is known inherently about the process is that over its course it must essentially reverse mineralization: the iron(III)/oxy mineral must be dissolved from its solid state to aqueous ions and the iron(III) ions must be reduced to iron(II).

Proposed models for ferritin iron release include (1) an equilibrium between the iron stored in ferritin and the iron in the cytoplasm of the cell, (2) ferritin protein degradation, (3) spontaneous, direct dissolution of iron(III) from the mineral core from scavenging by iron(III) binding proteins, and (4) the reduction of the iron(III) mineral which is then complexed iron(II) by a chelating agent and transported out of ferritin.[4,12] The last model (4) lacks confirmation, yet is considered by many to be the physiological mechanism. This model is the most efficient method and the presence of reducing agents under physiological conditions.[4]

Except the second model (2), the physiological relevance of all above models is still to be seen.[12] The ferritin degradation model (2) is the only mechanism to have been observed under physiological conditions. However, since this model would require iron release to be dependent of the turnover and synthesis of ferritin, another model is suspected to be necessary.[12]

However iron is released from ferritin, studies indicate that the physical exit of the iron from ferritin takes place via the 3-fold channels. One proposal for exit based on observations in bacterial ferritin is the localized folding/unfolding of ferritin.[4] The ferritin channels can be unfolded without affecting the overall function or structure of the protein. Unfolding the channels and thus, widening the opening, would allow for quick release of demineralized iron. The channels become highly disordered when this occurs to the effect that they do not appear in crystal structures.[8]

Much remains to be determined about human ferritin. Other functions of ferritin in the body, and the mechanisms for how Fe^{2+} enters and binds to ferritin, how Fe^{2+} is oxidized to Fe^{3+} for storage, and how iron is released remain undetermined, among others, are thought to be non-universal—even within the same organism.[3,6]

While much of the chemistry behind ferritin is, as of now, unexplained, ferritin is still an important protein for all life. Wherever iron is noted as an essential nutrient, ferritin must also be present for management and storage. The elucidation of ferritin can lead to advancements in iron metabolism and neurological disorders and new uses of ferritin chemistry in nanochemistry and catalytic industrial applications.[3,4]

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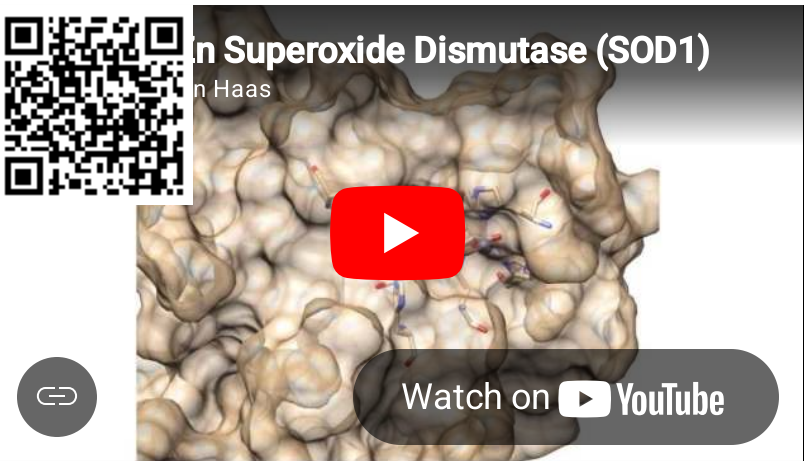
*This work was originally written by **Anna Shadid,** Spring 2018: Anna is currently (as of 2018) a junior chemistry major at Saint Mary's College in Notre Dame, IN.*

This work was originally edited by Dr. Kathryn Haas, Associate Professor, and Madison Sendzik, Teaching and Research Assistant, of Saint Mary's College.

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10.5: Antioxidant- Cu/Zn Superoxide dismutase (SOD1)

This is a video introduction to the Cu,Zn superoxide dismutase (SOD1), which acts as an antioxidant in the cytoplasm of mammalian cells. (PDB 1sxz)



The role of the copper-zinc superoxide dismutase system (SOD1) is to catalyze the conversion of the potentially toxic superoxide anion, $O_2^{\cdot-}$, to the less toxic substance hydrogen peroxide, H_2O_2. Dioxygen, O_2, is also a product of this reaction.[1] Superoxide is produced in aerobes as a product of metabolism. The superoxide anion can be an intermediate or a byproduct of metabolic processes such as respiration or photosynthesis.[2] Superoxide, $O_2^{\cdot-}$, is toxic when in the protonated form, $HO_2^{\cdot}$, and can cause damage to the cells.[1] Superoxide is involved in the oxidative damage phenomena also known as *oxidative stress*.[2] Oxidative stress is harmful and it is caused by radicals, such as superoxide, that can attack lipids, proteins, and DNA within the body. Oxidative stress is linked to many human diseases including hypertension, diabetes mellitus, ischemic diseases, and malignancies.[3] Cells use superoxide dismutase in order to prevent oxidative damage by removing superoxide free radicals.[2]

Superoxide dismutase participates in a dismutation reaction in order to convert superoxide into the less toxic substances of hydrogen peroxide and dioxygen. A dismutation reaction is a reaction in which one substance is oxidized and the other is reduced simultaneously.[5] There are two redox reactions that occur in the copper zinc superoxide dismutase system, and copper catalyzes these reactions. In one reaction Cu^{2+} is reduced to Cu^{1+}, while the superoxide molecule, O_2^{-}, is oxidized to O_2. In the second step Cu^{1+} is oxidized to Cu^{2+}, while a second superoxide molecule is reduced to hydrogen peroxide, H_2O_2.[7] A simplified catalytic cycle can be seen in the Figure below.

The overall reduction potential of the overall reaction is dependent on the half reactions which are:

$$O_2 \rightarrow e^- + O_2^- \tag{10.5.1}$$

with E = -0.16 V

$$O_2 + e^- \rightarrow 2H^+ + H_2O_2 \tag{10.5.2}$$

with E = +0.89 V

Therefore, the overall reduction potential of this reaction must be within -0.16V and 0.89V.[6]

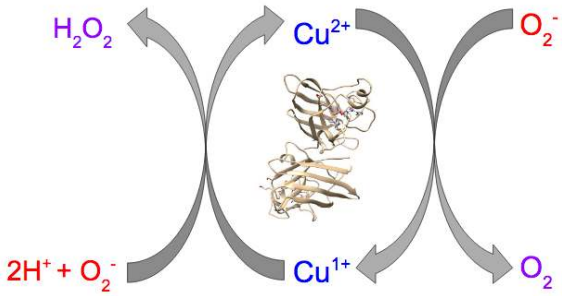
> ***The overall reaction catalyzed by superoxide dismutase enzymes is shown below. When catalyzed by Cu,Zn Superoxide Dismuase (SOD1), the reaction happens in two steps: In one step, Cu^{+2} at the enzyme active site is reduced to Cu^{+1} as superoxide is oxidized to dioxygen. (see right of simplified reaction cycle shown below) In another step, Cu^{+1} is oxidized to Cu^{+2} as superoxide is reduced to hydrogen peroxide. This step also requires two hydrogen ions (see left of simplified reaction cycle shown below).***

Overall Reaction:

$$2\,O_2^{\bullet -} + 2H^+ \rightleftharpoons H_2O_2 + O_2$$

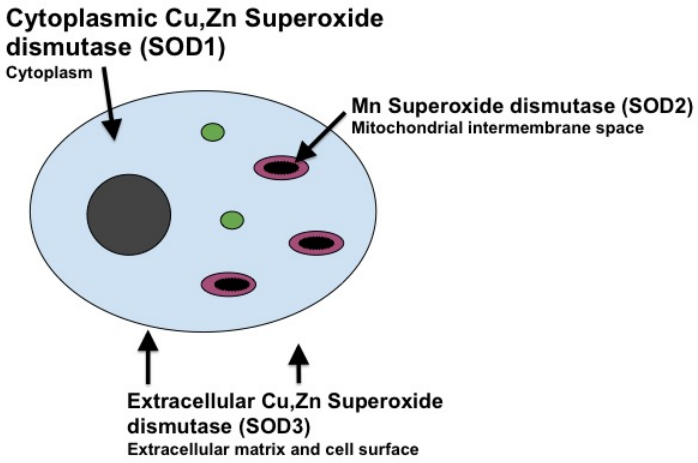
superoxide — hydrogen peroxide and dioxygen

Simplified Catalytic Cycle:



There are three different types of superoxide dismutase that are found in mammals. The primary form of superoxide dismutase is Cu,Zn superoxide dismutase, which is referred to as SOD1. SOD1 is primarily found in the cytoplasm of cells but a small portion is found in the intermembrane space of the mitochondria. A key feature of SOD1 is that is possesses a copper cofactor, which is used to catalyze the superoxide dismutation reaction. A second type of superoxide dismutase is manganese superoxide dismutase, which is referred to as SOD2. Manganese superoxide dismutase is found in the mitochondrial matrix of the cell. SOD2 is produced in the cytoplasm and then transported to the mitochondrial matrix. Manganese (Mn) is the metal cofactor used to catalyze the conversion of superoxide in SOD2. A third type of mammalian superoxide dismutase is the extracellular Cu,Zn superoxide dismutase, referred to as SOD3. SOD3 is primarily found in tissues on the extracellular matrix and on cell surfaces. There is a small amount of SOD3 that is found in plasma and extracellular fluids. SOD3 is similar to SOD1 in that it poseses copper at its active site.[4] This page focuses specifically on SOD1.

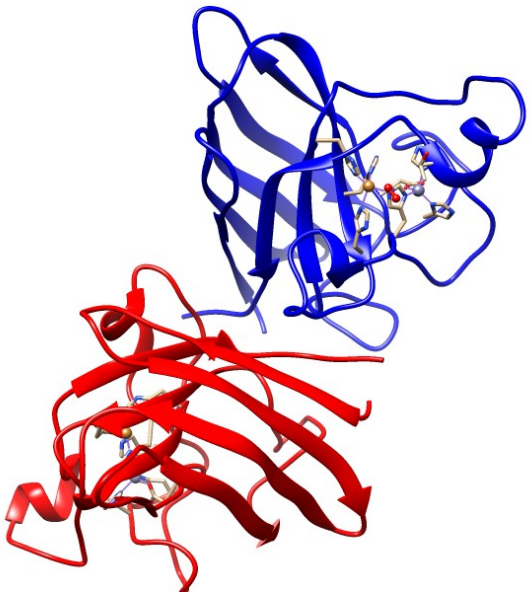
This figure illustrates the three types of SOD found in mammals, and their primary localization in reference to the cell.



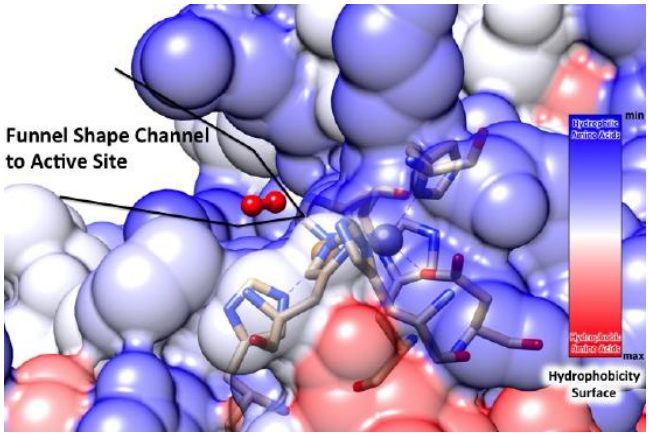
Amyotrophic lateral sclerosis (ALS), the disease commonly referred to as Lou Gehrig's disease, can be caused by a genetic mutation in SOD1. About one tenth of all cases of ALS are hereditary, and in these hereditary cases of ALS there are mutations in the SOD1 gene. Much research has been aimed at understanding how this mutation in SOD1 causes ALS, with hopes of developing better treatments or a potential cure for this disease.[5]

The SOD1 protein is a dimer composed of two identical subunits (homodimer). The two subunits are differentiated in red and blue in the Figure below. The two subunits are oriented so the two active sites are facing away from each other. Each subunit is composed of 151 amino acid residues. These amino acids are arranged in eight β-sheets and three exterior loops. Each subunit contains a copper ion and a zinc ion at the active site. The copper ion acts as an electron transfer center in this catalyst, while the zinc ion serves as a structural scaffold and a contributes to the positive charge of the active site, which attracts the negatively charged superoxide anion.

Ribbon diagram of the reduced form of Cu,Zn SOD with two subunits differentiated in blue and red. Active site side chains and metal cofactors are shown with superoxide bound. (Modified from PDB 1sxz). [6]



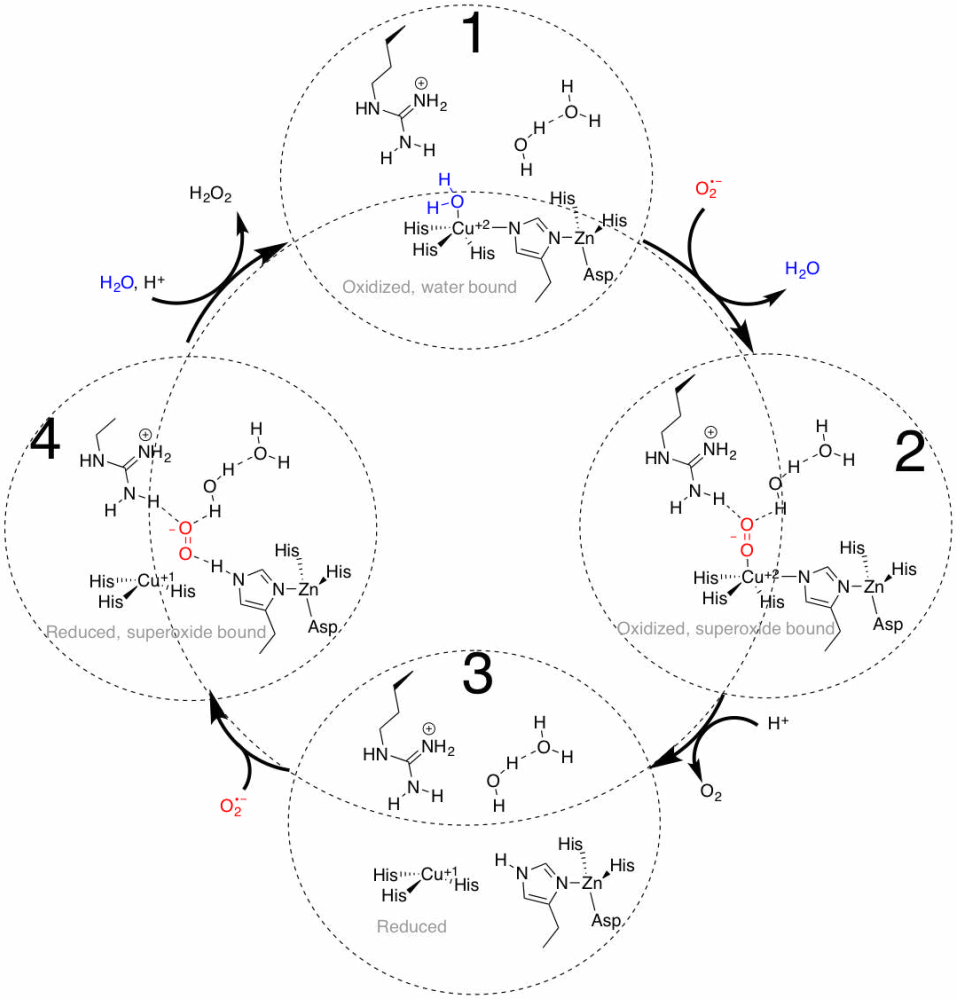
The placement of the active site of this complex as well as the geometry surrounding the copper metal centers are critical for this reaction to occur. The active site of this complex is at the bottom of a channel. The copper ion is exposed at the bottom of this channel to allow binding of superoxide to the copper ion, while the zinc ion is buried within the protein.[8] This funnel shape leading to the active site is very important to the superoxide dismutase function.[9] Superoxide dismutase has a very small active site compared to the entire size of the enzyme. The small funnel shape is selective towards small molecules such as superoxide, as seen in the Figure below. In the funnel shaped channel are copper and zinc cations as well as two positively charged hydrophilic amino acids, histidine and arginine. The strong positive charge provided by these amino acids and metal ions attracts the negatively charged superoxide to the active site where the superoxide can be converted into less toxic substances.[5]



At the active site of Cu,Zn superoxide dismutase, copper provides a redox-active binding site for the superoxide anion, while zinc provides structural support and positve charge.[1] **There are several histidine amino acids that surround the copper and zinc metal centers**. The copper ion is bound to either three or four histidine side chains, and may also be bound to either water or superoxide, depending on the copper oxidation state and the step in the catalytic cycle (see Figure below). The zinc coordination is more static, and zinc is consistently bound to three hisidine and one aspartate side chain (see Figure below).

The four steps of the detailed catalysts cycle are shown below. This catalytic cycle alternates between electron counts of 19 and 16. Structure 1 below is of the copper(II) metal center with a four histidine ligands and a water ligand. This five coordinate system yields an electron count of 19. Then the water molecule is displaced as the superoxide molecule binds to copper(II). This is a ligand substitution reaction and once again the structure that is formed, seen as the structure on the right of Figure 13, has 19 electrons. When copper(II) is reduced to copper(I), there are only three histidine ligands that are attached. This copper(I) structure in a trigonal planar geometry is illustrated below as tStructure 3. This copper(I) structure with three ligands attached yields an electron count of 16. Then superoxide binds near copper in the active site, and the copper(I) is oxidized to copper(II), while the superoxide molecule is reduced to hydrogen peroxide. A water binds to the oxidixed Cu^{+2}, to return to structure 1 with an electron count of 19. This continuous cycle converts the superoxide molecule to hydrogen peroxide and dioxygen.[9,10]

The detailed catalytic cycle at the active site of SOD1. Adapted from reference 9.



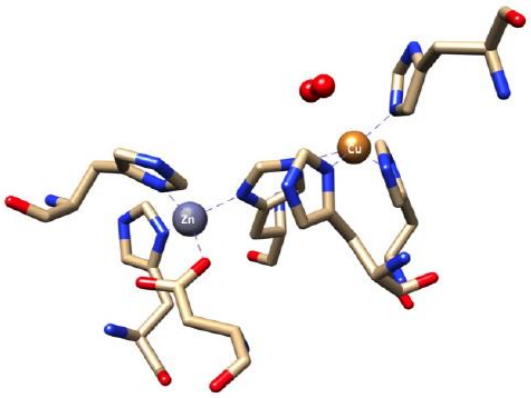
Hard-soft acid-base (HSAB) theory predicts that "like" classes of acids and bases prefer to interact (ex: hard acid + hard base is better than hard + soft), thus this binding site of primarily borderline bases is ideal for their borderline metal cations. The aspartate, which is bound to zinc and is a hard donor atom, may provide charge balance.According to Ligand Field Theory (LFT), histidine amino acids are strong σ donors and are π acceptors. Thus, histidine is a relatively strong field ligand ,compared to water and other

amino acid side chain ligands, and would encourage a relatively large Δ. The aspartate is both a σ donor and π donor, and is a weak field ligand.

Ligand field theory would predict the geometry surrounding the copper(II) metal center as Jahn-Teller distorted octahedron. This would create either a square pyramid or square plane geometry. The geometry that surrounds the copper(II) metal center, however, is a distorted square pyramid when ether water or superoxide is bound (see structures 1 and 2 in the figure above).[1] This distorted from the ideal geometry for a d^9 metal center such as copper(II). However, this causes a slight destabilization of the copper(II) metal center, which helps promote copper into its d^{10}, monovalent oxidation state. In other words, the destabilization of Cu(II) allows redox cycling to occur more easily (this is also related to Marcus theory, and this article should be elaborated to describe application of Marcus Theory). If the geometry was a perfect square pyramid, the Cu^{2+} would be more stable, and it would be more difficult to reduce to Cu^{+1}. In the redox reaction, the copper(II) metal center oxidizes the superoxide molecule to dioxygen, while the copper(II) metal center is reduced to copper(I). This step (from 2 to 3 in the figure above) occurs via an **inner sphere electron transfer** as the superoxide molecule is bound directly to the copper(II) metal center.[8] Upon reduction of copper, the dioxygen product is immediately released (structure 3, figure above). According to hard-soft acid-base theory, hard acids are attracted to hard bases and soft acids are attracted to soft bases. The superoxide molecule is a hard base and copper(II) is a borderline acid. Thus the binding of superoxide directly to the copper(II) metal is not surpising based on their close hard-soft acid-base character.

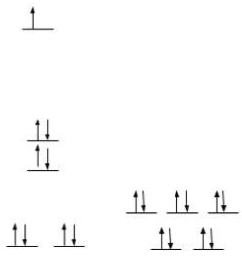
Ligand field theory cannot predict a preferred geometry surrounding the copper(I) metal center, as Cu^{+1} is a d^{10} metal, and there is no ligand-field stabilization energy. The geometry that surrounds the copper(I) metal center in SOD1 is a distorted trigonal plane (structures 3 and 4, figure above).[1] In conversion from structure structure 3 to 4 in the figure above, superoxide binds in the active site through H-bonding and electrostatic attraction, however does not directly coordinate to the copper center. In conversion of structure 4 to 1, the copper(I) metal center reduces the superoxide molecule to hydrogen peroxide, while copper(I) is oxidized to copper(II).[9] The fact that superoxide binds directly to copper(II) in the first part of the cycle (structure 1 to 2 above), but does not bind directly to copper(I) in the second part of the cycle (structure 3 to 4 above) is not surprising based on hard-soft acid-base principles. According to hard-soft acid-base theory, the soft copper(I) ion is not a preferred acid for the hard superoxide base.

A "snapshot" of the Cu,Zn SOD active site, adapted from PDB structure 1SXZ, is shown below. In the PDB structure, 1SXZ, azide is bound to the reduced copper center. We have converted azide to superoxide.



The active site of SOD1 has a zinc metal center that is present for structural support and stabilization. Ligand field theory does not play a role in the determination of the geometry surrounding the zinc metal center since zinc is a d^{10} metal and does not have ligand field stabilization energy. Instead. the geometry is determined by steric preference of ligands and structural constraints imposed by the protein. For example, the tetrahedral geometry, with bond angels of 109.5° is preferred in terns of sterics compared to a square plane, with smaller bond angles of 90°. Thus, the geometry that surrounds the zinc metal center is distorted tetrahedron which is the favored geometry due to sterics and structural constraints imposed by the polypeptide.[1]

The crystal field splitting diagrams for the copper metal center is a distorted square pyramid geometry and the zinc metal center in a tetrahedron geometry are shown below.



Cu^{2+} is a d^9 metal; therefore, there is an empty orbital for an electron to move up in energy as seen in Figure 11. Therefore, d-d transitions can occur in this molecule when superoxide dismutase is in its reduced form, Cu^{2+}. However, when superoxide dismutase is in its oxidized form, Cu^{1+}, d-d transitions cannot occur. This is because Cu^{1+} is a d^{10} metal. Therefore, all of the orbitals will be filled. Figure 12 is the crystal field splitting diagram of Zn^{2+} in a tetrahedral geometry. Zn^{2+} is a d^{10} metal; therefore, all of the orbitals are filled so d-d transitions cannot occur here. The square pyramidal crystal field splitting diagram indicates that there are electrons in the anti-bonding orbitals, therefore, weakening the bonds. This makes the molecule more labile and more reactive, making the reaction more likely to occur.

The copper-zinc superoxide dismutase system is a necessary molecule in the body that converts the toxic superoxide molecule into the less toxic substances of hydrogen peroxide and dioxygen. The superoxide molecule can cause oxidative damage in the body. There has recently been discovered a connection between a mutation in SOD1 and a hereditary form of Lou Gehrig's disease. This molecule catalyzes the dismutation reaction of the conversion of superoxide. This reaction occurs due to the destabilization of the copper(II) metal center due to the distorted square pyramid geometry and the lability of copper. The zinc metal center is a structural scaffold for this molecule. The copper, zinc superoxide dismutase system is a necessary for the body in order to prevent oxidative damage that can affect lipids, proteins, and DNA.

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This work was originally edited by Dr. Kathryn Haas, Assistant Professor at Saint Mary's College.

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10.6: Keep Cu Safe- Intracellular Copper Chaperones

Copper Chaperone Atx1

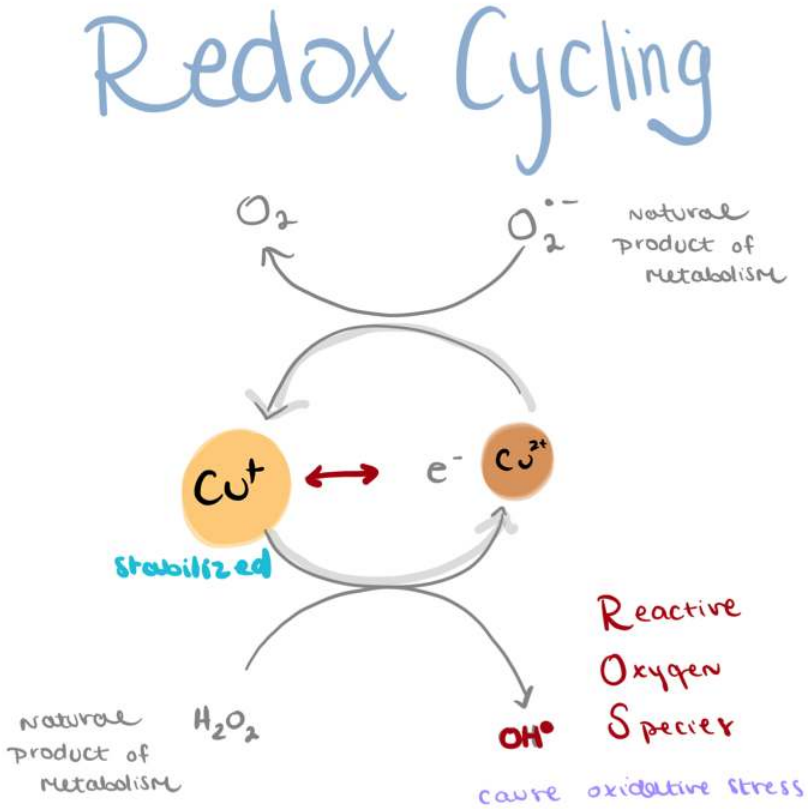
Copper chaperones are intracellular proteins that protect Cu along the pathway from Cu entry into the cell, through the cytoplasm, to its intracellular targets. This page focuses on the yeast Cu chaperone Atx1. Intracellular Cu chaperones, like Atx1, are well-conserved throughout eukaryotic species. The analogous protein in mammalian cells is Atox1.

This is a video introduction to the intracellular yeast Cu chaperone protein Atx1 (or Atox1 in mammals).



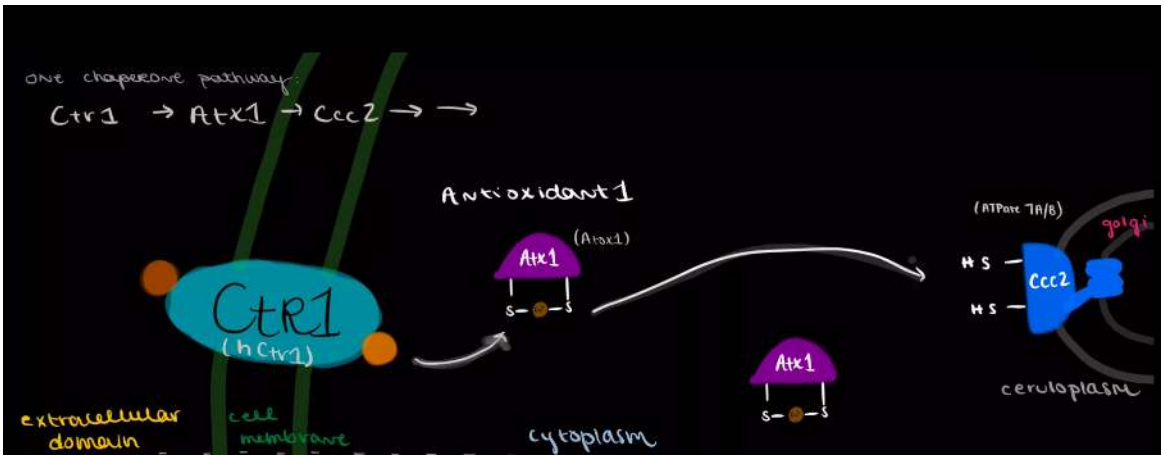
A copper chaperone is protein which binds intracellular copper and delivers it safely to essential intracellular locations. The primary function of a copper chaperone protein is to prevent unwanted, and dangerous, oxidizing reactions of copper as it travels through the cytoplasm. Unwanted redox cycling of copper causes a chain of aberrant chemical reactions that occur in the cell when unregulated Cu(I) interacts with oxidative species and then produces Cu(II) and reactive oxygen species, or ROS.[1] The reactive oxygen species, such as $HO^{\bullet}$, are hazardous to the health of the cell because the potential impact of oxidative stress when they interact with proteins and surfaces within the cell, overall leading to the aging and potential death of the cell. Figure 1 below provides a scheme for redox cycling in the cell. This reaction is continually harmful because the Cu(II) may be reduced to Cu(I) and the cycle continues to cause cell damage as long as the metal remains free. If copper chaperones do not properly transport and protect intracellular copper, the reactive products of redox cycling will irreversibly damage the cell. In order to prevent redox cycling, the copper chaperone stabilizes one oxidative state of copper; the Cu(I) oxidation state is selected because the cell is a reducing environment and prefers this case already.[1]

Redox cycling occurs when reactive products of metabolism meet free copper to produce oxidative species that may cause damages to the cell. (Original artwork by Adrienne Bruggeman)



This page focuses on the yeast copper chaperone, **Antioxidant1, or Atx1** in shorthand. Copper chaperone Atox1 is the homologous chaperone present in mammalian (human) cells.[2] Yeast (*Saccharomyces cerevisiae*) is a model system that is simpler to study than mammalian cells. Most of what we know about the copper transport pathways of mammalian cells is derived from yeast model studies. Atx1 in yeast is assumed to be identical in its function to the human protein, Atox1.[2] These proteins are part of an elaborate system dedicated to safe copper transport through the cellular cytoplasm. This system protects the cell by relaying copper from the plasma membrane protein Copper Transporter 1 (Ctr1), to Atx1, to the ATP-dependent Cross-Complements Ca^{2+} protein, abbreviated Ccc2, which takes Cu into the golgi.[3] In short, the Atx1 is a member of a team of proteins dedicated to copper transport, protection, and usage through the cell. In mammalian cells, the copper chaperone Atox1 accepts copper from hCtr1 and delivers to proteins ATP7A and ATP7B. Atx1 and all copper chaperones are integral features of copper transport within the cell, most importantly stabilizing the Cu(I) oxidation state in order to prevent the harm caused by redox cycling.

The figure below illustrates one of the yeast intracellular Cu pathways which is mediated by the Cu Chaperone Atx1 (or Atox1 in mammals). Atx1 shuttles Cu from its cellular entry point at Ctr1 to the golgi, where it can be incorporated into enzymes destined for outside the cell. Ctr1 is the plasma membrane Cu transporter that is responsible for transporting Cu from the extracellular environment to the cytoplasm (hCtr1 in human). Ccc2 is the ATP-dependant protein that recieves Cu from Atx1 and transports Cu into the golgi. ATPase7A and ATPase7B are the human analogs to yeast Ccc2. (Original artwork by Adrienne Bruggeman)

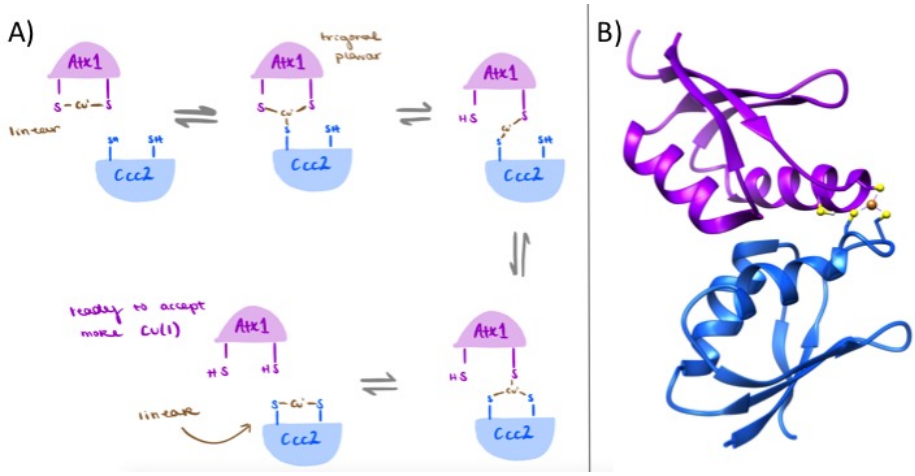


Hard soft acid base (HSAB) theory can be applied to explain how the chaperone's donor atoms help to stabilize Cu(I) over Cu(II) to prevent redox cycling. The theory of HSAB categorizes acids and bases according to ionic radius, charge/ion balance, and charge of ions to predict the binding capacity between an acid and a base.[4] The HSAB theory follows the convention that soft acids and bases prefer to interact while hard acids and bases prefer to interact compared to a hard-soft mixed interaction. According to this theory, the thiolate (S^-) ligand of a deprotonated cysteine is a soft base due to its large ionic radius and small charge. Similarly due to radius and charge, Cu(I) is characterized as a soft acid, while Cu(II) is characterized as a borderline acid. Thus, the soft binding site of Atx1 prefers to bind with the soft Cu(I) rather than the borderline Cu(II), and in the presence of both, the sulfur will prefer the Cu(I) and not the Cu(II). This strong preference for Cu(I) over Cu(II) increases the stability of Cu(I) in the cell, and helps prevent it from being oxidized to Cu(II). This stabilization of Cu(I) discourages undesirable redox cycling.

Ligand Field Theory (LFT) is another principle of coordination chemistry that can be applied to explain how Atx1 stabilizes the Cu(I) oxidation state. The d^{10} electron filling of Cu(I) results in a ligand field stabilization energy (LFSE) of zero.[5] The value of zero comes from the balance of a full set of electrons in higher energy orbitals and in lower energy orbitals. A zero LFSE indicates that there is no stabilization energy for any particular geometry, and thus gives the Cu(I) freedom to bind in any geometry.[2] When bound to Atx1, Cu(I) takes a linear geometry between two cysteine residues. Cu(II) is a d^9 metal with a LFSE of -0.6Δ. This negative stabilization energy indicates that the Cu(II) will have geometric preference for octahedral-type geometry, and thus would disfavor 2-coordinate binding geometries.[5] Thus the geometry of the Atx1 binding site is disfavorable to Cu(II), further stabilizing the preference of Cu(I) in the cell.

The zero LFSE of Cu(I) also assists in the transfer mechanism from the copper chaperone to another protein, such as Ccc2. During the docking and transfer process to Ccc2, copper bound to Atx1 forms an additional bond with an adjacent cysteine residue of the docked Ccc2 protein before breaking any initial bonds with Atx1.[3] Part A of the figure below provides an illustration of the transfer mechanism from Atx1 to Ccc2. Note that the geometry transitions from linear to trigonal planar before breaking the bonds with Atx1 and returning to a linear geometry at the Ccc2 site.[3] The two-coordinate linear and three-coordinate trigonal planar complexes are both favorable to the Cu(I) over Cu(II) due to the LFSE preference. This mechanism again promotes stability of Cu(I) and disfavors Cu(II).

A) The cartoon diagram of the Atx1 transfer of copper to Ccc2. The complex begins as 2-coordinate, becomes 3-coordinate twice during the transfer and ends as 2-coordinate again. (Original artwork by Adrienne Bruggeman) B) A ribbon diagram of the three-coordinate complex of Atx1 (purple) to Ccc2 (blue).



C) Below is an animation of the transfer mechanism illustrated above.



The Cu chaperone transfer mechanism also makes sense in terms of electron counting (think 18-electron rule). As previously mentioned, Cu(I) is a full shell d^{10} metal and is bound to two sulfurs of the Atx1 chaperone. Each of the sulfur ligands will donate two electrons to the copper. Thus the total electron count of the metal binding site is 14. A metal's capacity for electrons is 18, and since the copper does not yet have 18, it is able to accept electrons until it reaches this capacity. This ability to accept electrons is relevant to the copper chaperone system because at its binding step, which docks the copper to Ccc2, the copper accepts an additional sulfur bond before breaking either of the preexisting cysteine bonds with Atx1. Cu(I)'s ability to accept an additional ligand from Ccc2 while it is still coordinated to Atx1 means that that the metal will not be released as a free ion into the cell.[3] Thus Cu is always "protected" by Atx1 and/or Ccc2 coordination, preventing redox cycling.

The LFSE and geometry-fluidity of Cu(I) not only impacts the transfer mechanism towards greater stability of Cu(I) over Cu(II), but also reduces the thermodynamic energy cost during the transfer of Cu between Atx1 and Ccc2. Through the geometry-fluidity of Cu(I), the metal will bind to the chaperone reversibly and easily change its geometry when necessary. Thus at the end of the mechanism, an unbound Atx1 is produced.[6] If Cu(I) tended to bind with a specific preferred geometry, it would be more difficult to change out of that geometry. Thus the zero LFSE allows the Cu(I) to change geometry with low thermodynamic cost.

Finally, the lability of the Cu(I) reduces the energy cost of the transport from Atx1 to Ccc2. When a metal ion is labile, this means that it reacts at a high kinetic rate and may readily replace ligands in coordination complexes.[7] Copper, both as Cu(II) and as Cu(I) is especially labile. This lability comes as a result of the presence of d-electrons in the complex's high energy antibonding orbitals. When these electrons are present in the high energy orbitals, they contribute to high lability (the complex exchanges ligands at a high rate). When the Cu(I) enters the cell through Ctr1, the copper chaperone complex binds and transports the copper through the cell to the metal's next binding site. The copper's high lability is necessary so that the metal is able to change ligands readily, thus encouraging the ongoing binding and transport of the metal between chaperones and target proteins.[7]

The protective function of the copper chaperone is realized by the application of many chemical principles towards the prevention of redox cycling in the cell. In order to best prevent redox cycling, Atx1 stabilizes one oxidation state of copper. Because the cell is a reducing environment, it prefers Cu(I) over Cu(II), and because Ctr1 delivers copper in this form into the cell, the copper chaperone Atx1 is best suited to stabilize Cu(I). According to HSAB Theory and Ligand Field Theory, the binding site of Atx1, composed of two linear cysteines, stabilizes Cu(I) over Cu(II). Similarly, the mechanism of copper transfer from Atx1 to Ccc2 is used to further stabilize Cu(I) over Cu(II) in the cell and to prevent the exposure of free copper to the cell. Through coordination geometries only accessible to Cu(I) and the high lability of copper, the copper chaperone is able to transfer copper stably and with low energy costs. The ability for Atx1 and any copper chaperone to bind stably with copper not only successfully transports biologically needed metal ions, but also proactively reduces the damaging effects of free copper, redox cycling, and oxidative stress to the cell.

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10.6: Keep Cu Safe- Intracellular Copper Chaperones is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

10.7: Cytochrome C

All cells require energy in the form of ATP, Adenosine Triphosphate, to drive essential metabolic processes for survival. When an aerobic organism digests its food, glucose ($C_6H_{12}O_6$) is broken down into two molecules of pyruvate in the process of glycolysis. The reduced electron carriers, NADH and $FADH_2$ are produced as a byproduct of this reaction.

NAD^+ gains two electrons ($2e^-$) and a hydrogen ion (H^+) to form NADH. Similarly, FAD accepts two hydrogen ions ($2H^+$) and two electrons ($2e^-$) to form $FADH_2$. These electrons from NADH and $FADH_2$ then enter the complexes of the Electron Transport Chain. The Electron Transport Chain (ETC) is a series of electron transport proteins located in the inner membrane of the mitochondria--the powerhouse of the cell (Figure 1). Embedded in the mitochondrial membrane is a series of redox-active proteins, which act like a wire by shuttling electrons through the ETC. Through a series of redox reactions, these proteins pump protons (H^+) from the mitochondrial matrix to the intermembrane space. The accumulation of protons in the intermembrane space generates an electrochemical gradient which powers the synthesis of ATP by the enzyme ATP Synthase. The Electron Transport Chain produces a total of 34 molecules of ATP which the cell can use to carry out its metabolic processes for survival. [1]

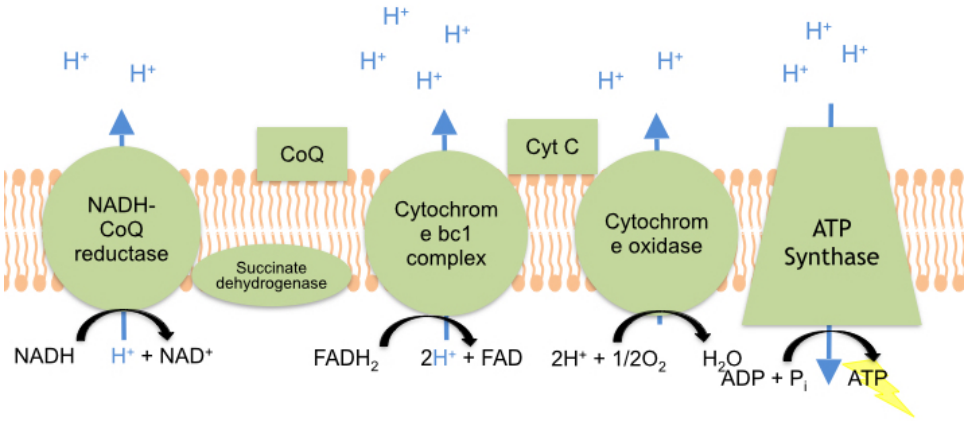


Figure 1. The Electron Transport Chain

This is a general overview of The Electron Transport Chain (ETC). The ETC is a series of four protein complexes: NADH dehydrogenase, succinate dehydrogenase, cytochrome bc_1, and cytochrome c oxidase, embedded in the inner membrane of the mitochondria. As electrons are transferred through these protein complexes, a proton (H^+) gradient accumulates in the intermembrane space of the mitochondria. ATP Synthase uses this proton gradient established by the ETC to synthesize energy in the form of ATP.

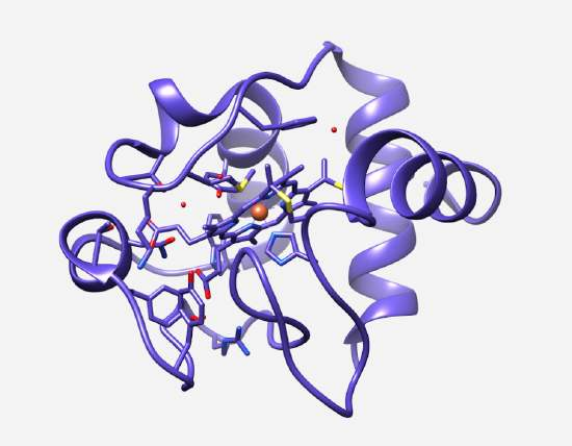


Figure 2. Full Length Ribbon Structure of Cytochrome C (PDB 3cyt).[3] This is the biological assembly of one cytochrome c monomer. Within the central heme is an iron ion shown in orange. The heme is covalently bonded to the protein via disulfide bonds made possible by the recurring Cys-X-Y-Cys-His motif found in cytochromes.

Cytochrome c is an important component of the Electron Transport Chain for the synthesis of ATP (Figure 2). Cytochrome c is a water soluble electron transport protein that is loosely associated with the mitochondrial inner membrane. In the Electron Transport Chain, cytochrome c transfers one electron at a time via its heme group from the third complex of the electron transport chain, cytochrome bc_1, to the fourth complex of the electron transport chain, cytochrome c oxidase.[2]

Cytochrome c contains a heme iron metal center that is essential to its function. During the electron transport process, this heme iron interconverts between the Fe^{3+} and Fe^{2+} oxidation states, which allows for electrons to be accepted and donated.[4] When cytochrome c is in its oxidized form, an electron is transferred from the cytochrome bc_1 complex to the heme Fe^{3+}, reducing it to Fe^{2+}. Finally, cytochrome c releases the electron to the final electron carrier of the ETC, cytochrome c oxidase. At this point, the iron center will return to its Fe^{3+}oxidation state.

The iron metal center of cytochrome c represents an octahedral geometry due to the coordination of six ligands around the central iron ion (Figure 3). An octahedral geometry is preferred for cytochrome c because each of the 6 electron rich ligands contribute to stabilizing the positively charged metal iron ion. The heme iron shown in orange is coordinated by four nitrogen atoms of a rigid square planar porphyrin ring and two axial ligands: the sulfur atom of a methionine residue and a nitrogen atom of a histidine imidazole ring. The porphyrin ring of cytochrome c is considered to be a tetradentate chelating ligand because the four nitrogen atoms of the porphyrin ring bind to the central iron, forming a stable organometallic complex. Based on the chelate effect, this tetradentate ligand binding site is more entropically favorable compared to the affinity of a monodentate ligand for the same metal ion. [5]

The ligands of cytochrome c are appropriate based on Hard Soft Acid Base Theory. (HSAB). HSAB categorizes acids and bases as hard, soft, or borderline. Soft acids and bases are larger and easily polarizable while hard acids and bases are smaller and less polarizable. Species that lie in between hard and soft are considered borderline. [6] Based on HSAB, it is logical that the borderline iron coordinates with the nitrogen of the histidine imidazole ring (a borderline base), the nitrogen atoms provided by the porphyrin ring (borderline bases), and the sulfur of the methionine (a soft base).

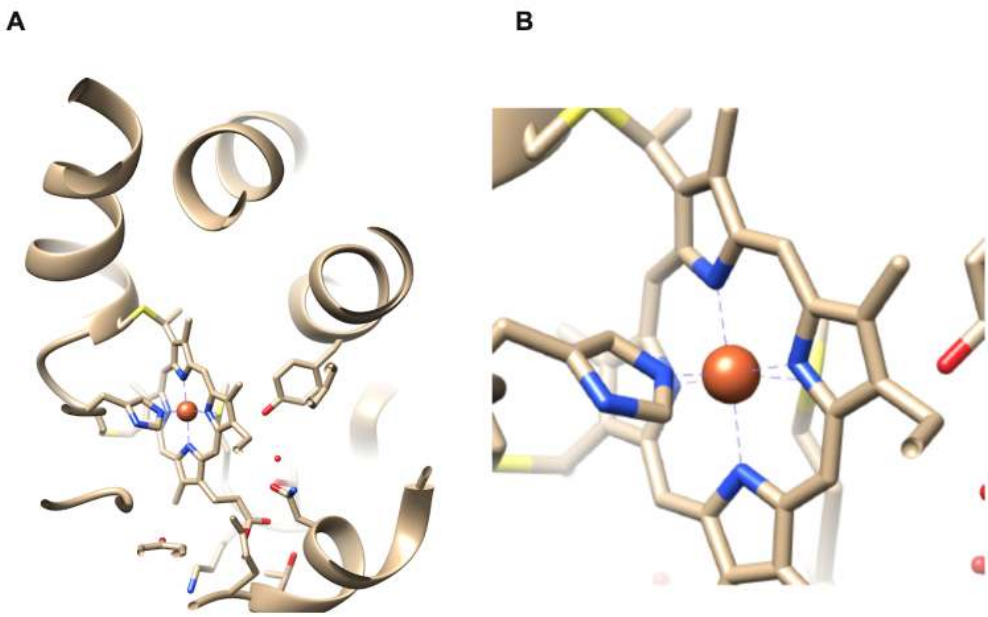


Figure 3. Iron Metal Center of Cytochrome C[3]

Figure 3A shows the entire structure of cytochrome c while Figure 3B is a magnified inset of the heme iron metal center essential to the electron transport function of cytochrome c. The heme iron shown in orange is coordinated by four nitrogen atoms of a rigid square planar porphyrin ring (blue) as well as two axial ligands: a sulfur atom of a methionine residue (yellow) and a nitrogen atom of a histidine imidazole ring (blue).

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Although the heme iron metal center changes oxidation state during the electron transport proces, cytochrome c always adopts an octahedral, low spin geometry regardless of the oxidation state on the iron. [7] This geometry is preferred based on Ligand Field Stabilization Energy (LFSE). LFSE is the total energy of the d-electrons of a metal complex relative to the theoretical barycenter. The formula for determining LFSE is shown in Equation 1 below, where x= number of d-electrons in the low energy t_{2g} orbitals and y= the number of d-electrons in the high energy e_g orbitals.

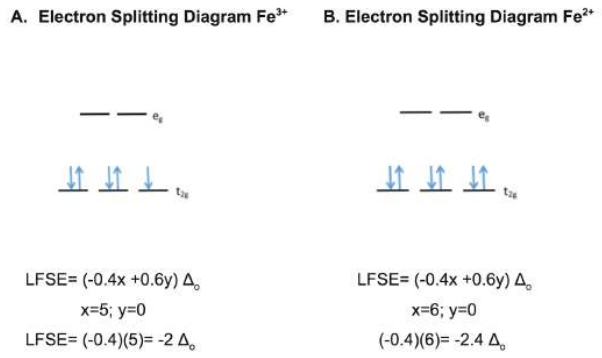


Figure 4. LFSE Splitting Diagram of Low Spin Fe^{3+} and Fe^{2+}

The electron splitting diagrams and calculations for low spin Fe^{3+} and Fe^{2+} are shown in figures A and B, respectively. The more negative LFSE values for low spin iron compared to high spin iron indicate that this low spin conformation is more energetically favorable and is therefore the configuration that the complex will adopt.

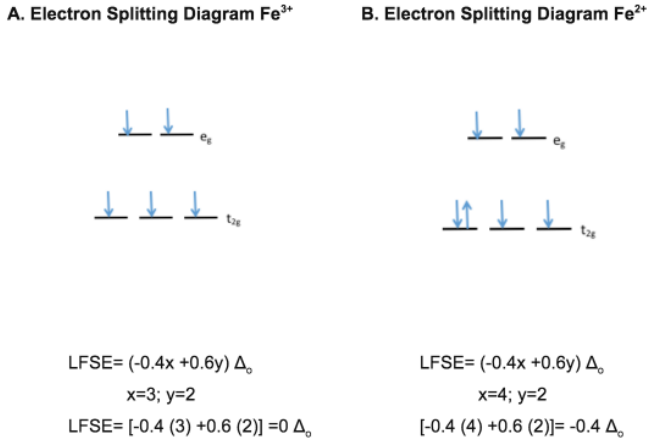


Figure 5. LFSE Splitting Diagrams of high spin Fe^{3+} and Fe^{2+}

The theoretical electron splitting diagrams and calculations for high spin Fe^{3+} and Fe^{2+} are shown in figures A and B, respectively. However, the LFSE values are more negative for low spin iron than for high spin iron, regardless of the oxidation state. Therefore, the heme iron metal center of cytochrome c will always adopt a low spin octahedral geometry regardless of the oxidation state on the iron.

In the low spin state, the d-electrons pair in the low energy t_{2g} orbitals before occupying the higher energy e_g orbitals, which increases stability. In the high spin state, the d-electrons singly occupy both the t_{2g} and e_g orbitals, without regard to the energy of the orbitals, and then pair up. The more negative the LFSE, the more stable the complex. The LFSE values for low spin iron are more negative than the LFSE values for high spin iron, regardless of the oxidation state present on the iron. Thus, the iron metal center of cytochrome c will always adopt the more energetically favorable low spin conformation.

During the electron transport process, the heme iron of cytochrome c cycles between the +2 and +3 oxidation states. As cytochrome c accepts an electron from the third complex of the electron transport chain, cytochrome bc_1, the Fe^{3+} iron metal center is reduced to Fe^{2+}. When cytochrome c releases this electron to the final complex of the electron transport chain, cytochrome c oxidase, the Fe^{3+}oxidation state is restored. However, despite this change in the oxidation state of the iron, the heme coordination does not change; the iron ion is “locked in place” and undergoes minimum reorganization.

Reduction potential also facilitates the electron transport function of cytochrome c in the ETC. Reduction potential (E°’) is the tendency for a chemical species to acquire electrons and therefore be reduced. The more positive the reduction potential, the greater the tendency for that chemical species to accept an electron and to be reduced. The reduction potential for cytochrome bc_1 (complex III of the ETC) is 0.194 V. Cytochrome bc_1 donates one electron to the oxidized form of cytochrome c (Fe^{3+}), reducing the iron of cytochrome c by one oxidation state to become Fe^{2+}. The reduction potential for cytochrome c is 0.254 V. The reduction potential for cytochrome c oxidase (Complex IV of the ETC) is 0.562 V. [8] Cytochrome C Oxidase accepts an electron from the reduced cytochrome c (Fe^{2+}) returning cytochrome c to its oxidized form (Fe^{3+}). The complexes of the Electron Transport Chain are arranged in order of increasing redox potential (each complex has higher affinity for electrons than the previous), which drives the flow of electrons towards the final complex of the Electron Transport Chain, Cytochrome C Oxidase.

E°’donor < E°’ electron transfer protein/center < E°’acceptor: Must be true for reaction to be spontaneous!

In conclusion, cytochrome c is an essential electron transfer protein which shuttles electrons between complexes III and IV of the ETC. The heme iron metal center readily interconverts between the Fe^{3+} and Fe^{2+} which allows for electrons to be accepted and donated. If this electron transfer did not occur, the ATP required to power many metabolic processes such as muscle movement, DNA synthesis, and active transport would not be produced. Therefore, cytochrome c is an important component in facilitating the production of this ATP through its electron transfer to Cytochrome C Oxidase, which provides cells the energy they need to carry out these vital processes necessary for survival.[9]

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10.8: Cytochrome Oxidase

The electron transport system (ETS) is an energy production system for aerobic organisms found in the mitochondria of cells. It is the third and final step in cellular respiration, which is the process by which the cell produces energy. When an organism takes in carbohydrate nutrients, they are converted to glucose which can be further broken down through a set of chemical reactions to pyruvate through glycolysis. After glycolysis, this pyruvate molecule is oxidized in the Kreb's cycle which in turn produces ATP and high energy molecules, NADH, and $FADH_2$. Only a few ATP are produced directly from the Kreb's cycle; however the NADH and $FADH_2$ are transported to the ETS where they can be oxidized to produce more ATP (Figure 1).[1]

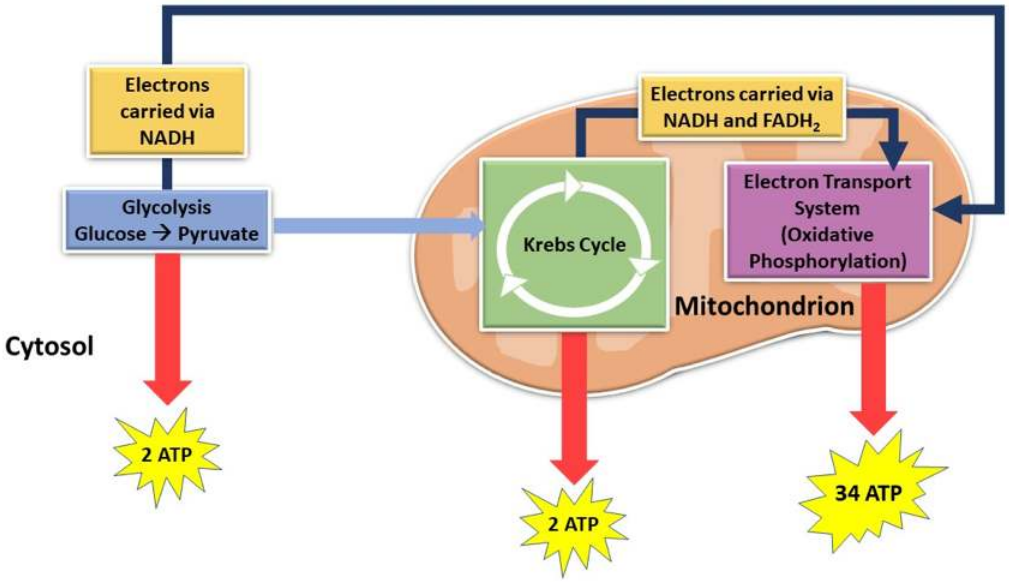


Figure 1. The Process of Cellular Respiration. Cellular respiration is the process used by aerobic organisms to break down sugars to produce energy. The process begins with glycolysis where glucose is broken down into pyruvate producing 2 ATP. Next, the pyruvate moves into the Kreb's cycle in the mitochondria and goes through a series of reactions producing 2 ATP and high energy molecules, NADH and $FADH_2$. These high energy molecules are then transferred to the electron transport system where they are oxidized and start a series of reactions that will ultimately produce 34 ATP.

After the NADH and $FADH_2$ are oxidized to NAD^+ and FAD, the electrons that are removed from NADH and $FADH_2$ and are transported through the four electron transport complexes of the ETS. The movement of electrons provides energy to pump hydrogen ions (H^+) across the inner mitochondrial membrane into the intermembrane space through four complexes.1 The four complexes are NADH-CoQ (ubiquinone reductase), succinate dehydrogenase, cytochrome bc1, and cytochrome oxidase (Figure 2).[2]

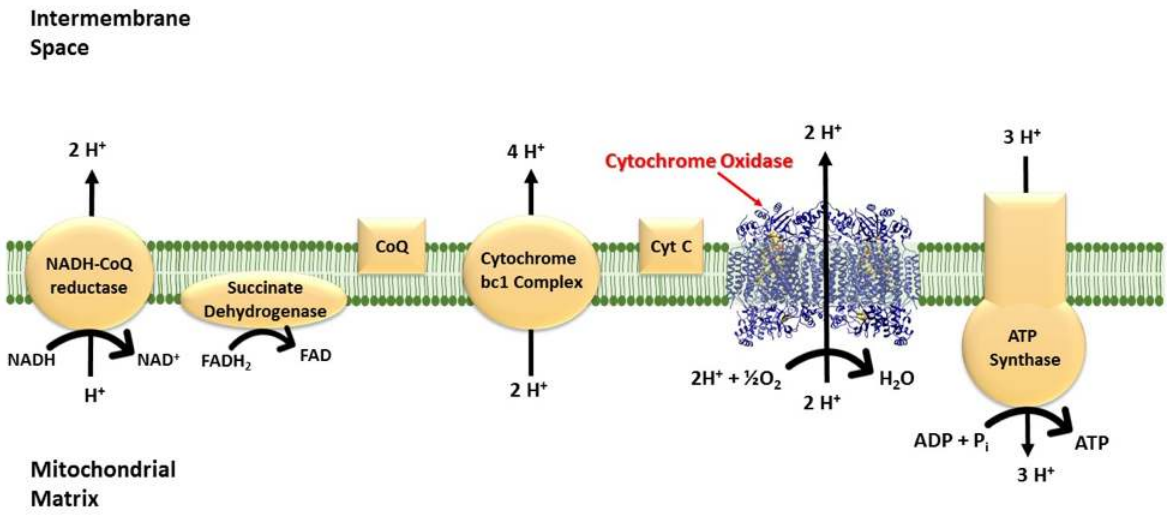


Figure 2. The electron transport system (ETS). The ETS is involved in energy production and occurs in the inner mitochondrial membrane of the mitochondrial matrix. NADH and $FADH_2$ are oxidized allowing electrons to travel through the membrane to the four complexes, NADH-CoQ reductase, succinate dehydrogenase, cytochrome bc1, and cytochrome oxidase (shown in ribbon depiction, PDB 1OCC), pumping H^+ ions across the membrane. The H^+ concentration in the intermembrane space increases and H^+ ions travel through the ATP Synthase to the mitochondrial matrix providing energy to convert ADP to ATP.

The pumping of hydrogen ions through the four complexes stores potential energy by creating a concentration gradient, with higher hydrogen ion concentration in the intermembrane space. This energy is captured as hydrogen ions cross back over to the matrix of the mitochondria, via the ATP synthase, producing energy for the cell in the form of ATP.[1] The hydrogen ion concentration will then increase in the mitochondrial matrix and travel through the three complexes again when another NADH and $FADH_2$ are introduced to the ETS. This process will continue to cycle and produce high numbers of ATP for the cell to use as energy (Figure 2).[1]

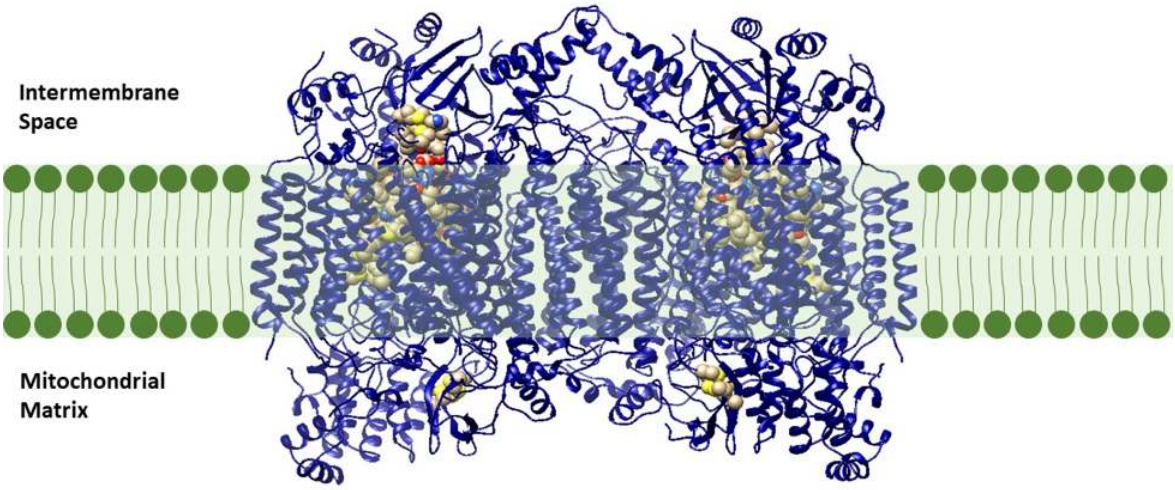


Figure 3. Structure of cytochrome oxidase (1OCC) in the inner mitochondrial membrane. Cytochrome oxidase is a transmembrane protein in the inner mitochondrial membrane. It is a dimer with two identical chemical units containing two hemes,

three coppers, magnesium and a zinc.[2] The protein is shown in ribbon depiction, with atoms of the metal-containing electron transport centers shown in spheres.

Cytochrome oxidase, also known as complex IV, is the terminal, or final, enzyme of the electron transport system (this does not include ATP synthase). Cytochrome oxidase is a transmembrane molecule found in the mitochondria of eukaryotes and in the cellular space of aerobic prokaryotes. This molecule is a proton pump that plays a vital role in producing energy, in the form of ATP, via the ETS (Figure 3). In the last steps of the energy production process, cytochrome oxidase oxidizes the waste products from the end of the energy making process, converting reactive species, H^+ and dioxygen (O_2), to a more stable molecule, water (H_2O). In the absence of cytochrome oxidase, this energetically favorable reaction could be explosive and no energy production would occur.[2] Cytochrome oxidase allows this reaction to occur safely while harnessing energy to form the H^+ ion gradient. This energy produced from the reaction is used to pump H^+ ions from the matrix to the intermembrane space of the mitochondria (Figure 2).[1]

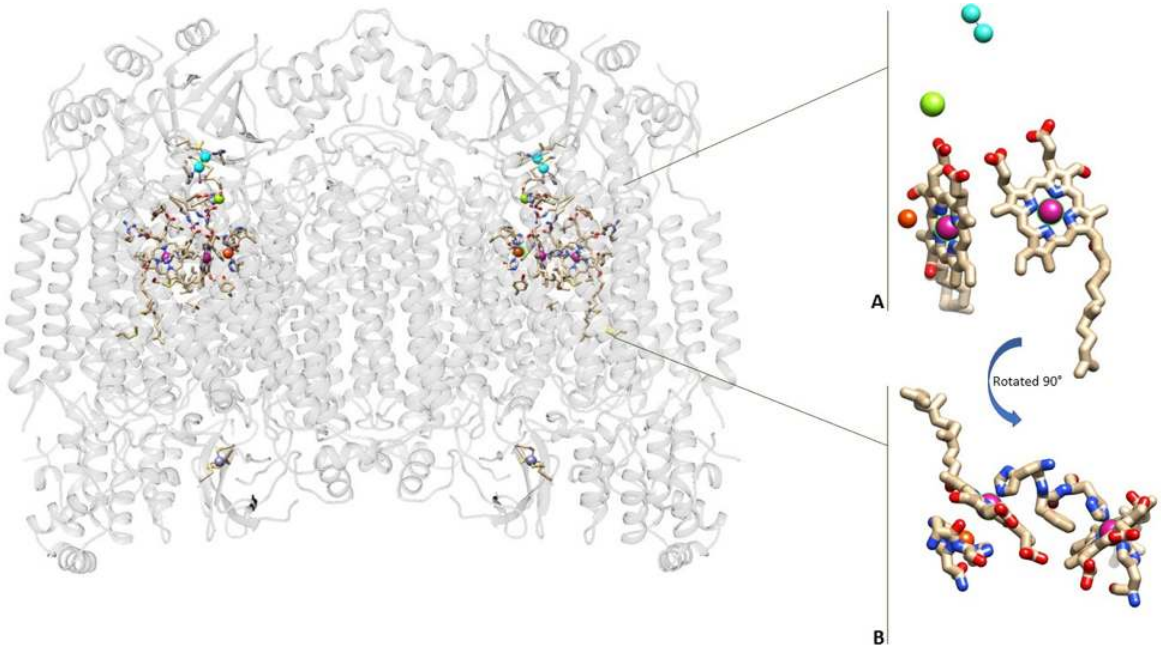


Figure 4. The structure of the metals and their ligands in cytochrome oxidase. This figure shows the two hemes and their irons (purple), two Cu_A (light blue), Cu_B (orange), one magnesium (light green), and one zinc (blue). Cytochrome oxidase is a dimer with its two sets of Cu_A, $heme_a$, $heme_{a3}$, Cu_B, and zinc. The metal complex dimer mirrors one another. Inset A shows a detailed view of Cu_A, magnesium, $heme_a$ (right), $heme_{a3}$ (left), and Cu_B and their spatial relation to one another. Inset B shows $heme_a$ bound to two imidazoles, and $heme_{a3}$ bound to an imidazole. $heme_{a3}$ and Cu_B are close to one another, but do not bind. This space between $heme_{a3}$ and Cu_B is where the oxygen then can bind to the iron. Cu_B is bound to three imidazoles. From PDB 1OCC.

Cytochrome oxidase is a dimer meaning it is made up of two identical proteins. The two proteins in cytochrome oxidase mirror one another. The system uses multiple metals to complete its function including the two irons in the two hemes, three coppers, one magnesium, and one zinc (Figure 4). The irons in the two hemes and the three copper molecules are vital to the success of the enzyme in aerobic respiration.[1]

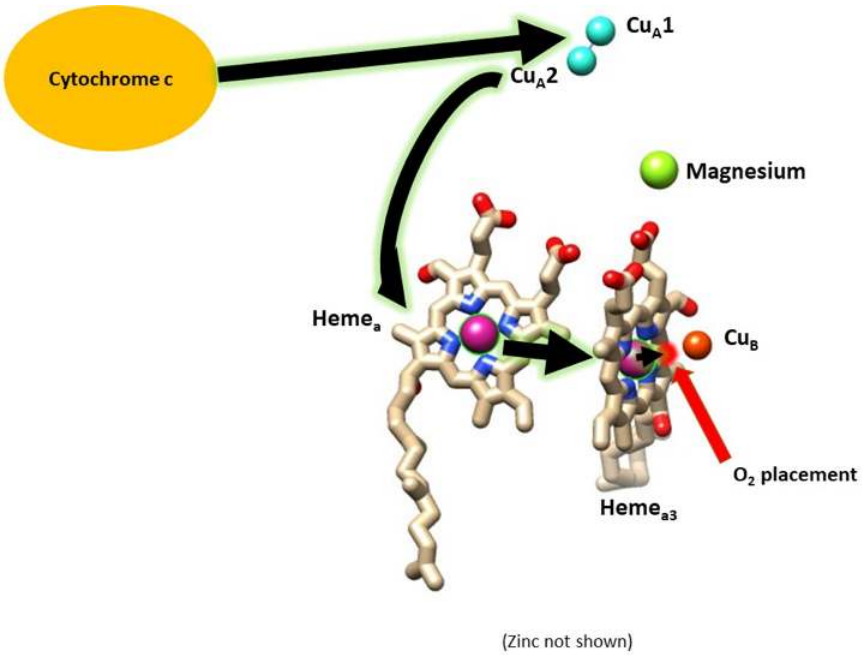


Figure 5. The transfer of electrons from cytochrome c to cytochrome oxidase. This figure shows the transfer of electrons the cytochrome c to the two Cu_A (light blue), to $heme_a$ (purple, left) to $heme_{a3}$ (purple, right), to finally to the oxygen molecule (red sphere). From PDB 1OCC.

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2 Cu_A molecules function in allowing the electrons to enter the enzyme from cytochrome c.2,3 The electrons travel from the Cu_A molecules to the first heme, also known as $heme_a$. $heme_a$ functions in allowing the electrons to be transferred from Cu_A to the second heme, $heme_{a3}$. The iron in $heme_{a3}$ functions in binding oxygen, with the help of Cu_B. The energy production system selects a heme iron group to bind the oxygen along with the other copper atom and is the location of oxygen reduction (Figure 5).3 The function of magnesium and zinc remains unknown.[4]

$$4e^- + 8H^+ + O_2 \rightarrow 4e^- + 4H^+ + 2H_2O.^{9} \text{ (1)}$$

The overall reduction that occurs in cytochrome oxidase is shown above (Reaction 1). The electron transfers from the electron donor, cytochrome c, to Cu_A to $heme_a$ to $heme_{a3}$ and finally to the electron acceptor, oxygen, are carried out mostly by redox reactions (Figure 5).[3]

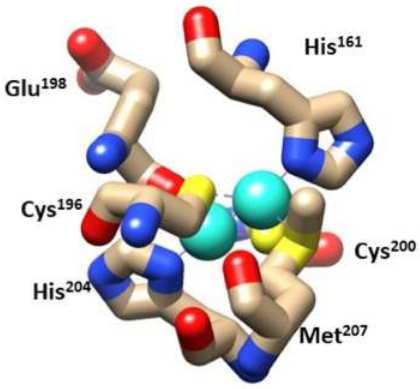


Figure 6. Cu_{A1} and Cu_{A2} with their ligands. This figure shows the two Cu_A (light blue) with their ligands. Cu_{A1} is bound by His^{204}, Cys^{200}, Cys^{196}, and Glu^{198}. Cu_{A2} is bound by His^{161}, Cys^{200}, Cys^{196}, and Met^{207}. From PDB 1OCC.

The electrons travel from cytochrome c to the two Cu_A molecules in the intermembrane space at a fast rate of 70,000 s^{-1} and with an E°' value of 0.27 V.[3,5,6] The Eo', or standard reduction potential, is a value indicating the likelihood a chemical species will be reduced, with a more positive value meaning it is more likely to be reduced. Literature has shown that Cu_A has a mixed oxidation state of I and II (or 1.5 each). Because of this mixed oxidation state when the electrons enter the cytochrome oxidase the charge is shared between the two Cu_A. Only a single electron is transferred from the cytochrome c to the Cu_A.[6] In the cell the environment is different than laboratory conditions, therefore the E°' value would be about +0.05 V.[3]

The two Cu_A molecules are what bring the electrons from the cytochrome c to $heme_a$. They both have tetradentate ligands with a tetrahedron shape.[7] Cu_{A1} is bound by His^{204}, Cys^{200}, Cys^{196}, and Glutamic $acid^{198}$. Cu_{A2} is bound by His^{161}, Cys^{200}, Cys^{196}, and Met^{207}. Both Coppers are bound by Cys^{196} and Cys^{200}, this chelating effect helps stabilize the molecule (Figure 6). The Hard Soft Acid Base (HSAB) theory helps explain the stability of the hemes. HSAB theory characterizes metals as hard, borderline, or soft acids and bases based upon their charge density. HSAB shows that chemical species like to bind with similar species, for example hard acids like to pair with hard bases and borderline acids like to pair with borderline bases. Cu_A applies to the HSAB theory as the copper binds to the imidazole residue on histidine which is borderline for HSAB. The two cysteine and glutamic acid residues that bind with Cu (I) or (II) are soft and hard bases, respectively, for HSAB and may still bind as they are next to borderline. Therefore HSAB may still be a selective method for the Cys and Glu ligands.[3]

As Cu (II) is a d^{10} metal its d orbital is full of electrons. As the d orbital is full the LFSE (ligand field stabilization energy) would be zero. The LFSE is a number that defines the energy of the electrons compared to the average energy of the orbitals. A more negative LFSE indicates lower energy and a more stable complex. As Cu(II) has an LFSE of zero this indicates that the geometry of the metal and its ligands it likely dependent upon sterics. Therefore the tetrahedral geometries of the Cu_{A1} and Cu_{A2} is a result of reducing steric hindrance between the ligands. Cu_{A1} and Cu_{A2} would have an electron count of 17-18. Both coppers each have four ligands with no charge thus having 8 ligand electrons. Copper can have an oxidation state of (I or II), and therefore will have 9-10 d electrons bringing the electron count to 17-18.3

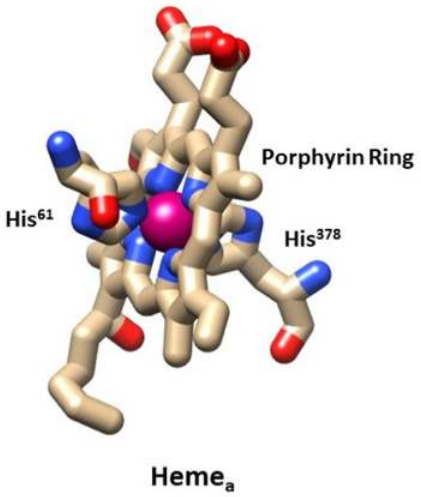


Figure 7. The structure of $heme_a$ and its ligands in cytochrome oxidase. This figure shows the $heme_a$ (purple) in the porphyrin ring and bound by the two histidine ligands, His61 and His378.

After the electrons have entered the cytochrome oxidase from the cytochrome c to the Cu_A molecules they will then transfer to $heme_a$ (Figure 7). This transfer is made possible by 14 covalent bonds and 2 hydrogen bonds spanning 19.5 Å and taking about 20,000 s-1.3 The iron transfers the electrons one at a time and changes from Fe (III) to Fe (II). However, literature shows that the iron only changes its charge about 10-15% as the change in charge is spread over the porphyrin ring decreasing the amount of energy needed.6

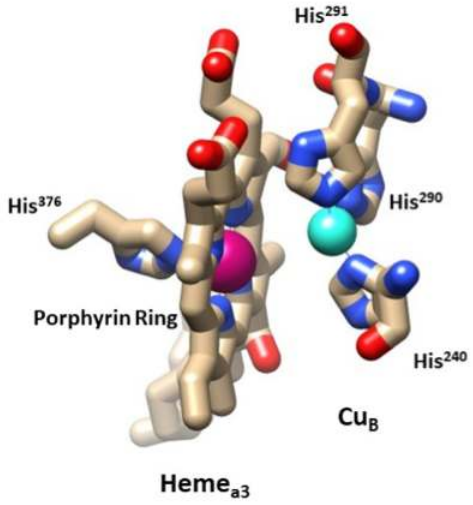


Figure 8. The structure of the heme$_{a3}$ and Cu$_B$ and their ligands in cytochrome oxidase. This figure shows the heme$_{a3}$ (purple) in the porphyrin ring with its histidine ligand and Cu$_B$ (light blue) with its three histidine ligands. Oxygen placement occurs between the heme$_{a3}$ and the Cu$_B$.

Next, the electrons transfer from heme$_a$ to heme$_{a3}$ (Figure 8). The hemes are perpendicular to one another and the edges are located 7 Å apart.[8] How the transfer of electrons from heme$_a$ to heme$_{a3}$ occurs is still not fully understood. Literature shows that electron tunneling stops at heme$_a$, and from heme$_a$ to heme$_{a3}$ the electrons are transferred from the edges of the heme and propelled by protons pumping to the intermembrane space.[6]

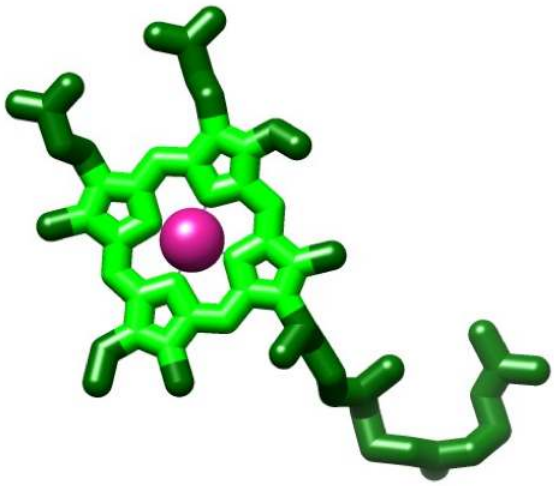


Figure 9. The structure of a porphyrin ring. This figure shows the structure of a porphyrin ring (light green) with its four pyrrole rings and planar geometry. The iron (purple) is in the center of the porphyrin ring and the side groups (dark green) vary depending on the type of heme.

The structure of the heme molecule is a porphyrin ring that is tetradentate chelating of an iron molecule with four nitrogens. Iron can form up to six bonds due to steric constraints that cost the molecule energy by not having enough space for the electrons which repel one another. A porphyrin ring is the building block for heme and is a planar structure composed of four pyrrole rings (Figure 9). Four of the bonds are with the nitrogens of the porphyrin ring, as previously stated, while the fifth coordination site is occupied by an imidazole in histidine, and the sixth coordination site is occupied by another imidazole for heme$_a$, or O_2 for heme$_{a3}$ (Figure 10). Both irons have a planar shape with the heme molecules, but with the addition of their ligands (two imidazole residues for heme$_a$ or an imidazole and an oxygen for heme$_{a3}$) they becomes an octahedral shape.3 The geometry of the hemes can be attributed

to LFSE as the the LFSE equals -0.4 for Fe(II) and -2.0 for Fe(III). This indicates that the geometry of the molecule may be a result of the high stability due to the lower energy of the electrons and their orbitals.[8]

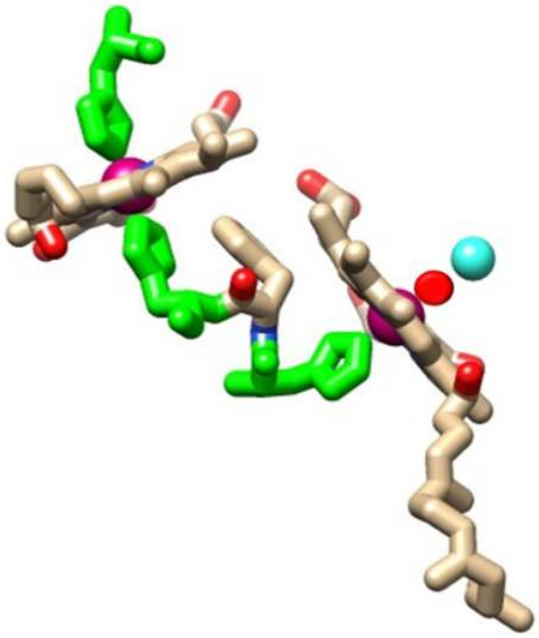


Figure 10. The structure of the metals and their ligands in cytochrome oxidase. This figure shows the two hemes in cytochrome oxidase, $heme_a$ (left) and $heme_{a3}$ (right). $heme_a$ is bound by two imidazoles from Histidines (light green) and $heme_{a3}$ is bound by an imidazole (light green) and an oxygen molecule (red).

Thermodynamic theories are important for ML binding as they provide ideas about the energy needed for breaking bonds and the stability of a molecule. The two hemes in cytochrome oxidase both maintain their stability largely due to their macrocyclic porphyrin ring. This porphyrin ring is made up of 4 pyrroles that bind their nitrogens to the iron. In cytochrome oxidase the iron never needs to leave the hemes and the stability of the porphyrin ring may help the iron stay in its place to properly transfer electrons to oxygen (Figure 10).[9]

The iron does not leave the porphyrin ring for either hemes and the ligands of $heme_a$ remain bound as well. The heme molecules are very stable due to the chelating effect of the porphyrin ring and is relatively inert meaning it holds its metal ion and maintains its planar geometry. The iron in $heme_{a3}$ has an imidazole ligand that remains bound to the iron, but also has a position for oxygen. The oxygen iron bond is broken when electrons are transferred to the oxygen and bound to two H^+ ions.[3] The high lability, or ability of the metal-ligand bond (Fe (II) and O_2) to be broken, is necessary for the water to be released from $heme_{a3}$ and for the cytochrome oxidase to reset for the next set of electrons. The high lability of the Fe (II) is likely a result of the low LFSE value of -0.4. The rate constant is unknown for the iron bound to oxygen. The HSAB theory applies to the iron and the porphyrin ring as Fe (II) and N (in the pyrrole ring) are both classified as having borderline acid character. Like prefers like, indicating that Fe (II) may be using this to select the right ligand to help it bind oxygen, which is hard base for the HSAB theory. The nitrogen in the pyrrole ring is likely a borderline base as it is in a ring structure like pyrimidine and imidazole which are borderline nitrogen containing ring structures as well.[8]

The iron in $heme_a$ transitions between two oxidation states, Fe (III) and Fe (II). The iron $heme_{a3}$ transitions from Fe (II, III, and IV).[10] The two irons in the heme a and a3 both have an electron count of 16-18, as the oxidation state changes. Both irons are bound by four nitrogens from a porphyrin ring, an imidazole nitrogen from His and an O_2 molecule. All of the nitrogen donor atoms are neutral. With six ligands bound to the Fe there would be a total of 12 ligand electrons (6e- x 2=12e-). Knowing that the iron may be missing 2-4 electrons, based on its oxidation state, there remains 4-6 d-electrons giving a total electron count of 16-18 (12 ligand e^- + 4-6 d e^- = 16-18 e^-) (Figure 11). Literature has shown that the iron in $heme_a$ is low spin as it is a 3d metal with a 3+ charge and because it has imidazole ligands that are pi acceptors which are strong field. While the other iron metal center in $heme_{a3}$ is high spin as it is a 3d metal with a 2+ charge.[10,11]

Lastly, the electrons transfer from heme$_{a3}$ to O_2. This transfer is made possible by the iron on the heme$_{a3}$, Cu_B, and a tyrosine. These set of molecules are also known as the bionuclear center (BNC).[3] Once the electron reaches the heme$_{a3}$, Fe(III) becomes Fe (II) and the oxygen binds to the Fe (II). The H^+ ion from the tyrosine ligand of Cu_B transfers to the oxygen bound to Cu_B (I) changing it to Cu_B (II). During this state the Fe (II) double bonds to the oxygen and becomes Fe (IV). The first H^+ and e^- enter the BNC and the H^+ binds to the oxygen on the Cu_B (II). During this step, while the electron places on the tyrosine oxygen the tyrosine oxygen moves to the Cu_B(II) oxygen. Next, the second H^+ and e- set enter with the new H^+ replacing an H^+ on the Cu_B(II) site and the e- placing on the Fe (IV) changing it to Fe (III). The replaced H^+ moves to the Fe (IV). The third set of H^+ and e^- move in with the third H^+ going on the tyrosine oxygen and the electron going on the Cu_B (II) causing it to become Cu_B (I). The final H^+ and e- enter the BNC and place on the Fe (III) causing it to become Fe(II). This stage is also where the two water molecules bound to Fe (III) and Cu_B(I) fall off. The cycle then restarts when oxygen binds to the Fe (II) (Figure 11).[12]

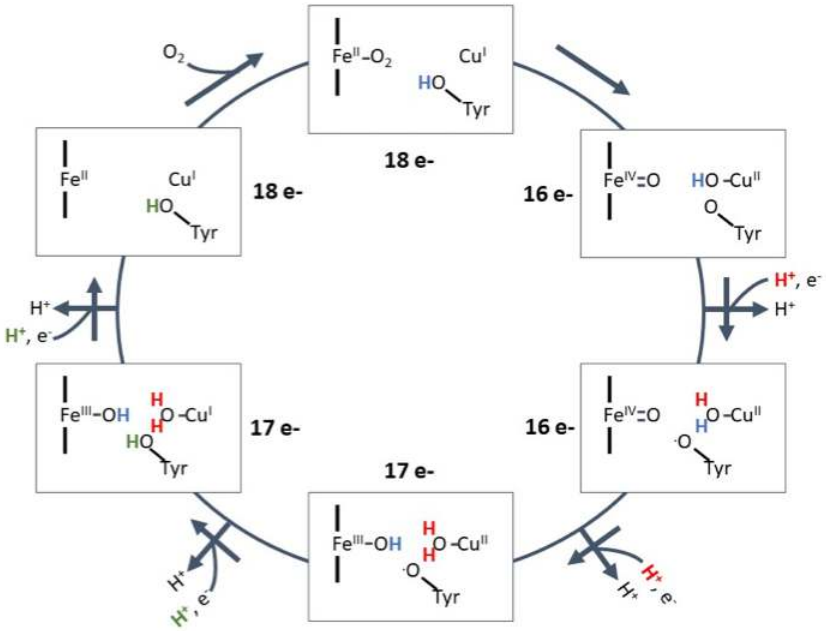


Figure 11. The catalytic cycle of the reaction of O_2 to H_2O in cytochrome oxidase. This figure shows the catalytic cycle that occurs when the oxygen in bound to the Fe (II). The electrons transferred in cytochrome oxidase are brought to the Fe (II) and used to react O_2 and H^+ ions to form water.

Cu_B is vital to the reaction of cytochrome oxidase and has tridentate ligands. All three ligands are imidazole side chains (His^{240}, His^{290}, and His^{291}). With the three imidazole ligands, Cu_B forms a trigonal planar shape and is stabilized by the chelating His^{290} and His^{291} ligands (Figure 8).[3] Similar to the Cu_A ions, Cu_B has an LFSE of 0 and has a trigonal planar geometry due to steric hindrance of the three His ligands. Copper can have an oxidation state of (I) or (II).[10] Cu_B would have an electron count of 14-16. This copper has three imidazole ligands with no charge therefore it has 6 ligand electrons. The HSAB theory also applies to the Cu (II) (Cu_B) center and the 3 imidazole ligands as both are considered borderline acids and bases, respectively, for HSAB and like attracts like, indicating that Cu (II) may be using this to select the right ligands. Cu (I) also occurs and may still be using HSAB to select the imidazole groups as it is close to borderline. Copper can have an oxidation state of +I, or +II, and therefore will have 9-10 d electrons bringing the electron count to 15-16. Cu_B takes on an oxygen and releases it after two H^+ ions are bound to it producing one molecule of water (Figure 11). The rate constant of the O-Cu_B bond is 3.5 x 108 $M^{-1}s^{-1}$ showing that the breaking of the bond is quick as and that it is a weak bond. As previously mentioned, the Cu_B has an LFSE of 0 indicating it is highly labile which correlates with the Cu_B's ability to react quickly with the oxygen.[3]

The reduction potential of the cytochrome oxidase reaction (Reaction 1) is +0.82 V. Beginning with the initial electron donor, cytochrome c, and ending with the final electron acceptor, O_2, we see that the reduction potential went from +0.27 V to +0.82 V. This increase in reduction potential from the electron donor to the electron acceptor makes the overall reactions of cytochrome oxidase spontaneous.[6]

Cytochrome oxidase is a colored protein. Cu_A has absorption bands at about 480 nm, 530 nm, and even one in the infrared spectrum at about 830 nm.[12] Literature has shown that although these absorbances reflect a blue/purple color in the lab, in an intact cytochrome oxidase the hemes hide the Cu_A absorbances with their own absorbances. Cu_A absorptions are charge transfer absorptions as ε>1000 cm-1 (ε=2000 cm^{-1}).[12]

$Heme_a$ has been found to have absorbances at 446 nm and 605 nm. $heme_{a3}$ has absorbances at 441 nm, 611 nm, and 656 nm.[12] The absorbances for both hemes mean the reflected light gives the hemes a reddish/purple color. The absorbances and colors of both hemes have been to found to be likely a result of charge transfers; however no ε value was found in the literature. Cu_B is not colored as it does not have any absorbances in the visual spectrum.[12]

Cytochrome oxidase is a key molecule in aerobic respiration and without a properly functioning enzyme can lead to cell death. The primary disorder associated with cytochrome oxidase is cytochrome oxidase deficiency which is a relatively rare, autosomal recessive disorder.[13] Leigh's Syndrome is a human disease caused by cytochrome oxidase deficiency and its symptoms include poor muscle tone and muscle movement, mental impairment, and lack of growth. These symptoms begin to manifest in infancy and the disorder usually results in death within two to three years of life. Although there is no cure for Leigh's Syndrome, treatment with Vitamin B1 has been shown to help prolong the patient's life. Therefore, cytochrome oxidase is very important to humans and all other aerobic organisms as it is the primary reason we breathe oxygen and is what helps our bodies produce energy to keep us alive.[14]

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Contributed by

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10.9: Potassium Channels

K+ Channels

Ion channels are large membrane-spanning proteins that allow selective transport of an ion. This can occur for ions like potassium, calcium, and sodium.[1] These channels are responsible for the electrical conduction in nervous systems to allow nerve and muscle cells to function properly. Neuron plasma membranes contain ion channels that have the ability to open and close based on these electric signals received from neuron activity. Electrical activity of neurons that send signals to the plasma membrane include conduction, transmission, and receiving of electric signals.[2] When there is an unequal distribution of charge across a membrane, ions will spontaneously diffuse across the membrane to equalize the charge (Figure 1).[1] Transport of ions across a membrane can be either active or passive depending on if energy is required. Ion channels are passive, or otherwise known as spontaneous, which allows the flow of ions to be transported across the a membrane based on when the signals are received.[1-2] The flow of the ions goes from the cytoplasm to the extracellular solution, and thus depolarizing the cell. Potassium channels are one of many different types of ion channels. Main cellular functions include cell volume regulation and electrical impulse formation.[3]

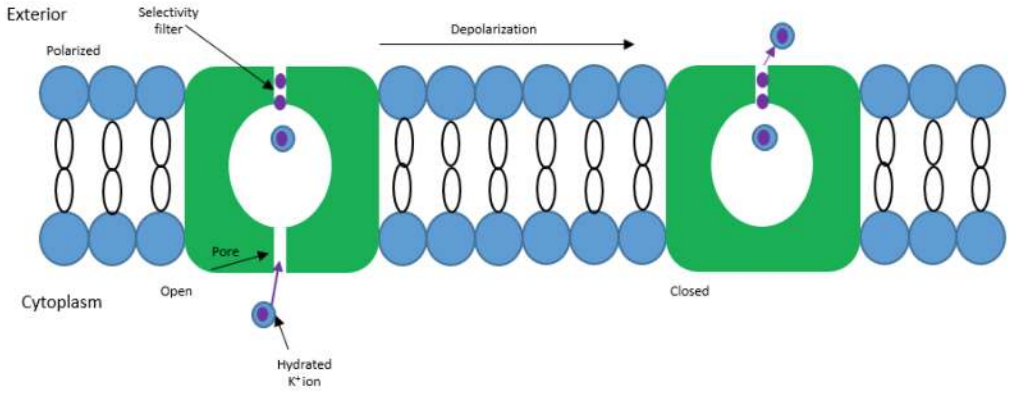


Figure 1. Schematic of how the membrane potential is diffused across the membrane. *This shows how the mechanism occurs. First, the potential difference across the membrane is sensed and signal is received causing the pore to open. Ions lose their water molecules before entering the selectivity filter. The pore then closes to allow for control of diffusion across the membrane once potassium ions are flowing the the filter.*[1]

There are many types of ion channels, but this paper will be focusing on potassium channels.The human genome contains over 90 genes that encode for potassium channels.[3] Dysfunction of potassium channels have been shown to link an individual to diseases such as the hyper-and hypokalemic periodic paralysis, myotonia, and epilepsy.[4] Potassium channels specifically allow potassium ions to penetrate the membrane when there is a response to a change in the membrane potential. This “specificity” means that no other ions can pass through this channel including sodium, which is very similar to potassium in regards to charge and size.[3] This selection is completed at rates that approach the diffusion limit. There are four main types of potassium channels which are as followed: calcium activated, inwardly rectifying, tandem pore domain, and voltage-gated. The differences between these types are mainly with how the gate receives its signal, whereas the structure of these channels is similar. A general structure for potassium channels can be seen below in Figure 2.[3]

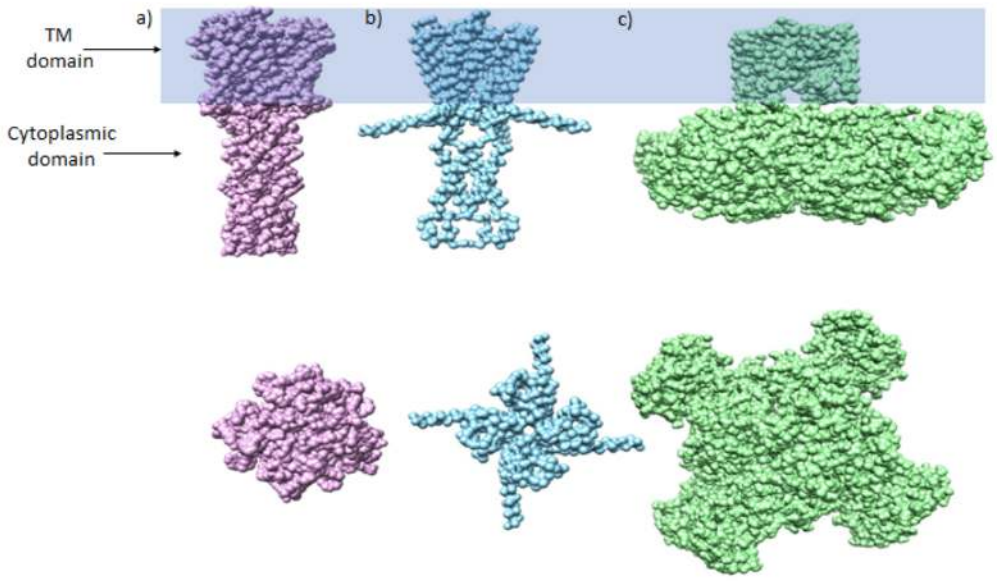


Figure 2. General structure of potassium channels showing the two conformations of the closed state (a and b) of KcsA vs. the open state of MthK. *Also, the transmembrane (TM) domain and the cytoplasmic domain of highlighted here. The gray rectangle represents the molecule would be located in the membrane. All three molecules are from bacteria, but have different gating dependence. KcsA is pH dependent, whereas MthK is voltage dependent. PDB 3EFF,* 1K4C, and 1LNQ.[3]

Potassium

Potassium is an alkali metal with a valence electron configuration of *n*s1 and contributes only one element to the molecular orbital band. There are some common trends that can be found from the periodic table, and there are specific ones that are for alkali metals. Alkali metals contain low first ionization energies and will want to form M^+ metals increasingly down the group. Potassium's thermodynamic tendency to become K^+ is due to the large and negative standard potentials that occur. Oxidation becomes more favorable going down the group because the enthalpies of sublimation and ionization decrease. Group 1 element ions are hard Lewis acids and mainly form complexes with hard donors like O and N.[1]

KcsA Channel: Structure

This paper will be focusing on KcsA, a potassium channel from *Streptomyces lividans*, which contains two domains. The first being the transmembrane portion, which contains 120 residues. This will be discussed in detail below. The second domain is a cytoplasmic domain that contains about 40 residues. The cytoplasmic domain contributes to the stability of the closed state. This is concluded based on data that shows a decrease in efficiency of channel folding and assembly and thermal stability being affect when the cytoplasmic domain is removed from the crystal structure.[5] As seen in Figure 2, the water filled C-terminal cytoplasmic domain is 4-helix bundle structure that extends linearly towards the cytoplasm.[5-6] It has been shown by electron paramagnetic resonance, EPR, data produced by Uysal, that the C-terminal has a stretch that bulges out where the C-terminal domain meets the transmembrane domain.[5] This stretch of helix that connects the two has a higher degree of flexibility than the other parts that potentially plays a role during the opening of the channel.[5] There is still much research that needs to be conducted to fully understand the functionality of the C-terminal domain. A suggested function of the domain is that it may serve as a receptor for an unidentified plasmic activator protein or ligand, but others argue that there is no significant effect on the permeation path for the ion. The structure does not yet contain orientation of any side chains, but the arrangement of the helices suggest electrostatic interactions in the subunit.[6] Figure 3, demonstrates how the cytoplasmic domain compares between an open channel vs. a closed channel with two bacteria channels.[7] The rest of the paper will be focusing on the transmembrane domain that selects for potassium.

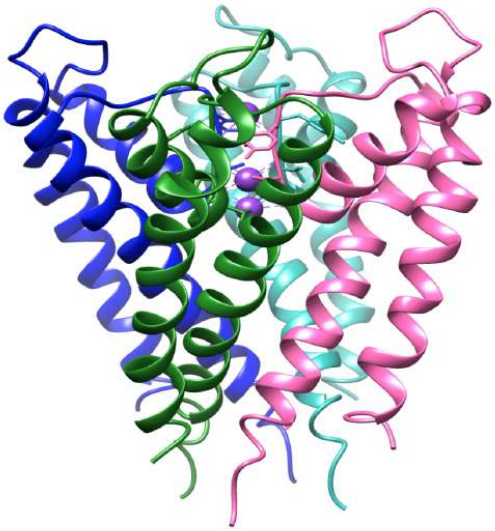


Figure 3. The transmembrane domain. *Each subunit is colored differently and the potassium ions are purple. PDB 1BL8.*

The selectivity for potassium ions relies heavily on the structure of the potassium channel selectivity filter. The coordination environment of the channel has selective ligands that bind specifically to potassium ions.[8] The potassium channel protein is a tetramer, that contains four identical subunits that form a central pore.[8-9] The ions flow into a pore that opens and closes, directing the ions to the central cavity. The subunits contain two alpha helices where one faces the central pore, inner helix, and one faces the lipid membrane, otherwise known as the outer helix.[3] Along with the inner and outer helices, each subunit includes a pore helix.[3,8] The subunits are tilted, as seen in Figure 3, where the selectivity filter is near the extracellular surface of the membrane. The four inner helices are structured in a way where they come together near the intracellular surface. Both the intra- and extracellular entryways are negatively charged by acidic amino acids. This allows for a higher concentration of cations near the membrane and less anions because of the opposing charges.[8]

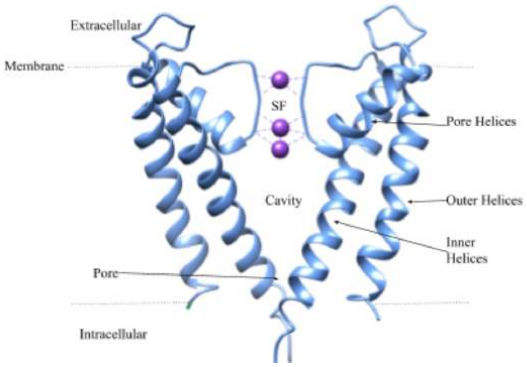


Figure 4. Potassium channel (KcsA structure from *Streptomyces lividans*) with key structural components labeled. *The main aspects to note are the pore, cavity, and selectivity filter (SF). These are the parts of the channel where potassium ions travel through. First, the ion flows through the pore and enters the cavity hydrated when the pore is open. Then a potassium ion is dehydrated and selected to travel through the SF where it will then enter the cell. Note that only two subunits are shown in this image for easier visualization. PBD 1K4C.*

The pore region was first identified with pore-blocking scorpion toxins. They interact with amino acids at the entrance of the pore causing blocking and dysfunction. The pore is where the potassium ion enters, where then it is transferred to the central cavity, as seen in Figure 4. During this time the potassium ion stays hydrated.[8] The intracellular pore is the feature of the channel that allows potassium ions to enter the cell when it is open, or be blocked from entering when closed. The channels opens when there is a change in membrane potential, allowing a influx of potassium ions into the cavity filter. Once selective binding occurs in the

selectivity filter, the potential drops across the membrane, thus closing the pore.[1] The pore and the cavity are hydrophobically lined, allowing the ability to lower electrostatic barrier. There needs to be a lower electrostatic barrier so the energetic cost of dehydration is compensated due to the large energy barrier for ion permeation (dielectric barrier). Thus, the water filled cavity allows for an energetically favourable environment.[3,8,10,11]

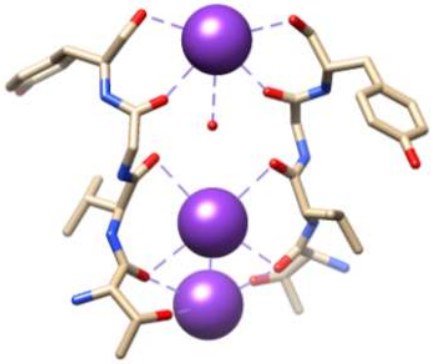


Figure 5. Binding of potassium ions (purple) to specific ligands by the backbone O's of Thr 75, Val 76, Gly 77, and Tyr 78. The full coordination is not shown here for easier visualization. *Reproduced from Samsom.*[11]

Next, the ions need to be selected into the selectivity filter (SF), which is lined with polar main chain atoms that belong to amino acids. The SF is so narrow that the ions must first be dehydrated before entering it. There are two essential features in the SF. First, the main chain atoms create suitable dimensions for coordinating a dehydrated potassium ion by stacking, thus making sequential oxygen rings. This creates a very small distance that the potassium ion must travel to reach each site while traveling through the filter. This forms a sequence of four cubic eightfold coordination sites, as seen in Figure 6.[3,8] At any time, these sites are occupied by two K^+ ions and two water molecules in an alternating sequence The second feature is the protein packing around the SF, which follows a sequence of T-V-G-Y-G, shown in Figure 5.[9] Conduction can then occur when two potassium ions enter the SF, causing a balance between attractive force that occurs from the SF to the ion with the repulsive force that occurs between the two potassium ions.[8] This repulsion helps potassium ions overcome its intrinsic affinity for binding tightly to the binding sites.[3] Further discussion of the selection mechanism will be discussed below.

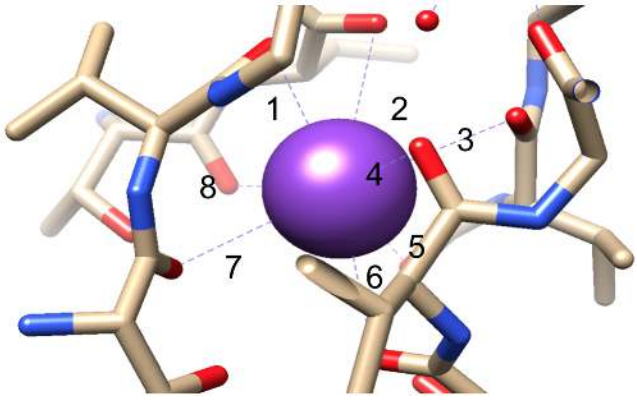


Figure 6. One example of a potassium ion (purple) in an eightfold coordination site. *Binding numbered for easier visualization.*

K+ Selectivity

The SF consists of four sites (S1-S4) that are formed by oxygen molecules, as seen in Figure 7.[11] The selectivity of potassium channels is of functional importance due to the fact that if sodium ions were to be selected, membrane repolarization would not

occur. Even though sodium ions are smaller than potassium, ~.95 Å and ~1.33 Å respectively, they are not able to penetrate the membrane.[12-13] This selection of potassium ions occurs by a factor of more than 1000 compared to sodium ions. Much research has been conducted to elucidate the mechanistic nature of how exactly potassium channels select for potassium ions, in which conclusions can vary by the type of potassium channel. This description will be based on KcsA..[9, 12, 13]

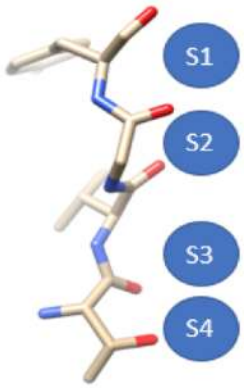


Figure 7. Showing one subunit demonstrating where the binding sites are in the selectivity filter. *Each site (S1, S2, S3, and S4) represents where an ion would be placed in the filter. PDB 1BL8.*

Selectivity of potassium ions has been attributed to the sequence motif TVGYG in positions 75-78 of each monomer. As stated above, potassium channels bind to ligands through an eight coordinate, octahedral coordination environment.[11] These are optimally placed to allow for the interaction with potassium ions, making the transfer of energy from the central cavity to the SF extremely low because the environment is not drastically changing.[8,11] When a potassium ion binds to the SF, eight water molecules are released from a hydrated potassium ion. The ion is then bound to eight carbonyl oxygens at each of the four sites in the SF. At the last site, the ion binds to four of the carbonyl oxygens as well as four water molecules, keeping the eightfold coordination number. Once the ion has completely diffused through the channel, the ion becomes rehydrated once again in the extracellular matrix.[3,8] This mechanism can be viewed in Figure 8.

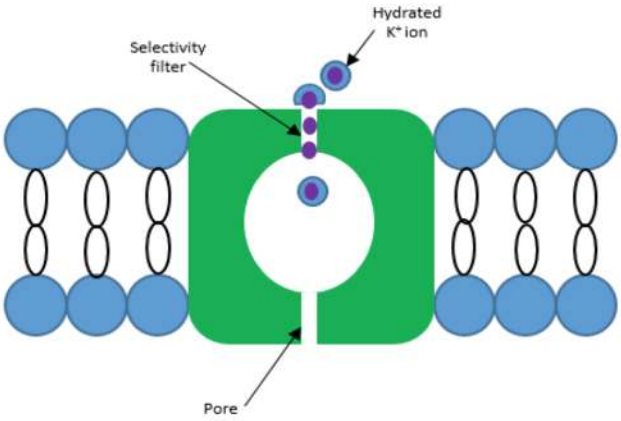


Figure 8. Mechanism of the diffusion of potassium ions through the channel, emphasizing when the potassium channel is hydrated. *The ion first goes through the pore where it resides in the central cavity. At this point the ion is still hydrated. When the ion is selected, it then moves to through the selectivity filter, where it becomes dehydrated. Following, the ion enters the extracellular matrix hydrated where it is hydrated once more.*

This simple reaction is favorable because of low energy cost to lose the water molecules and bind the to the selectivity filter. Potassium ions are normally surrounded by eight water molecules, which are stripped before entering the filter. The filter is designed to have similar dimensions that mimic the shell of water that encloses potassium by lining the pore with eight oxygen

atoms, as stated above. These are optimally placed to allow for the interaction with potassium ions. This makes the transfer of energy from the central cavity to the selectivity filter extremely low because the environment is not drastically changing.This static environment completely compensates for the energetic cost of K^+ ion dehydration when it enters the cavity.[9] The selection of the right metal allows for the ability for potassium channels to function correctly.

Atomic Radii: Na^+ vs. K^+

Sodium is a metal that is very similar in charge and size, as stated above, but sodium ions are not selected. This is due to the size of the ions.[3,8,11] Sodium ions are smaller in ionic radius. As seen in Figure 9, sodium ions have a smaller ion radius resulting in the inability to coordinate with the all eight oxygens at the first site. This demonstrates why sodium ions are not selected to go through the channel, even though the ions are smaller than potassium ions. This results in sodium ions favoring the shell of water.[9,12,13]



Figure 9. Comparison of potassium and sodium ion binding to a site in the selectivity filter. *The sodium ion has too small of an ionic radius to be fully coordinated to all the carboxylic groups in the filter. It should be noted that the figure for easier visualization only shows only four of the eight potential carbonyl oxygens available at each site. The red represents the amino acid.*

Additional Bio-inorganic Properties to Explain K+ Binding/Release

HSAB Theory

The potassium ion binds to carbonyl oxygens which are hard bases.[14] Hard Soft Acid Base theory characterizes metals as either “hard” or “soft”. This is dependent on the charge density, polarizability, and the type of bonding interactions. For example, hard metals tend to have higher charge density and/or form more electrostatic interactions, while soft metals tend to have lower charge density and/or more covalent bonding. Since potassium is characterized as a hard metal due to its electrostatic interactions, it would most likely bind to ligands that are hard. This theory helps explain why potassium binds to Thr 75, Val 76, Gly 77, and Tyr 78, which are mainly hard ligands.[11,14]

Lability

Lability refers to the ability for a metal-ligand bond to break. When a compound has bonds that are easily broken between the metal-ligand, then that metal is referred to as labile. A common trend that occurs is that alkali metals tend to be more labile compared to other metals that have higher charges. When metals have higher charges, they tend to be stronger Lewis acids. This would allow the metal to bind the ligands more tightly, resulting in harder bonds to break. Another trend that has been observed is that metals that have no d electrons tend to be more labile because of there are no electrons in the way for a new ligand to donate its electrons. Potassium channels are extremely labile because it has a $^+1$ charge, as well as a 0 ligand field stabilization energy (contains zero d electrons). Potassium being labile is extremely important since its diffusion rate is so high that the ion needs to be able to go from one site to the next. If the metal was not labile, the channel would not be able to flow potassium ions as quickly as it can because the metal-ligand complexes would not be as easily breakable.

Conclusions

Potassium channels are necessary for cellular function, especially assisting in neuronal signaling. There are many features that make up the channel, but the key feature is the selectivity filter. The SF is what keeps the channel functioning by specifically

selecting potassium ions. Overall, this selectivity for potassium over other ions can be attributed to the size of the ion and HSAB theory. The SF is the the correct fit to allow an eightfold coordination environment with potassium ions. The specific ligands assist with the binding of the potassium channels because the HSAB theory suggest that like binds to like and both the ligands and metals are characterized as hard. To conclude, there are many features of potassium channels, and this paper only began to touch on the functionality of the channels.

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Contributed By:

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10.10: Chemotherapy- Pt anticancer agents

Platinum complex drugs commonly used in chemotherapy as anticancer agents. Pt chemotherapeutics make up roughly 50% of all chemotherapeutic drug regimens. Platinum drugs are used in both Pt (II) and Pt(IV) oxidation states. Pt antitumor complexes have at least three components in common:

1. They are electrostatically neutral Pt coordination complexes.
2. They are either square planar Pt(II) compounds or octahedral Pt(IV) compounds with two donor groups that are either primary or secondary amines. These amine ligands are either two *cis* monodentate ligands or one bidentate chelating ligand.
3. They all have two donors groups that act as leaving groups. These donors are either Cl or O, and can be either two monodentate or one bidentate ligand.

Specific examples of both Pt(II) and Pt(IV) drugs will be discussed. Platinum itself is a soft metal, which based on the Hard Soft Acid Base (HSAB) Theory, has a higher affinity to softer ligands which is important in biological systems. It has been hypothesized that Pt drugs use copper transport systems including members of the Ctr family to enter and exit cells.[2] The exact mechanism of this process is still highly debated. Studies have shown that Pt drugs have an affinity towards methionine-rich Ctr1 motifs, which may suggest that Pt(II) has a similar affinity for the sulfur of methionine to that of Cu(I),[2] which is typically transported within the cell by the Ctr family. Pt ions within the drug complex are capable of binding to sulfur on amino acids because Pt is a soft acid and sulfur is a soft base. Pt(IV) complexes do not have the same level of affinity to bind to cysteine and methionine in biological systems as Pt (II) complexes.

Pt(II) Complexes

Common Pt (II) complexes are depicted in the figure below. Cisplatin and oxaliplatin are the most common and effective complexes in chemotherapy. These complexes are all in square planar d^8 configuration. These complexes only have four ligands, which limit the geometries to either square planar or tetrahedral, their splitting diagram is depicted below. Complexes in the square planar position tend to have more Ligand Field Stabilization Energy (LFSE) than those in tetrahedral due to their Δ values which separate their antibonding orbitals from the nonbonding. The Δ value is much higher for d8 complexes in the square planar geometry than those in tetrahedral, which affects the the complex's LFSE. Figures 2 and 3 below depict splitting diagrams for d8 Pt(II), in possible square planar and tetrahedral geometries, respectively. If this system is in a tetrahedral geometry, spin would be an irrelevant factor because Pt(II) is a d8 metal and its electrons must be in the anti-bonding orbitals because the first four electrons occupy the nonbonding orbitals. However, spin is a relevant factor for this system in the case of square planar geometry. In this configuration, the no electrons reside in the x2-y2 anti-bonding orbital because of high LFSE and large Δ value. This stabilizes the complex, which explains the affinity of Pt(II) complexes for square planar geometry. On cisplatin, the two Pt-NH3 bonds are kinetically inert and thermodynamically stable, while the Pt-Cl bonds are semi-labile and can act as leaving groups for nucleophiles. Lability refers to the rate at which the ligands can be replaced with other molecules. Because the Pt-Cl are considered labile, they have a greater ability to act as leaving groups and react with other molecules than non-labile bonds. In cisplatin, the NH3-Pt bonds are not as labile as the Pt-Cl bonds and therefore will not leave the metal complex at the same rate as the Pt-Cl bond would to react with other molecules. This is counterintuitive based on electrostatic theory. The Cl- ligands have a negative charge, which influences the overall charge of the complex. However the -NH3 ligands are neutrally charged and are more inert than the neighboring -Cl- ligands. Typically, this would cause the NH3 ligands to be more labile. But, ligand field theory (LFT) explains that Cl- is both a sigma and pi donor ligand, while NH3 is only a sigma donor ligand. Because Cl- is a sigma and pi donor, its electrons also fill antibonding orbitals when binding to Pt. Since NH3 is only a sigma donor, its electrons do not fill the antibonding orbitals when binding to Pt. Due to the presence of electrons in the antibonding orbitals, the Pt-Cl bonds are not as strong as the Pt-NH3 the Cl- ligands are more labile than NH3. During cisplatin's mechanism of action, the chloride ligands are substituted by water molecules, acting as nucleophiles through a process called aquation, which is important in the drug's efficacy3,4,5.

Cisplatin

Cisplatin $[Pt(II)Cl_2(NH_3)_2]^{2-}$ is one of the most widely used anticancer drugs used especially for testicular and ovarian cancers treatments. This was first discovered in 1965 by biophysicist, Barnett Rosenberg while attempting to investigate effects of electric

fields on cell division with Pt electrodes in a cell growth medium. Instead of the cells dividing properly, they formed filaments while undergoing electrolysis and undergoing subsequent reactions of Pt ions[1].

$$\text{Pt (electrode)} \xrightarrow{\text{electrolysis}} [\text{Pt(IV) Cl}_6]^{2-} \longrightarrow \text{NH}_4{}^{+} \xrightarrow{h\nu} [\text{Pt(IV) Cl}_4\ (\text{NH}_3)_2] \tag{10.10.1}$$

The initial product of electrolysis is bacteriostatic and therefore does not promote filamentous growth. Pt in oxidation state (IV) is kinetically inert, low-spin 5d6 and very slow while undergoing reactions. Because of this, Pt(II) was thought to be more effective. Cisplatin, the cis isomer of [Pt(II)Cl2(NH3)2]2- was not bacteriostatic and promoted filamentous growth among the cells, which then in turn, prevented further growth of cancer cells.

Cisplatin in unstable in water, so it is immersed in saline solution to prevent aquation within the body. Saline is a combination of NaCl and water which controls the water levels within the body. If aquation would occur, the water ligands would make the Pt(II) complex very acidic, with pKa values ranging from 5-8. Hydroxyl (-OH) ligands bind and are less reactive because they are more of a strong field ligand than a weak field, like Cl- , the previous ligands. This makes the complex more stable.

The cis conformation of cisplatin affects the distance of the chloro ligands and its drug efficacy as compared to transplatin. The two chloro ligands, the reactive sites, are further apart in transplatin (4.64 A) than cisplatin (3.29 A). This affects how Pt(II) cross-links at DNA sites, which affects its efficacy. Because the Pt ion binds to DNA to stop DNA production, if the Pt ion in transplatin cannot cross-link into DNA because of its ligands, it will not stop DNA production of the cancer cells, or at least not as well as cisplatin. Transplatin reacts very slowly because of the new trans oxygen ligand at its second aquation1.

To promote anticancer activity, the goal is that the Pt ion from the original cisplatin molecule binds to DNA, preventing replication of the cancer cells. After undergoing aquation, the hydroxyl groups leave the Pt ion allowing it to bind to N7 of guanine (G), DNA's major Pt- binding site. The N7 of guanine is one of DNA's major binding site because complexes can easily access this area via the major groove in DNA's B-form6, the most common DNA form. While this is the prefered binding site, cisplatin and other Pt(II) drugs can also bind to N7 of adenine and N3 of cytosine. During cisplatin treatment, cancer cell DNA undergoes 1,2 intrastrand cross-linking of two guanines and sometimes guanine and adenine. The second chloro group undergoes aquation and binds to the second guanine on the DNA strand creating a chelating effect. This cross-linking induced by Cisplatin causes DNA to bend or kink which then causes neighboring proteins to bind to the kinked DNA because they now recognize them as high mobility groups. When this occurs, these newly bound proteins often block these kinks from repair, which halts replication and causes cell apoptosis7. Unfortunately, cisplatin also affects healthy cells as well as cancer cells. Fortunately, healthy cells recognize the damage caused by the kink, where cancer cells do not. This allows enzymes to repair the DNA damage in healthy cells, so they do not undergo apoptosis7. in Figure 4 below shows a Chimera image of a DNA strand within DNA polymerase (ribbons) with the Pt ion, shown in purple, binding to guanine in the DNA strand. The blue atoms bound to the Pt represent the NH3 ligands. Figure 6 shows the same Chimera image, but focused on the binding site between Pt and guanine. The atoms are labeled.

Pt (IV) Complexes

Pt (IV) complexes, commonly referred to as Pt(IV) pro-drugs, are also used as chemotherapeutic agents. These complexes have some benefits over Pt(II) drugs including, they are stable enough to administered orally versus IV, their stability may diminish the side effects caused by Pt(II) drugs, and they may have higher affinity to structural modification via their axial ligands which can enhance their pharmacological properties. Some common Pt(IV) complex drugs are depicted to the right. Pt(IV) complexes differ from Pt(II) complexes in that they have a d6 octahedral geometry with monodentate ligand, except tetraplatin which has one bidentate ligand in addition to the other monodentate ligands. Pt resides in the 5d row of the transition metals. Typically, metals belonging in the 4d and 5d rows of the transition metals have a larger Δ value than those of the 3d metals. This is due to the increase in subshell and size of atoms going down the periodic table. As subshell increases, so does Δ. Another trend to mention is as positive charge on the metal increases, as does Δ. Since the charge on Pt in this system is +4 and it is in the 5d row of the transition metals, I speculate that this system will have a low spin based on the metal ion alone. The splitting diagram of Pt(IV) is depicted below. This image shows the effects of LFSE on the metal. Pt (IV) is low spin with a large Δ value and all electrons residing in the lower energy t2g orbital. This indicates high LFSE which also explains increased bond strength and overall stability of the complex. An increase in LFSE also increases inertness of the system, which decreases lability. The ligands of Pt(IV) will not be as labile as some of Pt(II) due to the difference in LFSE. Pt(II) do not have as much LFSE, therefore, their ligands are more labile and reactive.

Pt(IV) complexes in an octahedral geometry are said to be **substitution-inert**, which makes their interactions and reactions with biological nucleophiles such as cysteine and methionine, very slow. Pt(IV) complexes are considered pro-drugs because they are activated intracellularly in vivo by reduction that makes them act as their square-planar counterparts with the eliminations of their axial ligands.Figure 8 below shows the reduction process. The Pt(IV) complex begins as a Pt(II) complex during synthesis with four ligands in a square planar geometry. The Pt(IV) octahedral configuration is established with the addition of two axial ligands either during a chlorination reaction or an addition reaction with hydrogen peroxide and possible further reactions. When administered orally, Pt(IV) is reduced back to Pt(II) square-planar configuration intracellularly8. Because these complexes can only act as Pt(II) complexes within the cell, where they bind to DNA, they travel throughout the rest of the body as inert Pt(IV) complexes, they may reduce toxicity8.

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